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ASSOCIATION/DISSOCIATION PROCESSES IN DENSE GASES

By

M. R. Flannery

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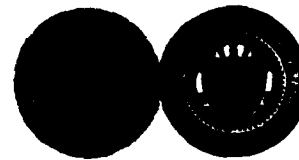
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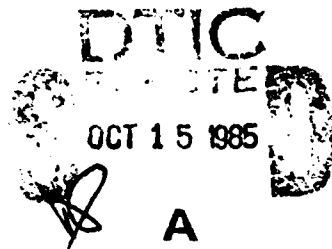
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A new basic microscopic theory of association/dissociation processes in dense gases has been developed. Expressions for the time-dependent rates $R^{A,D}(t)$ for the association/dissociation of atomic or molecular species A and B in a gas M are formulated in terms of the net probability $P_i^{A,D}$ for association/dissociation of bound energy level i of the pair (A-B).

A new Variational Principle for these rates is proposed and is applied to ion-ion recombination, as a benchmark, with very successful results.

The diffusional theory is examined and it is shown that highly accurate results can be obtained for general mass systems provided the new basic expression introduced here for $R_{A,D}(t)$ is adopted.

The microscopic basis of the macroscopic Debye-Smoluchowski Equation (DSE) is examined and analytical expressions for rates are derived for general interactions between A and B. —

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Dr. Ralph E. Kelley	(202) 767-4908	NP

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19. Abstract (continued)

A valuable relationship between the rates of recombination appropriate to the cases of ions generated with uniform frequency within a reaction volume and ions which approach each other from infinite separation is derived.

Contents

Abstract

During this first year of the new grant, research has been initiated and conducted on the development and implementation of a new basic microscopic theory of association/dissociation processes in dense gases. Expressions for the time-dependent rates $R^{A,D}(t)$ for the association/dissociation of atomic or molecular species A and B in a gas M are formulated in terms of the net probability $P_i^{A,D}$ for association/dissociation of bound energy level i of the pair (A-B).

A new Variational Principle for these rates is proposed and is applied to ion-ion recombination, as a benchmark, with very successful results.

The diffusional theory is examined and it is shown that highly accurate results can be obtained for general mass systems provided the new basic expression introduced here for $R_{A,D}(t)$ is adopted.

The microscopic basis of the macroscopic Debye-Smoluchowski Equation (DSE) is examined and analytical expressions for rates are derived for general interactons between A and B.

A valuable relationship between the rates of recombination appropriate to the cases of ions generated with uniform frequency within a reaction volume and ions which approach each other from infinite separation is derived.

1. Research Initiated and Completed

1.1 List of Topics

During the first year (7/1/84 - 6/30/85) of the Grant, theoretical research on the following topics was completed and written up for publication in scientific journals:

(A) General Microscopic Theory of Association/Dissociation Non-Equilibrium Processes in Dense Gases.

(B) Diffusional Theory of Association/Dissociation Non-Equilibrium Processes for General Systems.

(C) Microscopic Basis and Analytical and Numerical Solutions of the Debye-Smoluchowski Equation.

(D) Ion-Ion Recombination at High Ion Density.

1.2 Summary of Topics

A summary of each of the above topics (A) - (D) now follows. Full details of each topic are presented in Appendices (A) - (D) of this report.

<u>Topic (A)</u>: Sets of transport-collisional Master Equations for the two-particle non-equilibrium distribution function of subsystems (A-B) in a thermal bath of <u>dense</u> gas M are derived in various physical representations, corresponding to the full range of gas density. Expressions for time-dependent rates $R^{A,D}(t)$ for association/dissociation are formulated in terms of net probabilities $P_i^{A,D}$ for association/dissociation of bound energy level i of pair (A-B), so that association and dissociation are treated in a unified manner and that evolution in time t towards equilibrium is naturally achieved. The expressions for $R^{A,D}$ are also independent of whether or not a quasi-steady-state (QSS) distribution of highly excited levels is assumed and are particularly valuable when approximate probabilities $P_i^{A,D}$ are used. A

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new Variational Principle for the rates $R^{A,D}(t)$ is proposed and is applied to ion-ion recombination, as a benchmark, with very successful results. Contact of this Variational Principle (in general for chemical reactions in a gas) is established with Tellegen's Theorem for electrical networks and with Onsager's Principle of Least Dissipation for heat conduction.

Topic (B): Upon re-examination of the foundations of the diffusional treatment of association/dissociation processes involving a non-equilibrium distribution of (A-B) pairs in a gas M, it is shown that highly accurate results may be obtained for general mass systems provided a new and more basic expression for the time-dependent association/dissociation rates $R^{A,D}(t)$ is introduced. These rates $R^{A,D}(t)$ are derived here in terms of the probability $P_i^{A,D}(E_i)$ that (A-B) pairs with internal energy E_i has associative or dissociative character and are obtained without appeal to the quasi-steady-state (QSS) condition for highly excited levels E_i. Then association and dissociation can be treated in a unified way and evolution towards equilibrium with the gas is naturally achieved. Comparison is made between the exact probabilities $P_i^{A,D}$ obtained from the QSS-condition to the Exact input-output Master Equation and those obtained from the derived diffusional equational. $R^{A,D}(t)$ reduces to the constant-in-energy current $J(t)$ through the excited levels only for exact QSS of the Master Equation. When approximate probabilities are adopted, identification of $R^{A,D}(t)$ with $J(t)$ is not justified. The basic expression here for $R^{A,D}(t)$ is appropriate for both exact and approximate (diffusional) probabilities and yields excellent results for ion-ion recombination in a dilute gas over the full range of masses of the species involved and over various classes of ion-neutral interaction (polarization, hard-sphere and charge-transfer).

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<u>Topic (C)</u>: By explicitly including collisions and by operating at a level more basic than the macroscopic Debye-Smoluchowski Equation (DSE), various assumptions within the DSE-treatment of <u>transport-influenced reactions</u> between A and B in a dense medium M become naturally exposed. The appropriate modification of DSE to description of the kinetics within the region of the sink is provided.

Analytical expressions for probability densities and rates are derived which are exact solutions of DSE (a) at all times t and large internal separations R of the pair (A-B), (b) at long times t and all R and (c) at short times t and all R. Not only are the transient rates $\alpha_S(t)$ and $\alpha_L(t)$ exact at short and long times, respectively, but they are naturally bounded for all times with $\alpha_S(t\to\infty)$ and $\alpha_L(t\to 0)$ tending to the correct limit, albeit with an incorrect transience. Comparison with exact numerical solutions of DSE illustrates the effectiveness of a proposed solution over the full range of time.

<u>Topic (D)</u>: By appeal to a Thomson-type treatment of recombination, it is shown that the rate for recombination of ions generated with uniform frrequency within a reaction volume is a factor of (9/4) times greater than the rate for recombination of ions which approach each other from infinite separation. A valuable relationship connecting the two problems is uncovered. The analysis is pertinent to recombination involving dilute and high degrees of ionization.

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1.3 Papers Presented at Scientific Meetings

1. "Association/Dissociation in Dense Gases and Adsorption/Desorption on Surfaces" by M. R. Flannery.

2. "Analytical and Numerical Solutions of the Time Dependent Debye-Smoluchowski Equation" by M. R. Flannery and E. J. Mansky.

3. "Electron-Excited Hydrogen and Helium Collisions" by E. J. Mansky and M. R. Flannery.

4. "Symmetric Charge-Transfer Cross Sections in Rare Gas (Rg^+-Rg) Systems" by E. J. Mansky and M. R. Flannery.

All of the above papers were presented at the 37th Annual Gaseous Electronics Conference, October 9-12, 1984, held at the University of Colorado in Boulder.

The abstracts of the above papers now follow.

1.4 Abstracts of Papers Presented

LD-13 Association/Dissociation in Dense Gases and Adsorption/Desorption on Surfaces,* M. R. FLANNERY, Georgia Institute of Technology—A new comprehensive theory[1] is described for the time evolution towards equilibrium of association and dissociation in a dense gas. Expressions are formulated and are illustrated for the net probabilities of association to stable vibrational levels and dissociation to the continuum from an arbitrary bound vibrational level via collision with the thermal gas bath. A general variational principle emerges: The rate which corresponds to the overall direction of the process always adjusts itself to a minimum and the time evolution towards equilibrium is hindered. Analogy is established with Kirchhoff's Laws and Tellegen's Theorem for electrical networks, and with the Principle of Least Dissipation basic to thermodynamics, heat conduction, and fluid mechanics. The theory can also be modified to provide the first basic microscopic account of Associative Desorption of atoms from and Dissociative Chemisorption of molecules to surfaces.
*Research supported by AFOSR under Grant AFOSR-84-0023.
[1]M. R. Flannery, Phys. Rev. A, (1985).

LD-2 <u>Analytical and Numerical Solutions of the Time Dependent Debye-Smoluchowski Equation</u>,* M. R. FLANNERY and E. J. MANSKY, Georgia Institute of Technology--The macroscopic Debye-Smoluchowski Equation (DSE) with a radiation boundary condition has been derived[1] from a basic microscopic theory of association/dissociation processes, A+B $\rightarrow$ AB, between A and B in a thermal gas bath. There are at present no exact analytical solutions of DSE for general interactions V(R) between A and B for all separations R and time t. We formulate here exact analytical solutions for the conditional probability density and reaction rates (a) at long and short times for all R and (b) at all times for large R and compare the results with direct numerical solutions. We also propose highly accurate working expressions for the rates of transport influenced reactions at all times.

[1] M. R. Flannery, Phys. Rev. A (1985).

LC-1 <u>Electron-Excited Hydrogen and Helium Collisions</u>,* E. J. MANSKY and M. R. FLANNERY, Georgia Institute of Technology--The Multichannel Eikonal Treatment (MET) is modified so as to facilitate highly accurate description of various asymptotic long range dipole couplings important in electron excited atom collisions. MET is applied to excitation in e-H(2s), e-H(2p), e-He($2^{1,3}$S) and e-He($2^{1,3}$P) collisions at intermediate energies. Integral and differential cross sections together with various coherence and alignment parameters for the radiative decay of the n=2 and 3 collisionally-excited P and D states of H and He are determined from MET with 10 channels associated with n = 1, 2, and 3 sublevels. Comparison is made with various recent measurements.

LD-12 Symmetric Charge-Transfer Cross Sections in Rare
Gas (Rg$^+$-Rg) Systems,* E. J. MANSKY and M. R. FLANNERY,
Georgia Institute of Technology—Symmetric resonance
charge-transfer, elastic, diffusion and viscosity cross
sections for the ion-atom collisions: Rg$^+$ + Rg, Rg = He,
Ne, Ar, Kr, Xe are determined via a full quantal phase-
shift analysis using the pseudopotential of Sinha, et al.
[1] for He$_2^+$; and the spin-orbit ab-initio potentials of
Cohen and Schneider [2] for Ne$_2^+$, Wadt [3] for Ar$_2^+$, Kr$_2^+$,
and Xe$_2^+$; and Michels, et al. [4] for Ne$_2^+$, Ar$_2^+$, Kr$_2^+$,
and Xe$_2^+$ at lab energies ranging from 0.001 eV to 1 keV.
The long-range ion-atom polarization attraction is ex-
plicitly acknowledged in the full interaction and in a
JWKB correction to the numerical asymptotic phase shift.
Differential cross sections are also obtained. Comparison
is made with existing experimental and theoretical data.
[1] S. Sinha, S.L. Lin, and J.N. Bardsley, J. Phys. B
     12 (1979) 1613.
[2] J.S. Cohen and B. Schneider, J. Chem. Phys. 61
     (1974) 3230.
[3] W.R. Wadt, J. Chem. Phys. 68 (1978) 402.
[4] H.H. Michels, R.H. Hobbs, and L.A. Wright, J. Chem.
     Phys. 69 (1978) 5151.

1.5 <u>List of Publications</u> (in press and in preparation)

1. "General Microscopic Theory of Association/Dissociation Non-Equilibrium Processes in Dense Gases," M. R. Flannery (Phys. Rev. A).

2. "Diffusional Theory of Association/Dissociation Non-Equilibrium Processes for General Systems," M. R. Flannery (Phys. Rev. A).

3. "Microscopic Basis and Analytical and Numerical Solutions of the Debye-Smoluchowski Equation," M. R. Flannery and E. J. Mansky (Phys. Rev. A).

4. "Ion-Ion Recombination at High Ion Density," M. R. Flannery, J. Phys. B: Atom. Molec. Phys.

5. "Modified Multichannel Eikonal Treatment of Electron Excited Atom (H,He) Collisions," M. R. Flannery and E. J. Mansky (in preparation).

6. "Symmetrical Resonance Charge-Transfer in the Rare-Gas Sequence (Ne, Ar, Kr, Xe)," M. R. Flannery and E. J. Mansky (in preparation).

7. "Kinetic Theory Foundation of Ion-Ion Recombination in a Dense Plasma," M. R. Flannery and E. J. Mansky (in preparation).

8. "A Variational Principle in Dynamics of Relaxation," M. R. Flannery (in preparation).

9. "Classical Theory of Recombination," M. R. Flannery (in preparation).

10. "Selected Bibliography on Atomic Collisions: Data Collections, Bibliographies, Review Articles, Books, and Papers of Particular Tutorial Value," M. R. Flannery, E. W. Thomas and S. T. Manson, Atomic Data and Nuclear Data Tables <u>33</u> (1985) 1-148.

Papers #1-4 above are included as Appendices A-D of this report.

Reprints of paper #10 will be sent to AFOSR under separate package. Papers #5-10 will be also sent to AFOSR when completed.

1.6 Ph.D. Thesis Supervised

Mr. E. J. Mansky has been a Ph.D. graduate student supervised by the Principal Investigator (M. R. Flannery) and supported by the present and previous AFOSR grants (AFOSR-84-0233 and AFOSR-80-0055). He has now completed his thesis and is expected to graduate with a Ph.D. on September 1985. Copies of his thesis are being prepared and will be submitted in due course to the AFOSR as a separate bound report.

Appendices

In the following Appendices A-D are contained preprints of the following articles submitted for publication to scientific journals.

(A) General Microscopic Theory of Association/Dissociation Non-Equilibrium Processes in Dense Gases.

(B) Diffusional Theory of Association/Dissociation Non-Equilibrium Processes for General Systems.

(C) Microscopic Basis and Analytical and Numerical Solutions of the Debye-Smoluchowski Equation.

(D) Ion-Ion Recombination at High Ion Density.

Appendix A

General Microscopic Theory of Association/Dissociation

Non-Equilibrium Processes in Dense Gases

.

General Microscopic Theory of Association/Dissociation Non-Equilibrium Processes in Dense Gases

M. R. Flannery
School of Physics,
Georgia Institute of Technology,
Atlanta, Georgia 30332

Abstract. Sets of transport-collisional Master Equations for the two-particle non-equilibrium distribution function of subsystems (A-B) in a thermal bath of dense gas M are derived in various physical representations, corresponding to the full range of gas density. Expressions for time-dependent rates $R^{A,D}(t)$ for association/dissociation are formulated in terms of net probabilities $P_i^{A,D}$ for association/dissociation of bound energy level i of pair (A-B), so that association and dissociation are treated in a unified manner and that evolution in time t towards equilibrium is naturally achieved. The expressions for $R^{A,D}$ are also independent of whether or not a quasi-steady-state (QSS) distribution of highly excited levels is assumed and are particularly valuable when approximate probabilities $P_i^{A,D}$ are used. A new Variational Principle for the rates $R^{A,D}(t)$ is proposed and is applied to ion-ion recombination, as a benchmark, with very successful results. Contact of this Variational Principle (in general for chemical reactions in a gas) is established with Tellegen's Theorem for electrical networks and with Onsager's Principle of Least Dissipation for heat conduction.

I. Introduction

When a distribution of ion-ion $(A^+ + B^-)$ pairs, or of ion-atom $(A^+ + B)$ pairs or of any (ion or neutral) subsystem of dissociated species denoted in general by $(A + B)$ is introduced in a dense gas of thermal species M, a highly non-equilibrium situation exists. In this paper, a set of Master Equations is formulated for the relaxation from some initial non-equilibrium distribution of dissociated subsystems A + B (or of molecules AB) towards equilibrium with a dense thermal gas M via the pertinent energy-change processes,

$$A + B + M \rightleftharpoons AB + M \qquad (1.1a)$$

$$A^+ + B + M \rightleftharpoons AB^+ + M \qquad (1.1b)$$

$$A^+ + B^- + M \rightleftharpoons AB + M \qquad (1.1c)$$

i.e., by the collisional association (recombination) of the dissociated species, the forward direction of (1.1), or by the reverse of (1.1), the collisional dissociation of molecules AB with an initial distribution characterized by temperature T_{AB} which is higher than the temperature T_M of the dense gas M. A key component of this theory is inclusion of the essential coupling[1] between the macroscopic effects of transport and reaction between A and B in M via a comprehensive microscopic treatment of the process. Evolution of the two particle correlation function for subsystem (A-B) is provided in terms of the internal energy E, internal angular momentum L and internal separation R of the subsystem by explicitly including streaming (diffusion and drift) and discontinuous collisions with the heat bath M.

The present theory is a natural development of that previously proposed[1]

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for the rate of ion-ion recombination (1.1c) as a function of density N of the gas M. That theory[1] then emphasized the steady-state rate of recombination which can be expressed in terms of reaction and transport rates. Also the treatment intrinsically assumed that the relative speed v was purely radial and that the ratio of product concentrations of fully dissociated species, of concentration N_A and N_B, to their corresponding product $\tilde{N}_A\tilde{N}_B$ under thermodynamic equilibrium

$$N_A N_B / \tilde{N}_A \tilde{N}_B \gg N_{AB}/\tilde{N}_{AB} \tag{1.2}$$

is much larger than the corresponding ratio $N_{AB}/\tilde{N}_{AB}$ for fully associated species. The overall direction of (1.1) is then forward i.e., the overall rate of association is much greater than the rate of dissociation which is then neglected, by comparison. The aim of the present paper is to remove those restrictions and thereby provide a comprehensive account of the time evolution towards equilibrium of a highly non-equilibrium situation via the dynamic balance as in (1.1) between association and dissociation processes, which may then be treated in a unified way.

Because it remains a very basic problem in atomic and molecular physics both in its detailed theoretical elucidation and in its central significance to many physical situations of great current interest, solution of the general problem represented by (1.1) as a function of gas density is considered as a prototype textbook study[1] of a process in which collision theory and statistical mechanics can be coupled via some unified microscopic treatment.

Association and recombination, the forward direction of (1.1), are important in many instances, as for example, in gaseous discharges,[2] in electron-beam pumped exciplex lasers[2,3] (KrF, XeCl etc.), and in the recent Optoacoustic Effect[4] where the acoustic wave is generated by the conversion

into translational heating of a dense gas via termolecular association of the photofragments A and B produced originally by photodissociation of a dense molecular gas AB. For overall dissociation the reverse direction of (1.1), externally-induced non-equilibrium distributions of AB in excited vibrational levels can be produced by absorption by AB but not by M of short-duration high-intensity thermal radiation with temperature $T \gg T_M$, or by the passage of a shock wave through the gas. Here the translational and rotational degrees of freedom of all species will relax to thermal equilibrium at temperature T_S immediately behind the shock wave more rapidly than the much slower relaxation of the vibrational distribution of AB associated with the original and final temperatures T_M and T_S, respectively. Charge-transfer between molecular species $(AB^+ - AB)$ also produces[5] a non-equilibrium distribution of AB in various high vibrational levels. Absorption by AB of laser radiation will of course produce a vibrational distribution strongly peaked about a specific vibrational energy. The vibrational distribution will then relax by collisional association/dissociation processes.

In this paper, (1.1) is considered to be a closed system i.e., irreversible losses by curve crossings $AB \not\rightleftharpoons A + B$, quantum tunnelling, or by mutual neutralization $(A^+ - B^-) \not\rightleftharpoons A^* + B$ are specifically excluded. The concentrations N_A and N_B of subsystems are much less than the concentration N of the gas system M so that the main relaxation mechanisms are energy-changing collisions between the subsystem and gas. Relaxation via radiative transitions and subsystem-subsystem collisions may therefore be neglected. The gas is therefore regarded as a heat bath whose main function is to collisionally exchange energy and angular momentum with the subsystem, while maintaining its original thermodynamic state at temperature T_M at all times, thereby permitting the original dissociated or associated subsystems to relax

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to eventual equilibrium at temperature T_M. The above three assumptions help to keep the theory tractable but may, in principle, be all or individually removed via straightforward generalization of what remains, however, a fairly comprehensive theory presented here.

In the limit of low gas densities N, mutual transport of A towards B in the gas M is very rapid so that the process (1.1) is determined by the rate limiting step of reaction. The previous collisional input-output Master Equations of Bates and Moffett[6], of Bates and Flannery[7], of Bates and Mendas[8], of Flannery,[2,9-11] for ion-ion recombination (1.1c), of Bates and McKibbin[12] for ion-atom association (1.1b) and the weak (diffusional) collision treatment of Keck and Carrier[13] and of Anderson and Shuler[14] for association/ dissociation (1.1a) have all been designed specifically <u>for reaction only in the limit of low gas densities N</u>. As N is raised the transport rate decreases and the reaction rate increases until the rate limiting step of the overall process in the limit of high gas densities becomes transport. The present paper is therefore concerned with transport-influenced reactions and with the design of appropriate Master Equations which govern transport-reaction processes at all gas densities N. The Master Equation for the limit of low N is well documented and discussed[6-14] and the present theory yields this limit.

The organization of this paper is as follows. In §2, various representations of the basic equation governing the mutual streaming (transport) of A towards B in the dense gas are presented. The corresponding transport-collisional (reaction) Master Equations for the non-equilibrium distributions are then developed in §3. Simplifications introduced by assuming equilibrium associated with one or more of various physical variables as interseparation R, internal energy E, and internal angular momentum L of the pair A-B, are then discussed in §4. Expressions for the rates of

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association and dissociation are formulated in § 5 in terms of the solutions to the Master Equation. In § 6, the time evolution towards equilibrium is expressed in terms of the net probabilities of collisional association and dissociation of AB in high vibrational levels. A Variational Principle basic to evolution towards equilibrium then emerges and is discussed in §7. It is new and asserts that the conditional densities (or pair correlation functions) of pairs AB in various energy levels are so distributed that the rates $R^A(t)$ and $R^D(t)$ of association and dissociation, respectively, are extrema at time t. If conditions are such that the overall direction is association, then $R^A(t)$ is minimum and $R^D(t)$ is maximum; for overall direction of dissociation, $R^A(t)$ is maximum and $R^D(t)$ is minimum. Evolution towards eventual equilibrium is therefore hindered and the Principle of Least Dissipation (first derived by Onsager[15] for heat conduction) is satisfied. When equilibrium distributions are assumed for fully associated and dissociated pairs, the Variational Principle yields the quasi-steady state condition (i.e., a steady-state distribution of highly excited levels at all times) which rendered feasible the many pioneering studies[16] by Bates and colleagues of heavy-particle recombination[6-11] and of electron-ion collisional radiative recombination in a plasma[17,18] and in a gas.[19,20] Application of the Variational Principle to ion-ion recombination is made in §7.2.

Finally, in an effort to make this paper complete and comprehensive, Appendix A contains classical distributions corresponding to equilibrium in internal separation R, internal energy E and internal angular momentum L of the pair (A-B) together with various classical-quantal correspondences. In Appendix B are gathered various collision kernels and one-way equilibrium rates for energy-change collisions appropriate to various interactions (charge-transfer[6,10], hard-sphere,[11] polarization[8] and Coulombic) between the subsystem AB and the gas species M. The kernels are expressed in appropriate form for direct application of the present theory.

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2. Various Representations of the Transport Equation

The present theory is a natural development and generalization of the microscopic theory recently proposed[1] for the rate of ion-ion recombination (or of any chemical reaction in general) as a function of gas density N. The proposed theory[1] bridged the density gap between the previous quasi-steady-state theories[6-13] based on energy-relaxation alone and therefore valid in the low-density limit, and the macroscopic mobility/diffusion theory[2], valid in the limit of high gas densities N. It was also shown[1] that the steady-state rate of recombination is determined by the well known relation $\alpha = \alpha_{TR} \alpha_{RN}/(\alpha_{TR} + \alpha_{RN})$, between the macroscopic rates α_{TR} and α_{RN} of mutual transport and of reaction between the species, respectively. At low N when $\alpha_{TR} \gg \alpha_{RN}$ then $\alpha \to \alpha_{RN}$, the rate limiting step, while at high N when $\alpha_{RN} \gg \alpha_{TR}$, then $\alpha \to \alpha_{TR}$, the limiting rate. This relationship is also a natural consequence of the macroscopic Debye-Smoluchowski Equation[1] where α_{RN} is regarded as an externally assigned parameter, in contrast to the microscopic theory[1] where α_{RN} is internally determined.

At low N, equilibrium with respect to the internal separation R of the (A-B) pair (ion-atom or atom-atom) is very quickly established in comparison to the much slower relaxation in time t of both the angular momentum L and the internal energy E of the pair. The appropriate time dependent master equation would involve only the set (E, L^2, t) of variables for ion-atom and atom-atom association. For ion-ion recombination, the Coulombic attraction does not support an angular momentum barrier and equilibrium in L^2 is then very quickly established in comparison to energy relaxation so that the master equation involves only (E, t), as in the previous quasi-steady-state treatments.[6-13]

As the gas density N is increased, relaxation in internal separation R occurs in a time comparable to relaxation in internal energy E so that both transport and reaction are coupled. It has already been established[1,21] that a "Boltzmann-like" equation governs the development of the pair correlation function, or conditional probability density $n(\underset{\sim}{R}, \underset{\sim}{p}, t)$, which is such that $n \, d\underset{\sim}{R} \, d\underset{\sim}{p}$

is the probability that the internal momentum, $\underset{\sim}{p} = m\underset{\sim}{v}$, and internal

separation $\underset{\sim}{R}$ of the (A-B) pair of reduced mass m and relative velocity $\underset{\sim}{v}$, is

within the interval $d\underset{\sim}{R}\,d\underset{\sim}{p}$ about $(\underset{\sim}{R},\underset{\sim}{p})$ at time t. Thus[1,2]

$$\frac{d}{dt}\, n(\underset{\sim}{R},\underset{\sim}{p},t) \equiv \frac{\partial n}{\partial t} + \underset{\sim}{v}\cdot\nabla_{\underset{\sim}{R}}n - \left(\frac{\partial V}{\partial R}\right)\hat{R}\cdot\nabla_{\underset{\sim}{p}}n \tag{2.1a}$$

$$= \sum_{i=1,2}\int_{\underset{\sim}{P_M}}d\underset{\sim}{P_M}\int_{\Omega_i'}d\Omega_i\,[n(\underset{\sim}{R},\underset{\sim}{p}';t)N_0(\underset{\sim}{P_M}') - n(\underset{\sim}{R},\underset{\sim}{p};t)N_0(\underset{\sim}{P_M})][g_{iM}\,\sigma_{iM}(g_{iM},\psi)]$$

$$- n(\underset{\sim}{R},\underset{\sim}{p};t)\,\nu(\underset{\sim}{R},\underset{\sim}{p}) \tag{2.1b}$$

where V(R) is the interaction between A and B, where the momentum $\underset{\sim}{P_M}$ of the

gas species M is distributed according to a (time-independent) Maxwell

distribution $N_0(\underset{\sim}{P_M})$ at temperature Θ, and where $\sigma_{iM}d\Omega_i$ is the (center-of-mass)

cross section for A-M (i = 1) or B-M (i = 2) elastic scattering at relative

speed g_{iM} into solid angle $d\Omega_i$. If M is molecular, then σ_{iM} is augmented by

the collisional inelastic cross section for rotational and vibrational

transitions. The Ω_i-integration in (2.1b) is over that scattering region Ω'_i

accessible for the production of all final scalar momenta $p'(\underset{\sim}{p},\underset{\sim}{P_M},\Omega_i')$ and

$P_M'(\underset{\sim}{p},\underset{\sim}{P_M},\Omega_i')$ of the (A-B) pair and the gas, consistent with energy

conservation and with fixed $\underset{\sim}{p}$ and $\underset{\sim}{P_M}$. Included also in (2.1b) is a term, $n\nu$

which specifies loss of bound or free pairs via irreversible chemical reaction,

as mutual neutralization at frequency ν.

The emphasis of the earlier paper[1] was the steady state recombination

rate for the case when there were many more dissociated A-B species than the

associated neutrals such that the dominant process was association alone. In

this paper, we focus on the time evolution towards equilibrium which is

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established by the balance between collisional association of the free pairs and the collisional dissociation of the recombined pairs in a thermal gas bath. In order to facilitate appropriate theoretical development, the transport (streaming changes) portion (2.1a) and the collisional (discontinuous changes) portion (2.1b) of the above Master Equation will be formulated in various representations of physical interest.

2.1 $(\underset{\sim}{R},\underset{\sim}{p})$ Transport Equation.

With $\underset{\sim}{p}$ held fixed at angle θ to variable $\underset{\sim}{R}$, then after some analysis,

$$\underset{\sim}{p}\cdot\nabla_{\underset{\sim}{R}}n(\underset{\sim}{R},\underset{\sim}{p}) = \frac{1}{R^2}\frac{\partial}{\partial R}(R^2 np\cos\theta)_{p,\theta} + \frac{1}{R}\frac{\partial}{\partial(\cos\theta)}[np\,\sin^2\theta]_{p,R} \qquad (2.2)$$

$$+ \frac{\sin\theta}{R}\left[\cos\phi\left(\frac{\partial n}{\partial\theta_R}\right) + \frac{\sin\phi}{\sin\theta_R}\left(\frac{\partial n}{\partial\phi_R}\right) - \sin\phi\,\cot\theta_R\left(\frac{\partial n}{\partial\phi}\right)\right]$$

for general $n[\underset{\sim}{R}(R,\theta_R,\phi_R), \underset{\sim}{p}(p,\theta,\phi)]$, where $\underset{\sim}{p}(\theta,\phi)$ is directed along (θ,ϕ) of a spherical system with Z-axis along $\underset{\sim}{R}$ which, in turn, is directed along (θ_R, ϕ_R) of a space-fixed spherical reference frame. Since the interaction $V(R)$ is radial, then the probability density n is a function only of R, p and θ, the angle between $\hat{\underset{\sim}{R}}$ and $\hat{\underset{\sim}{p}}$. Under azimuthal (ϕ,ϕ_R) symmetry, and with the aid of (2.2) together with the corresponding expression for $\hat{\underset{\sim}{R}}\cdot\nabla_{\underset{\sim}{p}}n$, (2.1a) can be expressed as

$$\frac{d}{dt}n(\underset{\sim}{R},\underset{\sim}{p};t) = \frac{\partial n}{\partial t} + \frac{1}{R^2}\frac{\partial}{\partial R}(R^2\,n\,v\,\cos\theta)_{p,\theta} + \frac{1}{R}\frac{\partial}{\partial(\cos\theta)}(n\,v\,\sin^2\theta)_{p,R}$$

$$- \left(\frac{\partial V}{\partial R}\right)\left[\frac{1}{p^2}\frac{\partial}{\partial p}(p^2\,n\,\cos\theta)_{R,\theta} + \frac{1}{p}\frac{\partial}{\partial(\cos\theta)}(n\,\sin^2\theta)_{p,R}\right], \qquad (2.3a)$$

which may be cited as the <u>conservative form</u> of the transport equation in one dimensional spherical geometry, since the angular redistribution terms vanish when integrated over the full range $0 \leq \theta \leq \pi$ of the momentum direction $\hat{p}$ for fixed $\underset{\sim}{R}$. An alternative form of (2.3a) is

$$\frac{d}{dt} n(\underset{\sim}{R},\underset{\sim}{p};t) = \frac{\partial n}{\partial t} + v \cos \theta \left[\left(\frac{\partial n}{\partial R}\right)_{p,\theta} - \frac{m}{p} \left(\frac{\partial V}{\partial R}\right)\left(\frac{\partial n}{\partial p}\right)_{R,\theta} \right] \qquad (2.3b)$$

$$+ \frac{1}{2} v \sin^2\theta \left[\frac{2}{R} - \frac{1}{(E-V)} \frac{\partial V}{\partial R} \right] \frac{\partial n}{\partial(\cos\theta)}_{R,p}$$

where the internal energy E of the AB pair is

$$E = p^2/2m + V(R) = 1/2 \ mv^2 + V(R) = T + V(R) \qquad (2.4)$$

in terms of relative kinetic energy T and relative speed v.

2.2 $(R,p,|\cos\theta|)$-Transport Equations

Introduce the superscripts ($\pm$) to distinguish those pairs n^+ with $\hat{p}$ directed into the upper region, $0 < \theta < \frac{\pi}{2}$ where $\cos\theta > 0$ defines the positive (+) region, with outward directed radial speed, from those pairs n^- with $\hat{p}$ directed into the lower region, $\frac{\pi}{2} < \theta < \pi$ where $\cos \theta < 0$ defines the negative (-) region with inward directed radial speed. At $\theta = \frac{\pi}{2}$, the radial speed $v \cos\theta$ is zero (at the classical turning point of the relative motion).

The set of equations satisfied by,

$$n^{s,d}(\underset{\sim}{R},\underset{\sim}{p},|\cos\theta|;t) = n^+(\underset{\sim}{R},p,|\cos\theta|;t) \pm n^-(\underset{\sim}{R},p,|\cos\theta|;t), \qquad (2.5a)$$

the sum (s) and difference (d) of the ϕ-integrated quantities,

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$$n^+(\underset{\sim}{R},p,|\cos\theta|;t) = \int_0^{2\pi} n^+(\underset{\sim}{R},\underset{\sim}{p};t)d\phi \quad , \tag{2.5b}$$

is obtained from (2.3a) to yield,

$$\frac{d}{dt} n^S(\underset{\sim}{R},p,|\cos\theta|;t) = \frac{\partial n^S}{\partial t} + \frac{1}{R^2}\frac{\partial}{\partial R}(R^2 n^d v|\cos\theta|) + \frac{1}{R}\frac{\partial}{\partial(\cos\theta)}(n^S v \sin^2\theta)$$

$$- \left(\frac{\partial V}{\partial R}\right)\left[\frac{1}{p^2}\frac{\partial}{\partial p}(p^2 n^d|\cos\theta|) + \frac{1}{p}\frac{\partial}{\partial(\cos\theta)}(n^S \sin^2\theta)\right] \tag{2.6a}$$

and

$$\frac{d}{dt} n^d(\underset{\sim}{R},p,|\cos\theta|;t) = \frac{\partial n^D}{\partial t} + \frac{1}{R^2}\frac{\partial}{\partial R}(R^2 n^S v|\cos\theta|) + \frac{1}{R}\frac{\partial}{\partial(\cos\theta)}(n^d v \sin^2\theta)$$

$$- \left(\frac{\partial V}{\partial R}\right)\left[\frac{1}{p^2}\frac{\partial}{\partial p}(p^2 n^S|\cos\theta|) + \frac{1}{p}\frac{\partial}{\partial(\cos\theta)}(n^d \sin^2\theta)\right] \tag{2.6b}$$

2.3 $(\underset{\sim}{R},p)$-Transport Equations

Let

$$n^+(\underset{\sim}{R},p;t) = \int_0^{2\pi} d\phi \int_{0,-1}^{1,0} d(\cos\theta) \, n^+(\underset{\sim}{R},\underset{\sim}{p};t) \equiv \int_{(+,-)} n(\underset{\sim}{R},\underset{\sim}{p};t)d\hat{\underset{\sim}{p}} \tag{2.7}$$

be the conditional densities (per unit $d\underset{\sim}{R}\, p^2 dp$) of pairs that are radially expanding (+) or radially contracting (-) across a fixed element of surface S at radius $\underset{\sim}{R}$. The corresponding intramolecular currents

$$j^+(\underset{\sim}{R},p;t) = v \int_{(+,-)} n(\underset{\sim}{R},\underset{\sim}{p};t)|\cos\theta|d\hat{\underset{\sim}{p}} \tag{2.8}$$

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are the rates (per unit $dR\, p^2 dp$) that pairs expand (+) or contract (−) across a fixed surface S with normal $\hat{e}_S$ oriented along the fixed direction $\hat{R}$. In terms of (2.7) and (2.8), integration of the conservative form (2.3a) over each ($\pm$) region yields,

$$\frac{d}{dt}\, n^{+}(\underset{\sim}{R},p;t) = \frac{\partial n^{\pm}}{\partial t} \pm \frac{1}{R^2}\left[\left(\frac{\partial}{\partial R}\right)_p - \frac{m}{p^2}\left(\frac{\partial V}{\partial R}\right)_R p\right]\left[R^2\, j^{+}(\underset{\sim}{R},p;t)\right]$$

$$\mp \frac{1}{2}\, v\, n(\underset{\sim}{R},p,\ \theta = \tfrac{\pi}{2};t)\left[\frac{2}{R} - \frac{1}{(E-V)}\frac{\partial V}{\partial R}\right]\quad, \tag{2.9}$$

where, owing to ϕ-symmetry $n\ (\theta = \tfrac{\pi}{2})$ is $2\pi\, n^{+}(R,p;t)$ evaluated at $\theta = \tfrac{\pi}{2}$, which corresponds to turning point(s), the pericenter and apocenter (where appropriate) of the orbital motion.

This density $n(\tfrac{\pi}{2})$ corresponds to orbits (with angular momentum $L_t = |\underset{\sim}{R} \times \underset{\sim}{p}| = Rp$),which are tangential ($\theta = \tfrac{\pi}{2}$) to, but do not intersect the R-sphere i.e., $n(\tfrac{\pi}{2})$ is $n^{-}(\tfrac{\pi}{2})$ at the pericenter, and is $n^{+}(\tfrac{\pi}{2})$ at the apocenter of the appropriate orbits. As R increases from zero, the angular momentum L_t required to provide this tangential orbit must also increase, so that the orbit can only touch the R-sphere externally at its pericenter. For unbound orbits ($E > 0$), L_t can increase indefinitely so that $n(\tfrac{\pi}{2})$ remains $n^{-}(\tfrac{\theta}{2})$ for all R. For bound orbits of specified E, however, then $L_t = Rp$ required for a tangential orbit reaches a maximum at a radius A which is the root of

$$\frac{1}{R^2 p^2}\left[\frac{\partial}{\partial R}\, (R^2 p^2)\right]_E = \left[\frac{2}{R} - \frac{1}{(E-V)}\frac{\partial V}{\partial R}\right] \equiv \frac{2}{R} - \frac{1}{T}\frac{\partial V}{\partial R} = 0 \tag{2.10}$$

where T is the kinetic energy $(E-V)$.

As R increases beyond this radius A, L_t decreases, and the required

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L_t-orbits become internally tangential to the R-sphere at their apocenters; until R reaches the largest apocenter at R = B, the turning point of the L = 0 (straight line) motion determined by $|E| = |V(B)|$ for attractive interaction. Hence the density n in (2.9) is delineated as,

$$n(\underset{\sim}{R},p, \theta = \frac{\pi}{2};t) = \begin{cases} n^-(R,p, \theta = \frac{\pi}{2};t) & ; \ T > T^* = 1/2 \ R \ (\partial V/\partial R) \\ \\ \\ n^+(R,p, \theta = \frac{\pi}{2};t) & ; \ T < T^* = 1/2 \ R \ (\partial V/\partial R) \end{cases} \qquad (2.11)$$

Region I, characterized by $T < T^*$ corresponds to (E > 0, all R) and to (E < 0, $0 \leq R \leq A$) while Region II, characterized by $T < T^*$ corresponds to (E < 0, $A \leq R \leq B$).

Note that the coefficient of n in (2.9) vanishes at R = A and B. The radius of the bound circular orbit is given by the root of

$$\frac{\partial V_{eff}}{\partial R} \equiv \frac{\partial}{\partial R} \left[V + L^2/2mR^2 \right]_L = 0 \qquad (2.12)$$

which is identical with A, the root of (2.10) i.e., the circular orbit is associated with the largest value L_{max} of the allowed angular momentum, as expected. Hence, for R < A, the pericenters of all orbits with $L < L_t = Rp$ for given E lie within the R-sphere and that orbit with $L = L_t$ touches externally the R-sphere, and the apocenters for all L are all external to the R-sphere. For R = A, $L_t = L_{max}$ and the orbits are circular with the pericenters and apocenters lying on the R-sphere. For R > A, the pericenters of all L orbits

and the apocenters of those orbits with $L_t < L < L_{max}$ are within the R-sphere and the apocenters of orbits with $L < L_t$ lie without the R-sphere. The L_t-orbit is internally tangential to the R-sphere at the apocenter.

The radius A of the circular orbit for pure Coulomb attraction is $e^2/2|E|$ and the maximum turning point B is 2A. The turning points appropriate to fixed (E, L^2) are

$$R_{1,2}(E, L^2) = A[1 \pm \{1 - L^2/2m|E|A^2\}^{1/2}]; \quad A = e^2/2|E|, \qquad (2.13)$$

such that, at $R_{1,2} = A$ then $L^2[= 2m|E|A^2 = 1/2 \, me^4/|E|$ which is the maximum permissible value L_{max}^2 of L^2 for a given $|E|]$ decreases with stronger binding $|E|$. For $L = 0$, $R_1 = 0$ and $R_2 = B = 2A$. Also $T > T^* = e^2/2R$ for $E > E^* = (-e^2/2R)$. Hence (2.11) shows that $n(\frac{\pi}{2})$ is n^- for $E > 0$ at all R, is n^- for $E < 0$ and $R < A$, and is n^+ for $E < 0$ and $R > A$.

With the sum (s) and differences (d)

$$n^{s,d}(\underset{\sim}{R}, p; t) = n^+(\underset{\sim}{R}, p; t) \pm n^-(\underset{\sim}{R}, p; t) \qquad (2.14)$$

and with the <u>total</u> (s) current from, and with the <u>net</u> (d) outward current across,

$$j^{s,d}(\underset{\sim}{R}, p; t) = j^+(\underset{\sim}{R}, p; t) \pm j^-(\underset{\sim}{R}, p; t), \qquad (2.15)$$

a fixed $\hat{e}_s$-surface, then (2.9) is equivalent to the set,

$$\frac{d}{dt} n^s(\underset{\sim}{R}, p; t) = \frac{\partial n^s}{\partial t} + \frac{1}{R^2} \left[\left(\frac{\partial}{\partial R}\right)_p - \frac{m}{p^2}\left(\frac{\partial V}{\partial R}\right)\left(\frac{\partial}{\partial p}\right)_R p \right] \left[R^2 j^d(\underset{\sim}{R}, p; t) \right] \qquad (2.16a)$$

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and

$$\frac{d}{dt} n^d(\underset{\sim}{R},p;t) = \frac{\partial n^d}{\partial t} + \frac{1}{R^2}\left[\left(\frac{\partial}{\partial R}\right)_p - \frac{m}{p^2}\left(\frac{\partial V}{\partial R}\right)\left(\frac{\partial}{\partial p}\right)_R p\right]\left[R^2 j^s(\underset{\sim}{R},p;t)\right]$$

$$- \left[\frac{2}{R} - \frac{1}{(E-V)}\frac{\partial V}{\partial R}\right] n(\underset{\sim}{R},p; \theta = \frac{\pi}{2};t)v \qquad (2.16b)$$

in the $(\underset{\sim}{R},p)$-representation. The above forms are useful when $n^{\pm}(\underset{\sim}{R},p)$ are each independent of θ i.e., when the internal angular momentum states are in thermodynamic equilibrium (see Appendix A). Under this condition the set (2.16) with (2.7) and (2.8) reduces to

$$\frac{d}{dt} n^s(\underset{\sim}{R},p;t) = \frac{\partial n^s}{\partial t} + \frac{1}{2} v\left[\left(\frac{\partial n^d}{\partial R}\right)_p - \frac{m}{p}\left(\frac{\partial V}{\partial R}\right)\left(\frac{\partial n^d}{\partial p}\right)_R + \left(\frac{2}{R} - \frac{1}{(E-V)}\frac{\partial V}{\partial R}\right)n^d\right]$$
$$\qquad (2.17a)$$

for the total density n^s and to

$$\frac{d}{dt} n^d(\underset{\sim}{R},p;t) = \frac{\partial n^d}{\partial t} + \frac{1}{2} v\left[\left(\frac{\partial n^s}{\partial R}\right)_p - \frac{m}{p}\left(\frac{\partial V}{\partial R}\right)\left(\frac{\partial n^s}{\partial p}\right)_R\right]$$

$$+ \frac{1}{2} v\left[n^s - 2n(\theta = \frac{\pi}{2})\right]\left[\frac{2}{R} - \frac{1}{(E-V)}\frac{\partial V}{\partial R}\right]$$
$$\qquad (2.17b)$$

Since (2.17a) is appropriate to the L^2-equilibrium averaged value of $\underset{\sim}{\chi}$, it represents a generalization of Eqs. (2.12),(2.20) and (5.1a) of Ref. 1 which are associated only with the speed v_i along the radial direction $\hat{\underset{\sim}{R}}$.

2.4 (R,T)-transport equations.

When the kinetic energy T (= $p^2/2m$) rather than E is used as a variable,

then the corresponding densities and currents (per unit $d\underset{\sim}{R}\,dT\,d\hat{\underset{\sim}{p}}$) are

$$n(\underset{\sim}{R},T,\hat{\underset{\sim}{p}};t) = m\,p\,n(\underset{\sim}{R},\underset{\sim}{p};t) \tag{2.18}$$

and

$$j(R,T,\hat{\underset{\sim}{p}};t) = m\,p\,j(\underset{\sim}{R},\underset{\sim}{p};t) = v\,n(R,T,\hat{\underset{\sim}{p}};t) \tag{2.19}$$

respectively, such that the $\hat{\underset{\sim}{p}}$-integrated quantities which correspond to (2.14) and (2.15) satisfy,

$$\frac{d}{dt}n^{S}(\underset{\sim}{R},T;t) = \frac{\partial n^{S}}{\partial t} + \frac{1}{R^{2}}\left[\left(\frac{\partial}{\partial R}\right)_{T} - \left(\frac{\partial V}{\partial R}\right)\left(\frac{\partial}{\partial T}\right)_{R}\right]\left[R^{2}\,j^{d}(\underset{\sim}{R},T;t)\right] \tag{2.20a}$$

$$\frac{d}{dt}n^{d}(\underset{\sim}{R},T;t) = \frac{\partial n^{d}}{\partial t} + \frac{1}{R^{2}}\left[\left(\frac{\partial}{\partial R}\right)_{T} - \left(\frac{\partial V}{\partial R}\right)\left(\frac{\partial}{\partial T}\right)_{R}\right]\left[R^{2}\,j^{S}(\underset{\sim}{R},T;t)\right]$$

$$- \left[\frac{2}{R} - \frac{1}{T}\frac{\partial V}{\partial R}\right]n(\underset{\sim}{R},T,\,\theta = \frac{\pi}{2}\,;t)v \tag{2.20b}$$

In thermodynamic equilibrium (Appendix A) at temperature Θ, the conditional density factors as

$$\tilde{n}^{S}(\underset{\sim}{R},\underset{\sim}{p}) = (2\pi m\,k\,\Theta)^{-3/2}\exp(-p^{2}/2m)\exp(-V(R)/k\Theta), \tag{2.21}$$

and is independent of direction (such that $\tilde{n}^{S} = 2\tilde{n}^{+}$, $\tilde{n}^{d} = 0$). It therefore satisfies the set· (2.17), where each term vanishes separately, and the set (2.20) as expected.

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2.5 R-Transport Equations.

Integration of (2.16) over the full range $(0, \infty)$ of T therefore yields the set,

$$\frac{d}{dt} n^S(\underset{\sim}{R};t) = \frac{\partial n^S}{\partial t} + \frac{1}{R^2} \frac{\partial}{\partial R} \left[R^2 J^d(R) \right] \qquad (2.22a)$$

and

$$\frac{d}{dt} n^d(\underset{\sim}{R};t) = \frac{\partial n^d}{\partial t} + \frac{1}{R^2} \frac{\partial}{\partial R} \left[R^2 J^S(R) \right] - \left[\frac{2}{R} - \frac{2}{m} \frac{\langle v^{-1} \rangle}{\langle v \rangle} \left(\frac{\partial V}{\partial R} \right) \right] n(\underset{\sim}{R}, \theta = \frac{\pi}{2};t) \langle v \rangle$$

$$(2.22b)$$

where the macroscopic (configuration) densities are

$$n^{S,d}(\underset{\sim}{R};t) = \int_0^\infty n^{S,d}(\underset{\sim}{R},T;t) dT \qquad (2.23)$$

and the macroscopic (configuration) currents are

$$J^{S,d}(\underset{\sim}{R};t) = \int_0^\infty J^{S,d}(\underset{\sim}{R},T;t) dT \qquad (2.24)$$

The averaged speeds $\langle v^n \rangle$ in (2.22b) are determined by,

$$n(\underset{\sim}{R}, \theta = \frac{\pi}{2};t) \langle v^n \rangle = \int_0^{T^*} n^+(\underset{\sim}{R},T, \theta = \frac{\pi}{2};t) \ v^n \ dT + \int_{T^*}^\infty n^-(\underset{\sim}{R},T, \theta = \frac{\pi}{2};t) \ v^n \ dT \qquad (2.25)$$

where $T^*(R) = \frac{1}{2} R(\partial V/\partial R)$ is either the kinetic energy of a bound circular orbit of radius R, as in (2.11), or else is zero for unbound orbits, and where

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$$n(\underset{\sim}{R}, \theta = \frac{\pi}{2}; t) = \int_{0}^{T^*} n^+(\underset{\sim}{R}, T, \theta = \frac{\pi}{2}; t) dT + \int_{T^*}^{\infty} n^-(\underset{\sim}{R}, T, \theta = \frac{\pi}{2}; t) dT \qquad (2.26)$$

is the total macroscopic density at the turning points (apocenter for $T < T^*$ and pericenter for $T > T^*$).

The variable sets $(\underset{\sim}{R}, \underset{\sim}{p})$, $(\underset{\sim}{R}, p)$, $(\underset{\sim}{R}, T)$ and R are quite natural at higher gas densities N, since in the limit of high N, collisions are sufficiently rapid to establish equilibriun in p or T such that (2.3), (2.6), (2.16), (2.20) and (2.22) furnish quite naturally the appropriate non-equilibrium equations in the various variables. When there is T-equilibrium for example, $n^{\pm}$ are separately independent of p and satisfy the Maxwellian distribution

$$\frac{n^{\pm}(\underset{\sim}{R}, T; t)}{n^{\pm}(\underset{\sim}{R}; t)} = \frac{\tilde{n}{}^{\pm}(\underset{\sim}{R}, T)}{\tilde{n}{}^{\pm}(\underset{\sim}{R})} = \frac{2}{\sqrt{\pi}} \frac{1}{(k\theta)^{3/2}} T^{1/2} \exp(-T/k\theta) \qquad (2.27)$$

where the tildas ($\sim$) denote equilibrium values and where the configurational density is

$$n^{\pm}(\underset{\sim}{R}; t) = \int_{0}^{\infty} n^{\pm}(\underset{\sim}{R}, T; t) dT \qquad (2.28)$$

The appropriate non-equilibrium equations for $n^{s,d}(\underset{\sim}{R}, t)$ are then (2.22) where the currents are

$$J^{s,d}(\underset{\sim}{R}, t) = 1/2 \, n^{s,d}(\underset{\sim}{R}; t) \, \overline{v} = 1/2 \, [n^+(\underset{\sim}{R}, t) \pm n^-(\underset{\sim}{R}, t)] \, \overline{v} \qquad (2.29)$$

and where the averaged speed

$$<v> = \overline{v} = (8 \, k \, \theta/\pi m)^{1/2} \qquad (2.30)$$

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is simply the mean thermal speed. For T-equilibrium (2.27) holds such that

$$n(\underset{\sim}{R}, \theta = \frac{\pi}{2}; t)<v> = \overline{v}[n^{+}(\underset{\sim}{R},t) - n^{D}(\underset{\sim}{R},t) \{1 + (T^{*}/k\theta) \exp(-T^{*}/k\theta)\}] \quad (2.31)$$

and

$$\frac{2}{m} n(R, \theta = \frac{\pi}{2}; t)<v^{-1}> = (\overline{v}/k\theta)[n^{+}(\underset{\sim}{R},t) - n^{D}(\underset{\sim}{R},t) \exp(-T^{*}/k\theta)] \quad (2.32)$$

The macroscopic eq. (2.22b) therefore reduces to,

$$\frac{d}{dt} n^{d}(\underset{\sim}{R};t) = \frac{\partial n^{d}}{\partial t} + \frac{\overline{v}}{2R^{2}} \frac{\partial}{\partial R} [R^{2} n^{S}(R;t)]$$

$$- \frac{1}{2} \overline{v} \left[\frac{2}{R} - \frac{1}{k\theta} \frac{\partial V}{\partial R}\right][n^{S}(\underset{\sim}{R};t) + n^{d}(\underset{\sim}{R};t)] - \frac{2\overline{v}}{R} n^{d}(\underset{\sim}{R};t)\exp(-T^{*}(R)/k\theta)$$

$$(2.33)$$

which is, of course, coupled to its companion (2.22a), with J^{d} given by (2.29).

In R-equilibrium, $n^{S}(\underset{\sim}{R},t)$ is the Boltzmann distribution

$$\tilde{n}(\underset{\sim}{R}) = \exp[-V(R)/k\theta] \quad (2.34)$$

and $\tilde{n}^{S} = 2 \tilde{n}^{+}(R)$, $n^{d} = 0$. Hence both (2.22a) with (2.29) and (2.33) are satisfied in equilibrium, as expected.

At the higher gas densities N where relaxation in R becomes the rate limiting step and where collisions are sufficiently fast to promote equilibrium in p or T, then the sets of equations (2.6), (2.16), (2.20) and

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(2.22) derived above are appropriate for application from high N to intermediate N.

2.6 $(\underset{\sim}{R},E,\hat{\underset{\sim}{p}})$-Transport Equations

In the low N-limit, equilibrium in R (i.e., the Boltzmann distribution) is achieved instantaneously relative to the rate limiting step of collisional relaxation in the internal energy E. The set $(\underset{\sim}{R},E,\hat{\underset{\sim}{p}})$ of variables is therefore more natural to this situation. When the relaxation in E and in the internal angular momentum squared,

$$L^2 = R^2 p^2 \sin^2\theta = 2m[E-V(R)] R^2 \sin^2\theta \qquad (2.35)$$

are both slow in comparison with R-relaxation, then the set $(\underset{\sim}{R},E,L^2)$ of variables is more appropriate.

The probability densities germane to the various sets are related by (2.18) and by

$$n(\underset{\sim}{R},\underset{\sim}{p})d\underset{\sim}{R}\ d\underset{\sim}{p} \equiv n_1(\underset{\sim}{R},E,\hat{\underset{\sim}{p}})d\underset{\sim}{R}\ dE\ d\hat{\underset{\sim}{p}} \equiv n_2(\underset{\sim}{R},E,L^2)d\underset{\sim}{R}\ dE\ dL^2\ d\phi \qquad (2.36)$$

for the probabilities $n\ d\underset{\sim}{p}$, $n_1\ dE\ d\hat{\underset{\sim}{p}}$ and $n_2\ dE\ dL^2\ d\phi$ that the pair with internal separation in the interval $d\underset{\sim}{R}$ about $\underset{\sim}{R}$ has the physical quantities $\underset{\sim}{p}$, $(E,\hat{\underset{\sim}{p}})$, or (E,L^2,ϕ) in the associated intervals. Hence the various probability densities are related by

$$n(\underset{\sim}{R},\underset{\sim}{p}) = R^2 n_1(\underset{\sim}{R},E,\hat{\underset{\sim}{p}})v/R^2 p^2 = 2R^2\ n_2(\underset{\sim}{R},E,L^2)v\ \cos\theta \qquad (2.37)$$

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In what follows the ϕ-integrations are implied unless otherwise indicated. In (2.36) the bound levels (E,L^2) of the AB-pair are assumed to lie sufficiently close (relative to the thermal energy $k\Theta$ of the gas bath) that they form a quasi-continuum in energy E and angular momentum L. This restriction is not essential and can be removed by appropriate discretization of the continuous variables E and L^2.

With the recognition that

$$\left(\frac{\partial}{\partial R}\right)_E \equiv \left(\frac{\partial}{\partial R}\right)_p - \frac{m}{p}\left(\frac{\partial V}{\partial R}\right)\left(\frac{\partial}{\partial p}\right)_R \qquad (2.38)$$

where the subscript denotes that quantity held constant throughout the appropriate differentiation, then the basic $(\underset{\sim}{R},\underset{\sim}{p})$-equation,(2.3) with (2.4) and (2.36),in the $(R,E,\hat{\underset{\sim}{p}})$-representation is equivalent to,

$$\frac{d}{dt}\, n_1(\underset{\sim}{R},E,\hat{\underset{\sim}{p}};t) = \frac{\partial n_1}{\partial t} + \left[\frac{1}{R^2}\frac{\partial}{\partial R}\,(R^2\,n_1\,v\,\cos\theta)_{E,\theta} + \right.$$

$$\left.\frac{1}{2}\,v\,\{\frac{2}{R} - \frac{1}{(E-V)}\frac{\partial V}{\partial R}\}\,\frac{\partial}{\partial(\cos\theta)}\,(n_1\,\sin^2\theta)_{R,E}\right] \qquad (2.39)$$

which is the conservative form similar to (2.3a),since the angular redistribution term, when integrated over the full range of θ, vanishes as with (2.3a).

2.7 $(\underset{\sim}{R},E,L^2)$-Transport Equations.

The transformation $\underset{\sim}{p} \rightarrow (E,L^2,\phi)$ in

$$n(\underset{\sim}{R},\underset{\sim}{p}) = n(\underset{\sim}{R},E(p,R),\,L^2(p,R,\theta),\,\phi) \qquad (2.40)$$

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may be accomplished via use of the derived identities,

$$\left(\frac{\partial n}{\partial R}\right)_{p,\theta} = \left(\frac{\partial n}{\partial R}\right)_{E,L^2} + \left(\frac{\partial n}{\partial E}\right)_{\underset{\sim}{R},L^2} \left(\frac{\partial E}{\partial R}\right)_p + \left(\frac{\partial n}{\partial L^2}\right)_{R,E} \left(\frac{\partial L^2}{\partial R}\right)_{p,\theta} \tag{2.41a}$$

$$\left(\frac{\partial n}{\partial p}\right)_{\underset{\sim}{R},\theta} = \left(\frac{\partial n}{\partial E}\right)_{p,L^2} \left(\frac{\partial E}{\partial p}\right)_R + \left(\frac{\partial n}{\partial L^2}\right)_{\underset{\sim}{R},E} \left(\frac{\partial L^2}{\partial p}\right)_{R,\theta} \tag{2.41b}$$

$$\left[\frac{\partial n}{\partial(\cos\theta)}\right]_{\underset{\sim}{R},p} = \left(\frac{\partial n}{\partial L^2}\right)_{\underset{\sim}{R},E} \left[\frac{\partial L^2}{\partial(\cos\theta)}\right]_{R,p} \tag{2.41c}$$

Also the derived identity

$$\left(\frac{\partial}{\partial R}\right)_{E,L^2} = \left(\frac{\partial}{\partial R}\right)_{E,\theta} + \frac{\sin^2\theta}{2\cos\theta} \left\{ \frac{2}{R} - \frac{1}{(E-V)} \frac{\partial V}{\partial R} \right\} \left[\frac{\partial}{\partial(\cos\theta)}\right]_{R,E} \tag{2.41d}$$

is valuable for transformation between derivatives taken with respect to fixed L^2 and fixed θ, respectively.

Hence (2.3a) reduces after some analysis simply to

$$\frac{d}{dt} n(\underset{\sim}{R},\underset{\sim}{p};t) = \frac{\partial n}{\partial t} + v\cos\theta \left[\frac{\partial}{\partial R} n(\underset{\sim}{R},\underset{\sim}{p};t)\right]_{E,L^2} \tag{2.42a}$$

for $n(R,p;t)$, or with the aid of (2.37) for $n_1(\underset{\sim}{R},E,\hat{\underset{\sim}{p}})$ to

$$\frac{d}{dt} n_1(\underset{\sim}{R},E,\hat{\underset{\sim}{p}};t) = \frac{\partial n_1}{\partial t} + \frac{(R^2 p^2 \cos\theta)}{R^2} \frac{\partial}{\partial R} \left[R^2 n_1(\underset{\sim}{R},E,\hat{\underset{\sim}{p}};t) v/R^2 p^2\right]_{E,L^2} \tag{2.42b}$$

which, with the aid of (2.41d) can be shown to be identical with the conservative form (2.39) for $n_1(\underset{\sim}{R},E,\hat{\underset{\sim}{p}};t)$. In the $(\underset{\sim}{R},E,L^2)$-representation, (2.42a) is equivalent to

$$\frac{d}{dt} n_2(\underset{\sim}{R},E,L^2;t) = \frac{\partial n_2}{\partial t} + \frac{1}{R^2} \frac{\partial}{\partial R} \left[R^2 n_2(\underset{\sim}{R},E,L^2;t) v\cos\theta\right]_{E,L^2} \tag{2.43a}$$

for $n_2(\underset{\sim}{R},E,L^2;t)$ of (2.36) in terms of quantities (E,L^2) which are naturally

conserved in the absence of collisions with the gas. An equivalent and useful

form of (2.42a) is obtained from (2.37) and (2.42b) as,

$$\frac{d}{dt} n_2(\underset{\sim}{R},E,L^2;t) = \frac{\partial n_2}{\partial t} + \frac{1}{2R^2} \frac{\partial}{\partial R} \left[n_1(\underset{\sim}{R},E,\hat{\rho};t) v/p^2 \right]_{E,L^2} \qquad (2.43b)$$

In contrast to (2.3) for $n(\underset{\sim}{R},\underset{\sim}{\rho})$, and to (2.39) for $n_1(\underset{\sim}{R},E,\hat{\rho})$, the

microscopic vector current

$$\underset{\sim}{j_2}(\underset{\sim}{R},E,L^2;t) = n_2(\underset{\sim}{R},E,L^2;t)\underset{\sim}{v} \quad , \qquad (2.44)$$

associated with the density n_2 of particles with fixed internal energy E and

angular momentum L, across a fixed surface therefore satisfies the simple

transport equation

$$\frac{dn}{dt} = \frac{\partial n}{\partial t} + \frac{1}{R^2} \frac{\partial}{\partial R} (R^2 J_R) \qquad (2.45)$$

where $n = n_2(\underset{\sim}{R},E,L^2)$, the microscopic density, and J_R is the outward radial

component of the microscopic current (2.44).

In spite of the neat simplicity of (2.45) this is the first time to the

author's knowledge that the transport terms in the left-hand-side (2.3) of the

Boltzmann-like equation (2.1), have been written as (2.43a) in terms of the

conserved quantities (E,L^2) of a collisionless plasma being held fixed upon

the R-differentiation. The form (2.45) is normally reserved only for the

macroscopic net current $\underset{\sim}{J}(R)$ of all particles integrated over all vector

momenta $\underset{\sim}{\rho}$ (in magnitude and in direction). In equilibrium, $(R^2 n_2 v \cos\theta)$ is

a function only of E (cf. Appendix A) such that the streaming (gradient) term in (2.43) vanishes, as expected.

Introduce $n_2^{\pm}(\underset{\sim}{R},E,L^2;t)$ to distinguish those pairs with the same values of $(\underset{\sim}{R},E,L^2)$ and therefore of

$$|\cos\theta| = [1 - L^2/R^2 p^2]^{1/2} \quad , \tag{2.46}$$

but with $\hat{\underset{\sim}{p}}$ directed at θ with $\hat{\underset{\sim}{e}}_S$ into the positive (+) region, $0 < \theta < \frac{\pi}{2}$, or into the negative (-) region $\frac{\pi}{2} < \theta < \pi$. Under this distinction, the transport equation (2.43) is therefore equivalent to the set

$$\frac{d}{dt} n^{\pm}(\underset{\sim}{R},E,L^2;t) = \frac{\partial n^{\pm}}{\partial t} \pm \frac{1}{R^2} \frac{\partial}{\partial R} \left[R^2\, n^{\pm}(\underset{\sim}{R},E,L^2;t) v|\cos\theta|\right]_{E,L^2} \tag{2.47a}$$

for $n^{\pm}$, or to the set,

$$\frac{d}{dt} n^S(\underset{\sim}{R},E,L^2;t) = \frac{\partial n^S}{\partial t} + \frac{1}{R^2} \frac{\partial}{\partial R}\, [R^2\, j^d(\underset{\sim}{R},E,L^2;t)]_{E,L^2} \tag{2.47b}$$

$$\frac{d}{dt} n^d(\underset{\sim}{R},E,L^2;t) = \frac{\partial n^d}{\partial t} + \frac{1}{R^2} \frac{\partial}{\partial R}\, [R^2\, j^S(\underset{\sim}{R},E,L^2;t)]_{E,L^2} \tag{2.47c}$$

for the sum (s) and difference (d),

$$n^{s,d}(\underset{\sim}{R},E,L^2;t) = n_2^{+}(\underset{\sim}{R},E,L^2;t) \pm n_2^{-}(\underset{\sim}{R},E,L^2;t) \tag{2.48}$$

of those (E,L^2) pairs which are expanding (+) or contracting (-) across R with associated total (s) and net (d) currents

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$$j^{s,d}(\underset{\sim}{R},E,L^2;t) = n^{s,d}(\underset{\sim}{R},E,L^2;t)v|\cos\theta| \qquad (2.49)$$

with direction $\hat{\underset{\sim}{p}}$ at angle θ with the normal $\hat{\underset{\sim}{e}}_s$ to the fixed surface. The set (2.47) represents quite a formal simplification over the corresponding set (2.6) in the equivalent $(\underset{\sim}{R},p,|\cos\theta|)$-representation.

On integrating (2.43b) over the configuration volume between two spheres of radii $R_1(E,L^2)$ and $R_2(E,L^2)$, the turning points (pericenter and apocenter) for bound $(E < 0)$ orbits and on recalling that n at R_1 and R_2 is n^- and n^+ respectively, then,

$$\frac{d}{dt} n^{\pm}(E,L^2;t) = \frac{\partial n^{\pm}}{\partial t} \pm 2\pi\left[(v_2/p_2^2)n\,(\underset{\sim}{R}_2,E,\theta=\pi/2;t) - (v_1/p_1^2)n^-(\underset{\sim}{R}_1,E,\theta=\pi/2;t)\right]$$

$$(2.50)$$

where p_i and v_i are the momenta and speeds at $R_i(i=1,2)$. Hence

$$n^{s,d}(E,L^2;t) \equiv n^+(E,L^2;t) \pm n^-(E,L^2;t) = \int_{R_1(E,L^2)}^{R_2(E,L^2)} n^{s,d}(\underset{\sim}{R},E,L^2;t)\,d\underset{\sim}{R}$$

$$(2.51)$$

satisfy the set

$$\frac{d}{dt} n^s(E,L^2;t) = \frac{\partial}{\partial t} n^s(E,L^2;t) \qquad (2.52a)$$

and

$$\frac{d}{dt} n^d(E,L^2;t) = \frac{\partial n^d}{\partial t} + 4\pi\left[(v_2/p_2^2)n^+(\underset{\sim}{R}_2,E,\theta=\pi/2;t)\right.$$

$$\left. - (v_1/p_1^2)n^-(\underset{\sim}{R}_1,E,\theta=\pi/2;t)\right] \qquad (2.52b)$$

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The significance of the source/sink term in (2.52b) becomes transparent upon assuming $\underset{\sim}{R}$-equilibrium when (Appendix A),

$$\frac{n(\underset{\sim}{R},E,L^2;t)}{n(E,L^2;t)} = \frac{\tilde{n}(\underset{\sim}{R},E,L^2)}{\tilde{n}(E,L^2)} = \left[2\pi R^2 \ v|\cos\theta|\tau_R(E,L^2)\right]^{-1} \qquad (2.53)$$

where τ_R is the time to complete one radial orbit $(R_1 \to R_2 \to R_1)$ for fixed E and L^2. With the aid of (2.37), (2.52b) therefore reduces to

$$\frac{d}{dt} n^d(E,L^2;t) = \frac{\partial n^d}{\partial t} + 4n^d(E,L^2;t)/\tau_R(E,L^2) \qquad (2.54)$$

which with (2.51a) yields,

$$\frac{d}{dt} n^{\pm}(E,L^2;t) = \frac{\partial n^{\pm}}{\partial t} \pm 2(n^+-n^-)/\tau_R(E,L^2); \quad E < 0 \qquad (2.55a)$$

i.e., at every half periods, expanding (+) pairs in bound orbits are converted by transport at the apocenter into contracting-pairs, and contracting (-) pairs are converted at the pericenter into expanding (+) pairs. For unbounded ($E > 0$) orbits only the pericenter R_1 is relevant. Since $n^{\pm} \to \frac{1}{2} \tilde{n}$ as $R \to \infty$ then (2.55a) is replaced by

$$\frac{d}{dt} n^{\pm}(E,L^2;t) = \frac{\partial n^{\pm}}{\partial t} \mp 2n^-/\tau_R(E,L^2); \quad E > 0 \qquad (2.55b)$$

such that transport converts contracting (-) pairs to expanding (+) pairs at the pericenter. Hence each set (2.50) or (2.52) of transport equations yields quite naturally the radial period under $\underset{\sim}{R}$-equilibrium and therefore contains rather instructive information, particularly useful when orbital and collisional times are to be compared.

2.8 (R,E)-Transport Equations

Since L^2 in (2.35) varies between 0 and $L_t^2 = R^2p^2$ for fixed R and E as $\hat{p}$ varies within each __separate__ (+) or (−) region, the use of Leibnitz's rule[22] for R-differentiation of an integral with variable R-limits yields,

$$\int_0^{R^2p^2} \frac{1}{R^2} \frac{\partial}{\partial R} (R^2 n_2 v \cos\theta)_E dL^2 = \frac{1}{R^2} \frac{\partial}{\partial R} \left[R^2 \int_0^{R^2p^2} n_2 v \cos\theta \ L^2 \right]_E$$

$$- \left[n_2 v \cos\theta \right]_{\theta=\pi/2} \left[\frac{\partial}{\partial R} (R^2p^2) \right]_E \quad (2.56)$$

With the aid of (2.37)

$$j(\underset{\sim}{R},E,L^2;t) = n_2(\underset{\sim}{R},E,L^2;t)v \ |\cos\theta| = n_1(\underset{\sim}{R},E,\theta;t)v/(2R^2p^2) \quad (2.57)$$

and with the aid of (2.10), the L^2-integration of (2.43) over the range $(0 \rightarrow L_t^2)$ therefore yields

$$\frac{d}{dt} n^{\pm}(\underset{\sim}{R},E;t) = \frac{\partial n^{\pm}}{\partial t} \pm \frac{1}{R^2} \frac{\partial}{\partial R} \left[R^2 \ j^{\pm}(\underset{\sim}{R},E;t) \right]_E \mp \frac{1}{2} v \left[\frac{2}{R} - \frac{1}{(E-V)} \frac{\partial V}{\partial R} \right]$$

$$n_1(\underset{\sim}{R},E,\theta= \frac{\pi}{2};t) \quad (2.58)$$

for the integrated densities

$$n^{\pm}(\underset{\sim}{R},E;t) = \int_0^{L_t^2} n_2^{\pm}(\underset{\sim}{R},E,L^2;t)dL^2 \quad (2.59)$$

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and currents

$$j^{\pm}(\underset{\sim}{R},E;t) = v \int_{o}^{L_t^2} n_2^{\pm}(\underset{\sim}{R},E,L^2;t) |\cos\theta| dL^2 \equiv n^{\pm}(\underset{\sim}{R},E;t) \, v<|\cos\theta|> \qquad (2.60)$$

The equivalent set of equations for

$$n^{s,d}(\underset{\sim}{R},E;t) = n^{+}(\underset{\sim}{R},E;t) \pm n^{-}(\underset{\sim}{R},E;t) \qquad (2.61)$$

and the corresponding currents

$$j^{s,d}(\underset{\sim}{R},E;t) = j^{+}(\underset{\sim}{R},E;t) \pm j^{-}(\underset{\sim}{R},E,t) \qquad (2.62)$$

which are the total (s) and net(d) rates (per unit $d\underset{\sim}{R}$ dE) at which particles with speed v leave or cross a surface with normal $\hat{e}_S$ oriented along the fixed direction $\underset{\sim}{R}$, is

$$\frac{d}{dt} n^{s}(\underset{\sim}{R},E;t) = \frac{\partial n^{s}}{\partial t} + \frac{1}{R^2} \frac{\partial}{\partial R} \left[R^2 \, j^{d}(\underset{\sim}{R},E;t) \right]_E \qquad (2.63a)$$

and

$$\frac{d}{dt} n^{d}(\underset{\sim}{R},E;t) = \frac{\partial n^{d}}{\partial t} + \frac{1}{R^2} \frac{\partial}{\partial R} \left[R^2 \, j^{s}(\underset{\sim}{R},E;t) \right]_E$$

$$- v \left[\frac{2}{R} - \frac{1}{(E-V)} \frac{\partial V}{\partial R} \right] n_1(\underset{\sim}{R},E,\frac{\pi}{2};t) \qquad (2.63b)$$

On integration of (2.39) for $n_1(\underset{\sim}{R},E,\hat{\underset{\sim}{p}};t)$ over the positive (+) region $0 < \theta < \frac{\pi}{2}$, and the negative (-), $\frac{\pi}{2} < \theta < \pi$, region of $\hat{\underset{\sim}{p}}$, the above set (2.58) for

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$$n^{\pm}(\underset{\sim}{R},E;t) = \underset{(+,-)}{\int} n_1(\underset{\sim}{R},E,\hat{\rho};t)d\hat{\rho} \qquad (2.64)$$

$$j^{\pm}(\underset{\sim}{R},E;t) = v\underset{(+,-)}{\int} n_1(\underset{\sim}{R},E,\hat{\rho};t)|\cos\theta| \, d\hat{\rho} \qquad (2.65)$$

and the set (2.63) for $n^{s,d}$ also follow directly, since the $\underset{\sim}{R}$-differential

operator in (2.39) and the $\hat{\rho}$-integral operator in (2.64) simply commute. On

integrating (2.63) over the full range $-V(R) \leq E \leq \infty$ of energies E, and with

the use of Leibnitz's rule, the macroscopic set (2.22) of equations, for

$$n^{s,d}(\underset{\sim}{R}) = \int_{-V(R)}^{\infty} n^{s,d}(\underset{\sim}{R},E;t) \, dE \qquad (2.66)$$

and

$$J^{s,d}(\underset{\sim}{R}) = \int_{-V(R)}^{\infty} j^{s,d}(\underset{\sim}{R},E;t) \, dE \qquad (2.67)$$

is also reproduced with the averaged speeds determined by

$$n_1(R, \theta = \tfrac{\pi}{2};t)<v^n> = \int_{-V}^{E^*} n_1^+(R,E, \theta = \tfrac{\pi}{2};t)v^n \, dE + \int_{E^*}^{\infty} n_1^-(\underset{\sim}{R},E, \theta = \tfrac{\pi}{2};t)v^n \, dE \qquad (2.68)$$

where

$$E^* = 1/2 \, R \left(\frac{\partial V}{\partial R} \right) - V(R) \qquad (2.69)$$

corresponds to T^* of (2.11), and is the energy of a bound circular orbit of

radius R.

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For pure Coulombic attraction, $E^* = -e^2/2R < 0$; for $V \sim R^{-2}$, E^* is zero; and for $V = -\alpha e^2/2R^4$ then E^* is $\alpha e^2/2R^4 > 0$.

2.9 E-Transport Equations

On integrating (2.63) over all accessible $\underset{\sim}{R}$, then the equations satisfied by,

$$n^{s,d}(E;t) = \int_0^{R_i} n^{s,d}(\underset{\sim}{R},E;t) \; d\underset{\sim}{R} \tag{2.70}$$

where R_i is either the outermost turning point B determined by $|E| = |V(R_i)|$ for $E < 0$ or is infinity for $E > 0$, are

$$\frac{d}{dt} n^s(E;t) = \frac{\partial}{\partial t} n^s(E;t) \tag{2.71a}$$

for n^s, since the <u>net</u> flux $4\pi R^2 j^d(R,E;t)$ vanishes at both R_i and zero and

$$\frac{d}{dt} n^d(E \geqslant 0;t) = \frac{\partial n^d}{\partial t} + \lim_{R\to\infty} [4\pi R^2 j^s(\underset{\sim}{R},E;t)] - 4\pi \int_0^\infty n_1^-(\underset{\sim}{R},E, \theta = \frac{\pi}{2};t)$$

$$\times \left[\frac{v}{p^2} \frac{\partial}{\partial R} (R^2 p^2)_E \right] dR \tag{2.71b}$$

$$\frac{d}{dt} n^d(E \leqslant 0;t) = \frac{\partial n^d}{\partial t} - 4\pi \left[\int_0^A n_1^-(R,E, \theta = \frac{\pi}{2};t) + \int_A^{R_1} n_1^+(\underset{\sim}{R},E, \theta = \frac{\pi}{2};t) \right]$$

$$\times \left[\frac{v}{p^2} \frac{\partial}{\partial R} (R^2 p^2)_E \right] dR \tag{2.71c}$$

for n^d since the <u>total</u> current j^s vanishes at both 0 and R_i. Also A in

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(2.71c) is the root of (2.10) for constant E i.e., where $\frac{\partial}{\partial R}$ $(R^2 p^2)_E$ vanishes.

The physical significance of the above terms becomes apparent upon examination under thermodynamic equilibrium in $\underset{\sim}{R}$ and θ when (Appendix A)

$$\frac{n(\underset{\sim}{R},E)}{n(E)} = \frac{\tilde{n}(\underset{\sim}{R},E)}{\tilde{n}(E)} \tag{2.72}$$

such that (2.71b,c) reduce in this limit to

$$\frac{d}{dt} n^d(E \geq 0;t) = \frac{\partial n^d}{\partial t} - n^-(E;t)\Big[E-V(A)\Big]A^2 / \int_o^B pR^2 dR \tag{2.73a}$$

exactly, since the total transport can be shown to vanish for $\underset{\sim}{R}$-equilibrium, and to

$$\frac{d}{dt} n^d(E<0;t) = \frac{\partial n^d}{\partial t} + n^d(E;t)[E-V(A)]A^2 / \int_o^B p\ R^2\ dR \tag{2.73b}$$

For Coulombic attraction, $A = e^2/2|E|$ is the semi-major axis and

$$\Big[E-V(A)\Big]A^2 \left[\int_o^B pR^2 dR\right]^{-1} = \frac{1}{2}\ 2\pi\left[\frac{e^2}{2|E|}\right]^{3/2} \left(\frac{m}{e^2}\right)^{1/2} = \frac{1}{2}\ \tau(|E|) \tag{2.73c}$$

is simply half the time period τ for a bound orbit of energy E. For Coulomb attraction therefore

$$\frac{d}{dt} n^d (E \geq 0;t) = \frac{\partial n^d}{\partial t} - 4n^-(E;t)/\tau(E) \tag{2.74a}$$

$$\frac{d}{dt} n^d (E<0;t) = \frac{\partial n^d}{\partial t} + 4n^d (E;t)/\tau(E) \tag{2.74b}$$

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which, with (2.71a) yields

$$\frac{d}{dt} n^{\pm}(E>0;t) = \frac{\partial}{\partial t} n^{\pm} \mp 2n^{-}/\tau(E)$$

$$\frac{d}{dt} n^{\pm}(E<0;t) = \frac{\partial}{\partial t} n^{\pm} \pm 2(n^{+}-n^{-})/\tau(E)$$

(2.75)

i.e., after every half-period $(\frac{\tau}{2})$ expanding (+) pairs in bound orbits (E < 0) are naturally converted at the apocenter into contracting (−) pairs which in turn (for bound and unbounded orbits) are converted at the pericenter into expanding (+) pairs. This result is quite general in that it can also be deduced from the corresponding eq. (2.54) for (E,L^2)-nonequilibrium in terms of the averaged radial frequency

$$\nu_R(E) = 1/\tau_R(E) = \int [n(E,L^2)/\tau(E,L^2)]dL^2/n(E) \qquad (2.76)$$

In this section the basic transport eq. (2.1a) has therefore been represented in various forms (2.6), (2.17), (2.20), 2.22), (2.39), (2.47), (2.52), and (2.63) appropriate, respectively, to the sets - $(\underset{\sim}{R},\underset{\sim}{p})$, $(\underset{\sim}{R},p)$, $(\underset{\sim}{R},T)$, $\underset{\sim}{R}$, $(\underset{\sim}{R},E,p)$, $\underset{\sim}{R},E,L^2)$, (E,L^2) and $(\underset{\sim}{R},E)$ - of variables all pertinent to various ranges of gas densities N. At low → intermediate N, the set $(\underset{\sim}{R},E,L^2)$ is more natural than the set $(\underset{\sim}{R},T)$ which in turn becomes more appropriate for intermediate → high N. The transport equation assumes for the set $(\underset{\sim}{R},E,L^2)$ a particularly simple form (2.43a) normally reserved only for configuration densities (i.e., phase densities $n(\underset{\sim}{R},\underset{\sim}{p})$ integrated over $\underset{\sim}{p}$). This form is also preserved by $n^s(\underset{\sim}{R},E;t)$ in (2.63a) but not by $n^d(\underset{\sim}{R},E;t)$ in (2.63b) due to the conversions at the turning points.

The coupled equations (2.22a) and (2.22b) must in principle be solved to yield the net current $j^d(R)$ in configuration space. It has already been shown[1] via the continuity and momentum equations [which are $\underset{\sim}{v}^s$ velocity

averaged moments (s = 0 and 1, respectively) of Boltzmann's eq. (2.1b)] that J^d may be expressed, to a very good approximation, in terms of the total density n^S, by

$$\underset{\sim}{J}^{d}(\underset{\sim}{R},t) = \int n(\underset{\sim}{R},\underset{\sim}{\rho};t)\underset{\sim}{v}\, d\underset{\sim}{\rho}$$

$$= - D \underset{\sim}{\nabla} n^{S}(\underset{\sim}{R},t) - (K/e)(\underset{\sim}{\nabla}V)n^{S}(\underset{\sim}{R};t) \qquad (2.76)$$

where $D = D_A + D_B$ is the diffusion coefficient and $K = K_A + K_B$ is the mobility for the relative diffusional-drift of A and B in the gas M, in terms of the individual coefficients $D_{A,B}$ and mobilities $K_{A,B}$ for each individual species A or B in the gas. This recognition permitted [1] the overall rate α of the process to be analyzed[1] in terms of rates, α_{RN} and α_{TR}, for reaction and transport rates, respectively, which provided great insight to the overall variation of α with gas density. It also helps to establish (§5.3) the microscopic foundation of the Debye-Smoluchowski Equation.

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3. Full Transport-Collisional Equations

The collisional rate (2.1b) in the basic equation (2.1) for the development of the two-particle correlation function $n(\underset{\sim}{R},\underset{\sim}{p};t)$ for (A-B) pairs has been transformed to the $(\underset{\sim}{R},E,L^2)$-representation in Appendix B. With the aid of (2.47a) the full Transport-Collisional Master Equation is then

$$\frac{d}{dt} n_i^{\pm}(\underset{\sim}{R},E_i,L_i^2;t) = \frac{\partial n_i^{\pm}}{\partial t} \pm \frac{1}{R^2} \frac{\partial}{\partial R} [R^2 n_i^{\pm}(R,E_i,L_i^2;t)v|\cos\theta|]_{E_i,L_i^2}$$

$$= \int_{-V_i(R)}^{\infty} dE_f \int_{L_f^2=0}^{L_{tf}^2} dL_f^2 [n_f^{\pm}(\underset{\sim}{R};t)v_{if}(R) - n_i^{\pm}(\underset{\sim}{R};t)v_{fi}(R)] \qquad (3.1)$$

where the i-index specifies the combined internal energy E_i and internal angular momentum squared L_i^2 of the AB pair and where the direction cosine is

$$|\cos\theta| = |\hat{R}\cdot\hat{p}_i| = (1 - L^2/L_{ti}^2)^{1/2} \qquad (3.2)$$

in terms of the maximum internal angular momentum squared

$$L_{ti}^2 \equiv L_t^2(E_i,R) = 2m[E_i - V(R)]R^2 \qquad (3.3)$$

consistent with a fixed internal energy E_i and separation R. Also

$$V_i(R) = V(R) + L_i^2/2mR^2 \qquad (3.4)$$

is the effective radial interaction so that $-V_i(R)$ in (3.1) is the energy of the lowest vibrational level of AB consistent with separation R. The collision kernel $v_{if}(\underset{\sim}{R},E_i,L_i^2;E_f,L_f^2)dE_f dL_f^2$ is the frequency (s^{-1}) for the transitions

$(\underset{\sim}{R},E_i,L_i{}^2) \rightarrow (\underset{\sim}{R},E_f+dE_f, L_f{}^2+dL_f{}^2)$ in the AB pair by collision with the gas species M, under the assumption that $\underset{\sim}{R}$ remains fixed during the encounter between (A-B) and M, an excellent approximation[9] for ion-ion recombination. The superscripts $(\pm)$ indicate, as before, pairs which are radially-expanding $(+)$, $\cos\theta > 0$, or radially-contracting $(-)$, $\cos\theta < 0$, under the provision (2.11) that $n_i(R,E_i,L^2_{ti};t)$ is $n_i{}^-(\frac{\pi}{2})$ when $E > E^*$ (region I) where

$$E^* = V + 1/2\ R(\partial V/\partial R) \qquad (3.5)$$

and is $n_i{}^+(\frac{\pi}{2})$ when $E < E^*$ (region II). Since a closed system is assumed, the irreversible loss term $n_i \nu_i$ in (2.1b) can therefore be neglected in (3.1).

3.1 $(\underset{\sim}{R},E,L^2)$-Equations.

Introduce the distribution

$$\gamma_i^{s,d}(\underset{\sim}{R};t) = n_i^{s,d}(\underset{\sim}{R},E_i,L_i{}^2;t)/\tilde{n}_i(\underset{\sim}{R},E_i,L_i{}^2) \qquad (3.6a)$$

normalized to the conditional probability density $\tilde{n}_i$ for thermodynamic equilibrium (see Appendix A) so that

$$n_i^{\pm}(\underset{\sim}{R},E_i,L^2;t) = \frac{1}{2}\ (\gamma_i^s \pm \gamma_i^d)\ \tilde{n}_i(\underset{\sim}{R},E_i,L^2) \qquad (3.6b)$$

The distribution γ_i is then independent of whatever variable $\underset{\sim}{R},E_i$ or L_i^2 is associated with equilibrium. With the aid of the appropriate set (2.47b,c) of transport equations, the Master Equation (3.1) therefore yields the set

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$$\frac{d}{dt} n_i^s(\underset{\sim}{R},E_i,L_i^2;t) = \frac{\partial n_i^s}{\partial t} + \frac{1}{R^2} \frac{\partial}{\partial R} \left[R^2 \; j_i^d(\underset{\sim}{R};t)\right]_{E_i,L_i^2}$$

$$= \int_{-V_i(R)}^{\infty} dE_f \int_{0}^{L_{tf}^2} dL_f^2 \left[\gamma_f^s(\underset{\sim}{R};t) - \gamma_i^s(\underset{\sim}{R};t)\right] \; C_{if}(\underset{\sim}{R},E_i,L_i^2;E_f,L_f^2) \quad (3.7a)$$

and

$$\frac{d}{dt} n_i^d(\underset{\sim}{R},E_i,L_i^2;t) = \frac{\partial n_i^d}{\partial t} + \frac{1}{R^2} \frac{\partial}{\partial R} \left[R^2 \; j_i^s(\underset{\sim}{R};t)\right]_{E_i,L_i^2}$$

$$= \int_{-V_i}^{\infty} dE_f \int_{0}^{L_{tf}^2} dL_f^2 \left[\gamma_f^d(\underset{\sim}{R};t) - \gamma_i^d(\underset{\sim}{R};t)\right] \; C_{if}(\underset{\sim}{R},E_i,L_i^2;E_f,L_f^2) \quad (3.7b)$$

where $i \equiv (E_i,L_i^2)$. Also,

$$n_i^{s,d}(\underset{\sim}{R},E_i,L^2;t) = [n_i^+(\underset{\sim}{R},E_i,L^2;t) \pm n_i^-(\underset{\sim}{R},E_i,L^2;t)] = \gamma_i^{s,d} \; \tilde{n}_i(\underset{\sim}{R},E_i,L_i^2) \quad (3.8)$$

and

$$j_i^{s,d}(\underset{\sim}{R},E_i,L^2;t) = n_i^{s,d}(\underset{\sim}{R},E_i,L^2;t) \; v|\cos\theta| = \gamma_i^{s,d} \; \tilde{j}_i(\underset{\sim}{R},E_i,L_i^2) \quad (3.9)$$

are the densities and corresponding currents for fixed $(\underset{\sim}{R},E_i,L_i^2)$. The equilibrium rate for $i(E_i,L_i^2) \rightarrow f(E_f,L_f^2)$ collisional transitions at fixed internal separation $\underset{\sim}{R}$ is

$$C_{if}(\underset{\sim}{R},E_i,L_i^2;E_f,L_f^2) = \tilde{n}_i(\underset{\sim}{R}) \; \nu_{if}(R) = \tilde{n}_f(R) \; \nu_{fi}(R) = C_{fi}(\underset{\sim}{R},E_f,L_f^2;E_i,L_i^2),$$
$$(3.10)$$

and satisfies detailed balance. Dependence on the density N of the thermal gas M occurs both via the (transport) coupling between n_i^s and n_i^d in (3.7) and the linear dependence on N of the collision frequency (per unit $d\underset{\sim}{R} \; dE_i \; dL_i^2$),

$$\nu_{if} = N \, k_{if}(\underset{\sim}{R}, E_i, L_i{}^2; E_f, L_f{}^2) \tag{3.11}$$

where k_{if} is the ($cm^3 \, s^{-1}$) rate for $i \to f$ transitions by collision between one pair (A-B) with separation $\underset{\sim}{R}$ and one gas atom M (see Appendix B).

3.2 (R,E)-Equations.

With the aid of the appropriate set of transport Eqns. (2.63a,b), integration of (3.7) over all accessible $L_i{}^2$ yields the set,

$$\frac{d}{dt} n_i^s(\underset{\sim}{R}, E_i; t) = \frac{\partial n_i^s}{\partial t} + \frac{1}{R^2} \frac{\partial}{\partial R} \left[R^2 \, j_i^d(\underset{\sim}{R}; t) \right]_{E_i} \int_{-V(R)}^{\infty} dE_f \left[\gamma_f^s(\underset{\sim}{R}; t) - \gamma_i^s(\underset{\sim}{R}; t) \right] C_{if}(\underset{\sim}{R}) \tag{3.12a}$$

$$\frac{d}{dt} n_i^d(\underset{\sim}{R}, E_i; t) = \frac{\partial n_i^d}{\partial t} + \frac{1}{R^2} \frac{\partial}{\partial R} \left[R^2 j_i^s(\underset{\sim}{R}; t) \right]_{E_i} - n_1(\underset{\sim}{R}, E_i, \theta = \tfrac{\pi}{2}; t) v \left[\frac{2}{R} - \frac{1}{(E-V)} \frac{\partial V}{\partial R} \right]$$

$$= \int_{-V(R)}^{\infty} dE_f \left[\gamma_f^d(\underset{\sim}{R}; t) - \gamma_i^d(\underset{\sim}{R}; t) \right] C_{if}(R) \tag{3.12b}$$

in variables $\underset{\sim}{R}$ and E_i for the integrated densities,

$$n_1^{s,d}(\underset{\sim}{R}, E_i; t) = \int_0^{L_{ti}^2} n_1^{s,d}(\underset{\sim}{R}, E_i, L_i{}^2; t) dL_i{}^2 \tag{3.13}$$

and the integrated currents,

$$j_1^{s,d}(\underset{\sim}{R}, E_i; t) = v \int_0^{L_{ti}^2} n_1^{s,d}(\underset{\sim}{R}, E_i, L_i{}^2; t) |\cos\theta| dL_i{}^2 \tag{3.14}$$

$$= v \int n_1^{s,d}(R, E_i, L_i^2; t) |\cos\theta| d\hat{\underset{\sim}{R}} \equiv v \, n_1^{s,d}(\underset{\sim}{R}, E_i; t) \langle \cos\theta \rangle$$

Note in (3.12b) that n_1 is the angular density per unit $d\underset{\sim}{R} dE_i \, d(\cos\theta)$, as in (2.36), evaluated at $\theta = \frac{\pi}{2}$ i.e., at the turning points where $L_i^2 = L_{ti}^2$.

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The collisional frequency $\nu_{if}(R)$ for $(E_i,\underset{\sim}{R}) \to (E_f,\underset{\sim}{R})$ transitions integrated over all angular-momentum changes $(L_i{}^2, L_f{}^2)$ consistent with fixed E_i and E_f is given by

$$n_i(\underset{\sim}{R},E_i;t)\ \nu_{if}(R) = \int_0^{L^2_{ti}} dL_i{}^2\ n_i(\underset{\sim}{R},E_i,L_i{}^2;t) \int_0^{L^2_{tf}} dL_f{}^2\ \nu_{if}(\underset{\sim}{R},E_i,L_i{}^2,E_f,L_f{}^2) \quad (3.15)$$

with corresponding equilibrium collisional rates

$$C_{if}(\underset{\sim}{R}) = \int_0^{L^2_{ti}} dL_i{}^2 \int_0^{L^2_{tf}} dL_f{}^2\ C_{if}(\underset{\sim}{R},E_i,L_i{}^2;E_f,L_f{}^2) \quad (3.16)$$

in (3.12). Expressions for the averaged rates (3.16) for various interactions between AB and M can be formulated directly from collision theory (refs. 6-12 and Appendix B).

The normalized distribution in (3.12) is

$$\gamma_i^{S,d}(\underset{\sim}{R},E_i;t) = n_i^{S,d}(\underset{\sim}{R},E_i;t)/\tilde{n}_i(R,E_i)$$

$$= [\int_0^{L^2_{ti}} \gamma_i^{S,d}(\underset{\sim}{R},E_i,L_i{}^2;t)\ \tilde{n}_i(R,E_i,L_i{}^2)dL_i{}^2]/\tilde{n}_i(\underset{\sim}{R},E_i) \quad (3.17)$$

and becomes independent of E_i or $\underset{\sim}{R}$ when equilibrium is attained in E_i or $\underset{\sim}{R}$, respectively.

3.3 R-Equations.

On integrating (3.12) over the full range $-V(R) \le E_i \le \infty$ of E_i, then, on applying Leibnitz's rule, and on recognition of the null effect of collisions,

the following set

$$\frac{d}{dt} n^S(\underset{\sim}{R};t) = \frac{\partial n^S}{\partial t} + \frac{1}{R^2}\frac{\partial}{\partial R}\left[R^2 J^d(R)\right] = 0 \qquad (3.18a)$$

$$\frac{d}{dt} n^d(\underset{\sim}{R};t) = \frac{\partial n^d}{\partial t} + \frac{1}{R^2}\frac{\partial}{\partial R}\left[R^2 J^S(R)\right] = n_1(\underset{\sim}{R},\tfrac{\pi}{2};t) <v>\left[\frac{2}{R} - \frac{2}{m}\frac{<v^{-1}>}{<v>}\left(\frac{\partial V}{\partial R}\right)\right] \qquad (3.18b)$$

is obtained for the macroscopic densities (2.66) and currents
(2.67). The quantities $n_1 <v^n>$ are determined by (2.68). When
thermodynamic equilibrium exists in all variables except R, then J^d is E_i-
independent and is given by (2.29) so that (3.7a) upon E_i-integration yields
(3.18a) directly.

3.4 (E,L^2)-Equation

The appropriate set of transport-collisional equations is, with the use
of (2.52),

$$\frac{d}{dt} n_i^S(E_i,L_i^2;t) = \frac{\partial n_i^S}{\partial t} = \int_{-D}^{\infty}dE_f \int_{o}^{L_{mf}^2}dL_f^2\ (\gamma_f^S - \gamma_i^S)\ C_{if}(E_i,L_i^2;E_f,L_f^2) \qquad (3.19a)$$

where i specifies (E_i,L_i^2), and

$$\frac{d}{dt} n_i^d(E_i,L_i^2;t) = \frac{\partial n_i^d}{\partial t} + 4\pi\left[(v_2/p_2^2)\ n_1^+(\underset{\sim}{R}_2,E_i,\theta=\tfrac{\pi}{2};t)\right.$$

$$\left. - (v_1/p_1^2)\ n^-(\underset{\sim}{R}_1,E_i,\theta=\tfrac{\pi}{2};t)\right]$$

$$= \int_{-D}^{\infty}dE_f \int_{o}^{L_{mf}^2}dL_f^2\ (\gamma_f^D - \gamma_i^D)\ C_{if}(E_i,L_i^2;E_f,L_f^2) \qquad (3.19b)$$

where the equilibrium rate for $i \to f$ transitions,

$$C_{if} = \int_{R_1'}^{R_2'} C_{if}(\underset{\sim}{R},E_i,L_i^2;E_f,L_f^2)d\underset{\sim}{R} \tag{3.20}$$

is determined by $\underset{\sim}{R}$-integration of (3.10) between the limits $R_1' = \min[R_1(E_i,L_i^2), R_1(E_f,L_f^2)]$ and $R_2' = \min[R_2(E_i,L_i^2), R_2(E_f,L_f^2)]$. The lowest bound vibrational energy of the AB pair is $-D$ and L_{mf}^2 is the square of the maximum angular momentum $(2m|E_f|A^2)$ for $E_f < 0$ or infinity for $E_f > 0$ for a given energy E_f.

3.5 E-Equations.

On integrating (3.12) over all accessible $\underset{\sim}{R}$ consistent with (E_i,E_f), and on adopting the appropriate transport equation (2.71), the densities

$$n_i^{S,d}(E_i;t) = \int_0^{R_i} n_i^{S,d}(\underset{\sim}{R},E_i;t)d\underset{\sim}{R} \tag{2.70}$$

per unit dE_i then satisfy

$$\frac{d}{dt} n_i^S(E_i;t) = \frac{\partial n_i^S}{\partial t} = \int_{-D}^{\infty} dE_f \, [\gamma_f^S(t) - \gamma_i^S(t)] \, C_{if}(E_i,E_f) \tag{3.21a}$$

where $-D$ is the energy of the lowest bound level of AB, and either

$$\frac{d}{dt} n_i^d(E_i \geq 0;t) = \frac{\partial n_i^d}{\partial t} + \lim_{R \to \infty}[4\pi R^2 \, j_i^S(\underset{\sim}{R},E_i;t)] - 4\pi \int_0^{\infty} n_1^-(R,E_i, \theta = \frac{\pi}{2};t)$$

$$\left\{ \frac{v}{p^2} \frac{\partial}{\partial R} (R^2 p^2)_{E_i} \right\} dR \tag{3.21b}$$

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for $E \geq 0$, or

$$\frac{d}{dt} n_i^d (E_i < 0; t) = \frac{\partial n_i^d}{\partial t} - 4\pi [\int_0^A n^-(R,E, \theta = \frac{\pi}{2}; t) + \int_A^B n^+(R,E, \theta = \frac{\pi}{2}; t)$$

$$\frac{v}{p^2} \frac{\partial}{\partial R} (R^2 p^2)_E \quad dR \qquad (3.21c)$$

for $E < 0$, set equal to the collisional rate

$$\frac{d}{dt} n_i^d (E_i; t) = \int_{-D}^{\infty} dE_f [\gamma_f^d(t) - \gamma_i^d(t)] C_{if}(E_i, E_f) \quad . \qquad (3.21d)$$

The index i specifies only the energy E_i. The equilibrium rate C_{if} in (3.19) for $E_i \rightarrow E_f$ collisional transitions at all accessible R and angular momenta L^2 satisfies detailed balance and, in terms of (3.16), is

$$C_{if} = \int_0^{R_{if}} C_{if}(\underset{\sim}{R}) d\underset{\sim}{R} = C_{fi} \qquad (3.22)$$

where R_{if} is the minimum of the outermost turning points R_i and R_f associated with E_i and E_f, respectively. The normalized distributions in (3.21a,b) are

$$\gamma_i(t) = n_i(E_i; t)/\tilde{n}_i(E_i) = \int_0^{R_i} n_i(\underset{\sim}{R}, E_i; t) d\underset{\sim}{R} / \int_0^{R_i} \tilde{n}_i(\underset{\sim}{R}, E_i) d\underset{\sim}{R}$$

$$= \int_0^{R_i} \gamma_i(\underset{\sim}{R}, E_i; t) \tilde{n}_i(\underset{\sim}{R}, E_i) d\underset{\sim}{R} / \int_0^{R_i} \tilde{n}_i(\underset{\sim}{R}, E_i) d\underset{\sim}{R} \qquad (3.23)$$

in terms of (3.17), and become independent of E_i for E_i-equilibrium in n_i. The collision rate (3.15) integrated over $\underset{\sim}{R}$ is

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$$n_i(E_i;t) \, \nu_{if} = \int_0^{R_{if}} n_i(\underset{\sim}{R}, E_i; t) \, \nu_{if}(R) d\underset{\sim}{R} \qquad (3.24)$$

which reduces to (3.22) for C_{if} under full equilibrium.

In contrast to the above derived transport-collision equations, (3.7) in $(\underset{\sim}{R}, E_i, L^2)$, (3.12) in $(\underset{\sim}{R}, E_i)$ and (3.18) in $\underset{\sim}{R}$, eq. (3.21a) for n_i^s appears uncoupled from (3.19b). It however remains complex in principle since the collisional rates (3.24) and (3.15) are determined by the solutions $n_i^{s,d}(\underset{\sim}{R}, E_i, L^2; t)$ to the original set (3.7). The above sets are equations satisfied by the integrated quantities $n_i(\underset{\sim}{R}; E_i; t)$, $n(\underset{\sim}{R}; t)$ and $n_i(E_i; t)$ have all been derived from the basic set of Master Equations (3.7) for non-equilibrium in R, E and L_i^2. Assumption of equilibrium in at least one of the variables L_i^2, E_i and $\underset{\sim}{R}$ provides the following simplification via reduction in the dimensionality of the solutions.

4. Various Equilibrium Limits

4.1 L^2-equilibrium; (R,E)-nonequilibrium

When thermodynamic equilibrium among the angular momentum levels is established in n_i^+ and n_i^- independently much more rapidly than equilibrium associated with the remaining variables, E_i and $\underset{\sim}{R}$, then (Appendix A)

$$\frac{n_i^\pm(\underset{\sim}{R},E_i,L_i^2;t)}{n_i^\pm(\underset{\sim}{R},E_i;t)} = \frac{\tilde{n}_i^\pm(\underset{\sim}{R},E_i,L_i^2)}{\tilde{n}_i^\pm(\underset{\sim}{R},E_i)} = \left[2R^2p^2|\cos\theta|\right]^{-1} \tag{4.1}$$

and hence the normalized distributions $\gamma_i^{s,d}(\underset{\sim}{R},E_i,L_i^2;t)$ are independent of L_i^2. The current (3.9), reduces to

$$j_i^{s,d}(\underset{\sim}{R},E_i,L_i^2;t) = 1/2 \ v_i n_i^{s,d}(\underset{\sim}{R},E_i;t)/R^2p^2 \tag{4.2}$$

and is independent of L_i^2 so that the L_i^2-integrated current (3.14) is

$$j_i^{s,d}(\underset{\sim}{R},E_i;t) = 1/2 \ v_i n_i^{s,d}(\underset{\sim}{R},E_i;t) = 1/2 \ \gamma_i^{s,d} \ \tilde{j}_i \tag{4.3}$$

where $\gamma_i^{s,d}$ are the normalized distributions (3.17).

The equilibrium total current (Appendix A) and its gradient are

$$\tilde{j}_i(R) = \tilde{n}_i^s(\underset{\sim}{R},E_i)v_i = \frac{\exp(-E_i/k\Theta)}{\left[2\pi mk\Theta\right]^{3/2}} \ \left[8\pi m[E_i-V(R)]\right] \ , \tag{4.4a}$$

and

$$\frac{1}{R^2} \frac{\partial}{\partial R} (R^2 \tilde{j}_i) = \left[\frac{2}{R} - \frac{1}{(E-V)} \frac{\partial V}{\partial R}\right] \tilde{j}_i \tag{4.4b}$$

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a relation which is intimately connected with (2.10), since $R^2 \tilde{j}_i$ for constant E varies as $L_{max}^2 = R^2 p^2$. The derivative vanishes at $R = A$, the radius of the sphere which intersects the maximum number of bound (E, L^2) orbits possible at a given energy $E < 0$.

For L^2-equilibrium (4.1), the directional density (2.37),

$$n_1(\underset{\sim}{R}, E_i, \theta; t) = 2R^2 p^2 \cos\theta \, n_i(\underset{\sim}{R}, E_i, L_i^2; t) = n_i^{\pm}(\underset{\sim}{R}, E_i; t) \tag{4.5}$$

per unit $d\underset{\sim}{R} \, dE \, d(\cos\theta)$ is therefore independent of θ. The $(\underset{\sim}{R}, E_i)$-set of Master Equations (3.12) reduce, with the aid of (4.3) - (4.5) for L^2-equilibrium, to

$$\frac{d}{dt} n_i^S(\underset{\sim}{R}, E_i; t) = \frac{\partial n_i^S}{\partial t} + \frac{1}{R^2} \frac{\partial}{\partial R} \left[\frac{1}{2} R^2 \gamma_i^d(\underset{\sim}{R}; t) \tilde{j}_i(R) \right]_{E_i}$$

$$= \int_{-V(R)}^{\infty} dE_f \left[\gamma_f^S(R; t) - \gamma_i^S(R; t) \right] C_{if}(R) \tag{4.6a}$$

and to

$$\frac{d}{dt} n_i^d(\underset{\sim}{R}, E_i; t) = \frac{\partial n_i^d}{\partial t} + \frac{1}{R^2} \frac{\partial}{\partial R} \left[\frac{1}{2} R^2 \gamma_i(\underset{\sim}{R}; t) \tilde{j}_i(R) \right]_{E_i} - (\gamma_i^{S \mp} \gamma_i^d) \frac{1}{R^2} \frac{\partial}{\partial R} \left(\frac{1}{2} R^2 \tilde{j}_i \right)_{E_i}$$

$$= \int_{-V(R)}^{\infty} dE_f \left[\gamma_f^d(\underset{\sim}{R}; t) - \gamma_i^d(\underset{\sim}{R}; t) \right] C_{if}(R) \tag{4.6b}$$

where i now specifies E_i alone.

The upper (-) and lower (+) signs in the third term of (4.6b) respectively apply to region I ($E \geq 0$, all R; $E_i < 0$, $0 \leq R \leq A$) or to region II ($E < 0$, $A \leq B \leq B$). It is important to note that the four equations obtained by

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Bates and Mendas[23] from conservation considerations in the interval dEdR and from detailed balance arguments can be rewritten compactly in the form (4.6) with the explicit time dependences $\partial n_i^{s,d}/\partial t$ ignored for all E_i and R. Since (Eq. (2.3)),

$$\frac{1}{R^2}\left[\frac{\partial}{\partial R}\,(R^2 j_i^d)\right]_{E_i} = \frac{1}{R^2}\frac{\partial}{\partial R}\,(R^2 j_i^d)_{p_i} - v\,\frac{\partial V}{\partial R}\left(\frac{\partial j_i^d}{\partial p_i}\right)_R$$

it is now apparent that consideration[23] of the variation with R of the flux appropriate to constant E_i is equivalent to consideration of both streaming terms which separately give rise to diffusion and drift, respectively, in contrast to that earlier thought (ref. 1, p 449).

For Coulombic attraction, $V(R) = -e^2/R$, for example, the set (4.6) yields the coupled set,

$$\frac{d}{dt}\,n_i^s(\underset{\sim}{R},E_i;t) = \frac{\partial n_i^s}{\partial t} + \frac{1}{2}\left[\frac{\partial \gamma_i^d}{\partial R} + \frac{(2\,E_i-V)}{R(E_i-V)}\,\gamma_i^d\right]\tilde{j}_i$$

$$= \int_{-V(R)}^{\infty} dE_f\left[\gamma_f^s(R;t) - \gamma_i^s(R;t)\right] C_{if}(R) \qquad (4.7a)$$

where i denotes E_i, and

$$\frac{d}{dt}\,n_i^d(\underset{\sim}{R},E_i;t) = \frac{\partial n_i^d}{\partial t} + \frac{1}{2}\left[\frac{\partial \gamma_i^s}{\partial R} + \frac{|2E_i-V|}{R(E_i-V)}\,\gamma_i^d\right]\tilde{j}_i$$

$$= \int_{-V(R)}^{\infty} dE_f\left[\gamma_f^d(R;t) - \gamma_i^d(R;t)\right] C_{if}(R) \qquad (4.7b)$$

which can be solved by numerical techniques.

Since $\underset{\sim}{R}$-equilibrium is established at low gas densities N where relaxation in internal energy E is the rate limiting step, the set (4.6) for non-equilibrium R and E is naturally more appropriate for low to intermediate N. In the limit of high N, (Maxwell) equilibrium in scalar momentum p, [or kinetic energy $T \equiv E_i - V(R)$] is established, and relaxation in the separation R is the rate limiting step. Hence, a more natural set of variables for intermediate-high N is (R,T) and the associated transport equation is provided by (2.20). For L^2-equilibrium, the appropriate set satisfied by

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$$\gamma_i^{s,d}(\underset{\sim}{R},T_i;t) = n_i^{s,d}(\underset{\sim}{R},T_i;t)/\tilde{n}_i(\underset{\sim}{R},T_i) \qquad (4.8)$$

is therefore

$$\frac{d}{dt}\, n_i^s(\underset{\sim}{R},T_i;t) = \frac{\partial n_i^s}{\partial t} + \frac{1}{R^2}\left[\left(\frac{\partial}{\partial R}\right)_{T_i} - \left(\frac{\partial V}{\partial R}\right)\left(\frac{\partial}{\partial T_i}\right)_R\right]\left\{\frac{1}{2}\,R^2\gamma_i^d(\underset{\sim}{R},T_i;t)\,\tilde{j}_i(\underset{\sim}{R},T_i)\right\}$$

$$= \int_0^\infty dT_f\left[\gamma_f^s(\underset{\sim}{R};t) - \gamma_i^s(\underset{\sim}{R};t)\right]\,C_{if}(T_i,T_f) \qquad (4.9a)$$

where the equilibrium rate C_{if} is simply a function only of T_i and T_f but not of R
(see Appendix B), and

$$\frac{d}{dt}\, n_i^d(\underset{\sim}{R},T_i;t) = \frac{\partial n_i^d}{\partial t} + \frac{1}{R^2}\left[\left(\frac{\partial}{\partial R}\right)_{T_i} - \left(\frac{\partial V}{\partial R}\right)\left(\frac{\partial}{\partial T_i}\right)_R\right]\left\{\frac{1}{2}\,R^2\gamma_i^s(\underset{\sim}{R},T_i;t)\tilde{j}_i(\underset{\sim}{R},T_i)\right\}$$

$$- \frac{1}{2}\,(\gamma_i^s \mp \gamma_i^d)\,\frac{1}{R^2}\,\frac{\partial}{\partial R}\left\{(R^2\tilde{j}_i(\underset{\sim}{R},T_i)\right\}_{T_i}$$

$$= \int_0^\infty dT_f\left[\gamma_f^d(\underset{\sim}{R};t) - \gamma_i^d(\underset{\sim}{R};t)\right]\,C_{if}(T_i,T_f) \qquad (4.9b)$$

where $\tilde{j}_i(\underset{\sim}{R},T_i)$ is given by (4.4a) with $T_i = E_i - V(R)$. Thus, the complexity
is shifted from solution of Volterra-type[22] integro-differential equations
(4.6) with the first order differential taken with respect to one variable, R
and with the R-dependent function V(R) as an integration limit, to solution of
integro-partial differential equations (4.9) with first-order differentials
now taken with respect to two variables (R,T_i) but with fixed $(0,\infty)$ integration limits.
In the limit of high gas density N, the distribution in kinetic energy T

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is Maxwellian (2.27), $\gamma_i^{s,d}(\underset{\sim}{R};t)$ are independent of T_i and the collision sides of (4.9) vanish. On integration over T_i, (4.9) then reduces to the coupled set (2.22a) and (2.33) with $\tilde{j}(R)$ is given by (2.29).

4.2 $(L^2,\underset{\sim}{R})$-equilibrium; E-nonequilibrium

If, in addition to L^2-equilibrium, equilibrium in R is established for the total density n_i^s (but not for the net density n_i^d) so that relaxation in E is the rate limiting step, as at low gas densities N, then

$$\frac{n_i^s(\underset{\sim}{R},E_i;t)}{n_i^s(E_i;t)} = \frac{\tilde{n}_i(\underset{\sim}{R},E_i)}{\tilde{n}_i(E_i)} \tag{4.10}$$

and γ_i^s (but not γ_i^d) is therefore independent of R. The set (4.6) reduces in this limit to,

$$\frac{d}{dt} n_i^s(\underset{\sim}{R},E_i;t) = \frac{\partial n_i^s}{\partial t} + \frac{1}{R^2}\frac{\partial}{\partial R} \left[\frac{1}{2} R^2 \gamma_i^d(\underset{\sim}{R};t)\tilde{j}_i \right] = \int_{-V(R)}^{\infty} dE_f \left[\gamma_f^s(t) - \gamma_i^s(t) \right] C_{if}(R) \tag{4.11a}$$

and to,

$$\frac{d}{dt} n_i^d(\underset{\sim}{R},E_i;t) = \frac{\partial n_i^d}{\partial t} \pm \frac{\gamma_i^d(R;t)}{R^2}\frac{\partial}{\partial R} \left[\frac{1}{2} R^2 \tilde{j}_i \right] = \int_{-V(R)}^{\infty} dE_f \left[\gamma_f^d(\underset{\sim}{R};t) - \gamma_i^d(\underset{\sim}{R};t) \right] C_{if}(R) \tag{4.11b}$$

where (+) and (−) apply to regions I and II, respectively. Since $\gamma_i^d(R \rightarrow \infty, t)$ for $E_i \geq 0$, and $\tilde{j}_i$ at the turning point $R_i = B$ for bound levels ($E_i < 0$) both

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vanish, then integration of (4.11) over all accessible R yields, in terms of the integrated equilibrium collisional rate (3.20),

$$\frac{d}{dt} n_i^S(E_i;t) = \frac{\partial n_i^S}{\partial t} = \int_{-D}^{\infty} dE_f \left[\gamma_f^{\dot{S}}(t) - \gamma_i^S(t) \right] C_{if}(E_i,E_f) \qquad (4.12a)$$

for the total probability density which is decoupled both formally and in practice from its companion,

$$\frac{d}{dt} n_i^d(E_i;t) = \frac{\partial n_i^d}{\partial t} \mp \frac{1}{2} \int_o^{R_i} \tilde{j}_i(R) \left(\frac{\partial \gamma_i^d}{\partial R} \right) d\tilde{R}$$

$$= \int_{-D}^{\infty} dE_f \int_o^{R_i} d\tilde{R} \left[\gamma_f^d(\tilde{R};t) - \gamma_i^d(\tilde{R};t) \right] C_{if}(E_i,E_f,R) \qquad (4.12b)$$

for the net balance of expanding contracting pairs.

This set (4.12) corresponds to the case of equilibrium for n_i^S in $(\tilde{R},L_i^2)$, via (4.1) and (4.10), for n_i^d in L_i^2 alone via (4.1), and of non-equilibrium for both $n^{S,d}$ in E_i alone. This case is, in general, appropriate to ion-ion recombination at low gas densities N. It is not, however, appropriate to ion-atom or atom-neutral association since here, in contrast to Coulombic attraction in ion-ion recombination, the A-B interaction via the angular momentum barrier can support bound states with positive energies and angular momentum transitions are important.[12] When $\tilde{R}$-equilibrium is assumed for $n_i^{\pm}$, then γ_i^D in (4.12b) is zero.

Rates for association/dissociation can be determined directly (§ 5) from (4.12a) without recourse to (4.12b) which furnishes via (4.11b) the net densities $n_i^D(\tilde{R},E_i;t)$ and associated net currents (4.3). The above collisional input-output Master Equation, (4.12a), has been the governing basis of many studies of ion-ion recombination[6-11] and atom-atom association[13,14] at low gas

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densities, and was there deduced from simple arguments based on the net rate of growth of pairs in energy level E_i. The complementary Eq. (4.12b) or its basis (4.10b) is new and serves to complete the picture of recombination at low gas densities.

4.3 R-equilibrium; (E,L^2)-nonequilibrium

Even in the limit of low gas densities N, L^2-equilibrium is in general not obtained except for the specific cases of interactions (as Coulombic) which cannot support an angular momentum barrier at positive energies. For ion-neutral[12] and atom-neutral association, it is essential[12] to acknowledge departure from L^2-equilibrium. Low N implies R-equilibrium in n_i^S, i.e.,

$$\frac{n_i^S(R,E_i,L_i^2;t)}{n_i^S(E_i,L_i^2;t)} = \frac{n_i(R,E,L^2)}{n_i(E,L^2)} = \left[2\pi v R^2 \cos\theta \, \tau_R\right]^{-1} \tag{4.13}$$

where $\tau_R(E_i,L_i^2)$ is the time (see Appendix B) to complete one radial round trip between the turning points r_1 and r_2. Both the flux, which then reduces to

$$R^2 j_i^S(R,E_i,L_i^2;t) = n_i^S(E,L^2;t)[2\pi\tau_R(E_i,L_i^2)] \tag{4.14}$$

and γ_i^S are then all independent of R. The (R,E_i, L_i^2)-set (3.7) reduces to,

$$\frac{d}{dt} n_i^S(R,E_i,L_i^2;t) = \frac{\partial n_i^S}{\partial t} + \frac{1}{R^2}\frac{\partial}{\partial R}\left[R^2 j_i^d(R;t)\right]_{E_i,L_i^2}$$

$$= \int_{-V_i(R)}^{\infty} dE_f \int_0^{L_{tf}^2} dL_f^2 \left[\gamma_f^S(t) - \gamma_i^S(t)\right] C_{if}(R,E_i,L_i^2;E_f,L_f^2) \tag{4.15a}$$

where index i denotes (E_i,L_i^2), and to

$$\frac{d}{dt} n_i^d(\underset{\sim}{R},E_i,L_i^2;t) = \frac{\partial n_i^d}{\partial t} = \int\limits_{-V_i(R)}^{\infty} dE_f \int\limits_{o}^{L_{tf}^2} dL_f^2 \left[\gamma_f^d(\underset{\sim}{R},t) - \gamma_i^d(\underset{\sim}{R},t)\right]$$

$$C_{if}(\underset{\sim}{R},E_i,L_i^2;E_f,L_f^2) \qquad (4.15b)$$

which is fully decoupled from (4.14a).

The $\underset{\sim}{R}$-integration densities,

$$n_i^{S,d}(E_i,L_i^2;t) = \int\limits_{R_1}^{R_2} n_i^{S,d}(R,E_i,L_i^2;t)d\underset{\sim}{R} \qquad (4.16)$$

therefore satisfy the set

$$\frac{d}{dt} n_i^S(E_i,L_i^2;t) = \frac{\partial n_i^S}{\partial t} = \int\limits_{R_1}^{R_2} d\underset{\sim}{R} \int\limits_{-V_i(R)}^{\infty} dE_f \int\limits_{o}^{L_{tf}^2} dL_f^2 \left[\gamma_f^S(t) - \gamma_i^S(t)\right] \ C_{if}(R)$$

$$(4.17a)$$

since the current j_i^d vanishes at the end points, and

$$\frac{d}{dt} n_i^d(E_i,L_i^2;t) = \frac{\partial n_i^d}{\partial t} = \int\limits_{R_1}^{R_2} d\underset{\sim}{R} \int\limits_{-V_i(R)}^{\infty} dE_f \int\limits_{o}^{L_{tf}^2} dL_f^2 \left[\gamma_f^d(\underset{\sim}{R};t)-\gamma_i^d(\underset{\sim}{R};t)\right] \ C_{if}(R) \quad (4.17b)$$

which are now fully decoupled from one another.

The integrations in (4.17a) may then be re-arranged to yield

$$\frac{d}{dt} n_i^S(E_i,L_i^2;t) = \int\limits_{-D}^{\infty} dE_f \int\limits_{o}^{L_{mf}^2} dL_f^2 \left[\gamma_f^S(t) - \gamma_i^S(t)\right] \int\limits_{R_1'}^{R_2'} C_{if}(R)d\underset{\sim}{R} \qquad (4.18)$$

where $R_2' = \min\ [R_2(E_i,L_i^2),\ R_2(E_f,L_f^2)] > R_1' = \min[R_1(E_i,L_i^2),\ R_2(E_f,L_f^2)]$, where

L_{mf}^2 is the square of the maximum angular momentum, $(2m|E_f|A^2)$ for bound states or infinity for dissociated states],for fixed E_f and where $-D$ is the energy of the lowest bound vibrational level of the AB pair.

Rates for association/dissociation can be obtained (§ 5) directly from (4.17a) without recourse in principle or in practice to its decoupled companion (4.17b), which yield the <u>net</u> densities $n_i^d(R,E_i,L_i^2;t)$ and associated currents j_i^d.

In summary, coupled sets of Master Equations, (4.6), (4.9), (4.12), and (4.17) appropriate to non-equilibrium only in (R,E_i), (R,T_i), E_i, and (E_i,L_i^2) sets of variables have been systematically deduced from the basic set of Master Equations (3.7) for general (R,E_i,L_i^2)-non equilibrium. Even for the most reduced case (4.12) of non-equilibrium in E_i alone, the subject of many previous treatments[6-14], the present procedure has uncovered an additional equation (4.12b) valuable for providing the full description of the recombination process at low gas densities.

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5. Rates and the Macroscopic Transport-Collisional R-Equation

5.1 Various Energy Blocks

The full transport-collisional equation (3.12a) for the density $n_i^S(R,E_i;t)$ of (3.13) in terms of the net current j_i^d of (3.14) is

$$\frac{d}{dt} n_i^S(R,E_i;t) = \frac{\partial n_i^S}{\partial t} + \frac{1}{R^2} \frac{\partial}{\partial R} [R^2 j_i^d(R)]_{E_i} = -\int_{-V(R)}^{\infty} S_{if}(R,t)dE_f \qquad (5.1)$$

where

$$S_{if}(R,t) = n_i^S(R,E_i;t)\, \nu_{if}(R) - n_f^S(R,E_f;t)\, \nu_{fi}(R) = -S_{fi}(R,t) \qquad (5.2)$$

is the net two level collisional rate of depletion of energy level E_i or net rate of production of E_f. The minimum energy level consistent with fixed R is $-V(R)$ which always lies above $-D$, the lowest energy level.

Subdivide the full region of internal energy E_i into three blocks: the continuum block C with $0 \le E_i \le \infty$, an excited block E with $-S \le E_i \le 0$ and the block S of lowest excited levels in the range $-D \le E_i \le -S$. The block S in principle comprises all those levels between the lowest vibrational level $-D$ (~ 5 eV $\approx 20U$ k $(300/\Theta)$ at both temperature Θ and an intermediate level $-S$ defined as that level below which the net probability of direct dissociation by collision with the thermal bath is negligible. In practice, level $-S$ arises naturally from the collisional mechanics via the cut-off effect of the Maxwellian distribution of the gas at temperature Θ and generally lies ~ 10 kΘ below the dissociation limit (taken as zero energy). The central block E of highly excited bound levels is sandwiched (Fig. 1) between the continuum C - the fully dissociated block - and the fully associated block S and has no internal sources or sinks but is coupled by collision to both C and S. Each of C and S may be considered as a source/sink combination interconnected by E when

association is the dominant process, or as a sink/source combination when dissociation is dominant. Dissociation can therefore occur via stepwise collisional excitation through intermediate block E, as well as directly.

The macroscopic pair distributions

$$n_c(\underset{\sim}{R},t) = \int_0^\infty n_i^S(\underset{\sim}{R},E_i;t)dE_i \qquad (5.3a)$$

in block C,

$$n_e(\underset{\sim}{R},t) = \int_0^\infty n_i^S(\underset{\sim}{R},E_i;t)dE_i \qquad (5.3b)$$

in block E, and

$$n_s(\underset{\sim}{R},t) = \int_{-V(R)}^{-S} n_i^S(\underset{\sim}{R},E_i;t)dE_i \qquad (5.3c)$$

over those levels in the energy range $-V(R) \leq E_i \leq -S$ of block S accessible by collision at R, therefore satisfy

$$\frac{\partial}{\partial t} n_c(\underset{\sim}{R},t) + \nabla \cdot \underset{\sim}{J}_c = - \int_0^\infty dE_i \int_{-V}^\infty S_{if}(R,t)dE_f \quad , \quad \text{all } R \qquad (5.4a)$$

$$\frac{\partial}{\partial t} n_e(\underset{\sim}{R},t) + \nabla \cdot \underset{\sim}{J}_e = - \int_{-S}^0 dE_i \int_{-V}^\infty S_{if}(R,t)dE_f \quad , \quad R \leq R_s \qquad (5.4b)$$

$$\frac{\partial}{\partial t} n_s(\underset{\sim}{R},t) + \nabla \cdot \underset{\sim}{J}_s = - \int_{-V}^{-S} dE_i \int_{-V}^\infty S_{if}(R,t)dE_f \quad , \quad R \leq R_s \qquad (5.4c)$$

where R_s is the classical turning point associated with level $-S$. The corresponding contributions from blocks C, E and S to the net radial current

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$$J^d(R,t) = \int_{-V}^{\infty} j_i^{\ d}(R,E_i;t)dE_i = J_c(R,t) + J_e(R,t) + J_s(R,t) \qquad (5.5)$$

are J_c, J_e and J_s, respectively. Since $S_{if} = -S_{fi}$ the upper limit to the integration over E_f in (5.4a) is, in effect 0 while the lower E_f-limit -V is, in effect, -S for (5.4c).

Since the net effect of collisions is null for this closed system, summation of 5.35(a)-(c) yields the continuity equation,

$$\frac{\partial}{\partial t} [n_c(R,t) + n_e(R,t) + n_s(R,t)] + \nabla \cdot J^d = 0 \qquad (5.6)$$

which agrees with (3.18a). For $R \geq R_s$, block S does not exist and

$$\frac{\partial}{\partial t} n_e(R,t) + \nabla \cdot J_e = -\int_{-V}^{0} dE_i \int_{-V}^{\infty} S_{if}(R)dE_f \qquad , R \geq R_s \qquad (5.7)$$

holds instead of (5.4b,c). The lower E_f-limit-V in (5.7) is 0, in effect. Since $j_i^{\ d}$ vanishes at infinity (for $E_i \geq 0$) and at the classical turning point R_i (for $E_i < 0$), integration of (5.1) over all accessible R-space yields

$$\frac{\partial}{\partial t} n_i(E_i,t) = -\int_0^{R_i} dR \int_{-V}^{\infty} S_{if}(R,t)dE_f = -\int_{-D}^{\infty} dE_f \int_0^{R_{if}} S_{if}(R,t)dR \equiv -\int_{-D}^{\infty} S_{if}(t)dE_f \quad (5.8)$$

for the rate of change of density per unit energy interval. Within (5.8), the formal order of (R,E_f)-integrations has been interchanged, $R_{if} = \min(R_i,R_f)$ and

$$S_{if}(t) = \int_0^{R_{if}} S_{if}(R,t)dR = -S_{fi}(t) \qquad (5.9)$$

is the net frequency (per unit $dE_i dE_f$) of collisional transitions (i → f) between E_i and E_f. Hence, the rate of change in the configuration density

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$$n_c(t) = \int_0^\infty n_c(\underset{\sim}{R},t)d\underset{\sim}{R} = \int_0^\infty d\underset{\sim}{R} \int_0^\infty n_i^S(\underset{\sim}{R},E_i;t)dE_i = \int_0^\infty n_i(E,t)dE_i \quad (5.10)$$

of free pairs is exactly,

$$\frac{\partial}{\partial t} n_c(t) = - \int_0^\infty dE_i \int_0^\infty d\underset{\sim}{R} \int_{-V}^0 S_{if}(R,t)dE_f = - \int_0^\infty dE_i \int_{-D}^0 S_{if}(t)dE_f$$

$$= \int_{-D}^0 dE_i \int_0^\infty S_{if}(t)dE_f \quad (5.11)$$

which can also be obtained by R-integration of (5.4a). The corresponding rate of change in the density

$$n_S(t) = \int_0^{R_S} n_S(\underset{\sim}{R},t)d\underset{\sim}{R} = \int_0^{R_S} d\underset{\sim}{R} \int_{-V}^{-S} n_i^S(\underset{\sim}{R},E_i;t)dE_i = \int_{-D}^{-S} n_i(E_i,t)dE_i \quad (5.12)$$

of pairs bound in block S is exactly

$$\frac{\partial}{\partial t} n_S(t) = - \int_{-D}^{-S} dE_i \int_0^{R_i} d\underset{\sim}{R} \int_{-V}^\infty S_{if}(\underset{\sim}{R},t)dE_f = - \int_{-D}^{-S} dE_i \int_{-S}^\infty S_{if}(t)dE_f = \int_{-S}^\infty dE_i \int_{-D}^{-S} S_{if}(t)dE_f$$

$$(5.13)$$

which also follows from R-integration of (5.4c).

Integration of (5.1) over R from 0 to R_S yields,

$$\frac{\partial}{\partial t} \int_0^{R_S} n_i^S(\underset{\sim}{R},t)d\underset{\sim}{R} + 4\pi R_S^2 j_i^d(\underset{\sim}{R}_S,t) = - \int_0^{R_S} d\underset{\sim}{R} \int_{-V}^\infty S_{if}(\underset{\sim}{R},t)dE_f \quad (5.14)$$

which expresses continuity for each level E_i within the reaction sphere of radius R_S. Hence with the aid of (5.13),

$$\frac{\partial}{\partial t} \int_{-S}^\infty dE_i \int_0^{R_S} n_i^S(\underset{\sim}{R},t)d\underset{\sim}{R} + 4\pi R_S^2 \int_{-S}^\infty j_i^d(R_S,t)dE_i = - \int_{-S}^\infty dE_i \int_0^{R_S} d\underset{\sim}{R} \int_{-V}^{-S} S_{if}(\underset{\sim}{R},t)dE_f \quad (5.15a)$$

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$$= - \int_{-S}^{\infty} dE_i \int_{-D}^{-S} S_{if}(t) dE_f \qquad (5.15b)$$

$$= - \partial n_s(t) / \partial t \qquad (5.15c)$$

Eq. (5.15b) simply states that the flux entering the sphere equals the sum of the collisional rate of production of S-pairs and the rate of increase of the contribution from the reaction volume to the density of C and E pairs. Eq. (5.15c) also follows from (5.6) without the intermediate collisional step. Integration of (5.1) over R from R_s to R_i, the classical turning point (for E_i < 0) or infinity (for $E_i \geq 0$) yields

$$\frac{\partial}{\partial t} \int_{R_s}^{R_i} n_i{}^S(\underset{\sim}{R},t) d\underset{\sim}{R} - 4\pi R_s{}^2 j_i{}^d(\underset{\sim}{R}_s,t) = - \int_{R_s}^{R_i} d\underset{\sim}{R} \int_{-V}^{\infty} S_{if}(\underset{\sim}{R},t) dE_f, R_i > R_s \quad (5.16)$$

the continuity equation for each level E_i external to the reaction zone. Hence,

$$\frac{\partial}{\partial t} \int_{-S}^{\infty} dE_i \int_{R_s}^{R_i} n_i{}^S(\underset{\sim}{R},t) d\underset{\sim}{R} - 4\pi R_s{}^2 \int_{-S}^{\infty} j_i{}^d(\underset{\sim}{R}_s,t) dE_i = 0 \qquad (5.17)$$

due to the null effect of collisions. Addition of (5.15c) and (5.17) simply yields the conservation equation

$$\frac{\partial}{\partial t} [n_c(t) + n_e(t) + n_s(t)] = 0 \qquad (5.18)$$

for the sum of the densities (5.10) and (5.12) in blocks C and S and of

$$n_e(t) = \int_{-S}^{0} n(E_i,t) dE_i = \int_{-S}^{0} dE_i \int_{0}^{R_i} n_i(\underset{\sim}{R}, E_i; t) d\underset{\sim}{R} \qquad (5.19)$$

the density of pairs in block E, as expected for this closed system.

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5.2 Association and Dissociation Rates

From (5.11), the net rate of depletion of C-pairs (into all bound levels in E and S) is therefore

$$R_c(t) = -\int_0^\infty \left(\frac{\partial n_i}{\partial t}\right) dE_i = \int_0^\infty dE_i \int_{-D}^\infty S_{if}(t)dE_f = \int_0^\infty dE_i \int_{-D}^0 S_{if}(t)dE_f \qquad (5.20)$$

which is the net downward current across the dissociation neck at zero energy and which, with the aid of (5.9), equals the net rate of production

$$\int_{-D}^0 \left(\frac{\partial n_i}{\partial t}\right) dE_i = -\int_{-D}^0 dE_i \int_{-D}^\infty S_{if}dE_f \qquad (5.21)$$

of E and S-pairs, as expected for this closed system. The net rate (5.13) of production of S-pairs alone is

$$R_s(t) = \int_{-D}^{-S} \left(\frac{\partial n_i}{\partial t}\right)dE_i = -\int_{-D}^{-S} dE_i \int_{-D}^\infty S_{if}(t)dE_f = \int_{-S}^\infty dE_i \int_{-D}^{-S} S_{if}(t)dE_f \qquad (5.22)$$

so that, with the aid of (5.18),

$$R_c(t) = R_s(t) + \int_{-S}^0 \left(\frac{\partial n_i}{\partial t}\right) dE_i \qquad (5.23a)$$

$$= R_s(t) - \int_{-S}^0 dE_i \int_{-D}^\infty S_{if}(t)dE_f \qquad (5.23b)$$

Thus R_s and R_c are equal when $\partial n_i/\partial t \approx 0$ in block E i.e., constant (in energy) current flows through E which is in quasi-steady-state (QSS). For any fixed energies E_1 and E_2, then (5.9) yields

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$$\int_{E_1}^{E_2} dE_i \int_{E_1}^{E_2} S_{if}(t) dE_f = 0 \qquad (5.24)$$

which represents the null effect of collisions in the closed interval $E_1 \leq E_i \leq E_2$. The net downward current (5.20) across the dissociation neck can then be rearranged in terms of the net downward collisional current across arbitrary level -E as

$$R_c(t) = \int_{-E}^{\infty} dE_i \int_{-D}^{-E} S_{if}(t) dE_f + \int_{-E}^{0} (\partial n_i/\partial t) dE_i \qquad (5.25)$$

and the net downward current (5.22) across level -S can be similarly rearranged as

$$R_s(t) = \int_{-E}^{\infty} dE_i \int_{-D}^{-E} S_{if}(t) dE_f - \int_{-S}^{-E} (\partial n_i/\partial t) dE_i \qquad (5.26)$$

Note that (5.26) reduces to (5.22) directly when -E = -D, and that (5.25) reduces to (5.23a) and to (5.20) when -E = -S and when -E $\rightarrow \infty$ respectively. The expressions (5.25) and (5.26) provide alternative procedures which are valuable for accurate calculation of $R_c(t)$ and $R_s(t)$ particularly when block E is in QSS. In the absence of QSS, R_c and R_s are determined by the exact set (5.20) and (5.22) respectively.

On introduction of the (time-independent) probability P_i^A that pairs AB with internal energy E_i are considered as associated then the overall rate for association is,

$$R^A(t) = \int_{-D}^{\infty} P_i^A(E_i) \left(\frac{\partial n_i}{\partial t}\right) dE_i = R_s(t) + \int_{-S}^{0} P_i^A \left(\frac{\partial n_i}{\partial t}\right) dE_i \qquad (5.27)$$

since P_i^A is unity in block S and is zero in block C. The overall rate for

dissociation is similarly,

$$R^D(t) = \int_{-D}^{\infty} P_i^D(E_i) \left(\frac{\partial n_i}{\partial t}\right) dE_i = -R_c(t) + \int_{-S}^{0} P_i^D \left(\frac{\partial n_i}{\partial t}\right) dE_i \qquad (5.28)$$

where the probability P_i^D that E_i-pairs are considered dissociated is unity in the continuum block C, and zero in the fully associated block S. Pairs in block E are in the process of associating and dissociating with probabilities $P_i^{A,D} < 1$. Expressions (5.27) and (5.28) are exact for $R^{A,D}(t)$ under all conditions (cf §7.1, §7.2).

Since

$$P_i^A(E_i) + P_i^D(E_i) = 1 \qquad (5.29)$$

addition of (5.27) and (5.28) yields, with the aid of (5.23a),

$$R^A(t) + R^D(t) = 0 \qquad (5.30)$$

as expected for this closed system.

Provided block E is in QSS (i.e., $\partial n_i/\partial t \approx 0$), the association rate $R^A(t)$ is therefore identical to $R_S(t)$, the net rate collisional rate (5.22) or (5.26) for formation of S-pairs and the dissociation rate $R^D(t)$ is identical to $-R_c(t)$, the net collisional rate for formation of C-pairs. As shown by (5.23a), R_S and R_c are then equal. Otherwise (5.27) and (5.28) must be used for $R^{A,D}(t)$.

In § 7, extrema $R_*^{A,D}(t)$ to the rates $R^{A,D}(t)$ at time t implies the QSS condition. Hence these extrema in addition to (5.30) satisfy

$$R_*^A(t) = R_S(t) = \partial n_S(t)/\partial t \qquad (5.31a)$$

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$$= \alpha N_A(t)N_B(t) - k\, n_s(t) \tag{5.31b}$$

$$= \alpha N_A(t)N_B(t)\,[1 - \Gamma(t)] \tag{5.31c}$$

and

$$R_*^D(t) = -R_c(t) = \partial n_c(t)/\partial t \tag{5.32a}$$

$$= k\, n_s(t)\,[1 - \Gamma^{-1}(t)] \tag{5.32b}$$

where α is the effective two-body rate $(cm^3\, s^{-1})$ for association of dissociated species A and B with densities $N_{A,B}(t)$ cm^{-3} and where k is the frequency (s^{-1}) for dissociation of S-pairs AB with density $n_s(t)$. The quantity

$$\Gamma(t) = [\tilde{N}_A \tilde{N}_B / N_A(t)N_B(t)][n_s(t)/\tilde{n}_s] \tag{5.33}$$

is a measure of the departure of the densities from their corresponding time-independent values $\tilde{N}_{A,B}$ and $\tilde{n}_s$ achieved under full thermodynamic equilibrium $(\Gamma = 1)$ with the gas bath M.

The QSS rate α is therefore determined by the equivalent expressions

$$R_*^A(t) = \alpha N_A(t)N_B(t)[1 - \Gamma(t)] = \int_{-S}^{\infty} dE_i \int_{-D}^{-S} S_{if}(t)\,dE_f \tag{5.34a}$$

$$= -R_*^D(t) = \int_{o}^{\infty} dE_i \int_{-D}^{o} S_{if}(t)\,dE_f \tag{5.34b}$$

$$= \int_{-E}^{\infty} dE_i \int_{-D}^{-E} S_{if}(t)\,dE_f \tag{5.34c}$$

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which are respectively the rate R_s for formation of S-pairs, the rate R_c for depletion of C-pairs and the rate for formation of all pairs with energy $E_i \leq$ -E. The QSS-frequency k for dissociation is provided by the detailed balance relation

$$k \, \tilde{n}_s = \alpha \, \tilde{N}_A \tilde{N}_B \tag{5.35}$$

Evaluation of the exact expressions (5.20) for $R_c(t)$ and (5.22) for $R_s(t)$ require solution in general of the time-dependent coupled set (3.7) for the microscopic densities $n_i(\underset{\sim}{R}, E_i, L_i^2; t)$ or of the set (4.6) for $n_i(\underset{\sim}{R}, E_i; t)$ when equilibrium in L_i^2 can be assumed. It is only when block E is in QSS that (5.27) and (5.28) for the association and dissociation rates $R^{A,D}(t)$ are equal to R_s and $-R_c$ respectively such that the coefficients α and k are determined directly from (5.34) and (5.35).

<u>When block E is not in QSS</u>, then the exact rates (5.27)and(5.28) with (5.8) yields,

$$R^{A,D}(t) = \int_{-D}^{\infty} P_i^{A,D} dE_i \int_{-D}^{\infty} S_{fi}(t) dE_f \tag{5.36}$$

which is exact and which reduces to (5.31a) and (5.32a) only when the QSS-condition

$$\int_{-D}^{\infty} S_{if}(t) dE_f = 0 \tag{5.37}$$

is satisfied in block E $(0 \geq E_i \geq -S)$. When approximate or variational distributions (§7) are adopted, then (5.36), rather than (5.34), is the required expression.

5.3 Macroscopic Transport-Collisional R-Equation

With the aid of (5.4)-(5.7), the distribution

$$n(\underset{\sim}{R},t) = \int_{-S}^{\infty} n_i{}^S(\underset{\sim}{R},E_i;t)dE_i \equiv n_c(\underset{\sim}{R},t) + n_e(\underset{\sim}{R},t) \tag{5.38}$$

in combined blocks C and E, and the associated net current

$$J(\underset{\sim}{R},t) = \int_{-S}^{\infty} J_i{}^d(\underset{\sim}{R},E_i;t)dE_i \equiv J_c(\underset{\sim}{R},t) + J_e(\underset{\sim}{R},t) \tag{5.39}$$

then satisfy, for $R \geqslant R_s$.

$$\frac{\partial}{\partial t} n(\underset{\sim}{R},t) + \underset{\sim}{\nabla} \cdot \underset{\sim}{J} = 0 \quad , \quad R \geq R_s \tag{5.40a}$$

which agrees with (3.18a) since $n_s(R \geq R_s,t)$ vanishes. For $R \leqslant R_s$,

$$\frac{\partial}{\partial t} n(\underset{\sim}{R},t) + \underset{\sim}{\nabla} \cdot \underset{\sim}{J} = -\int_{-S}^{\infty} dE_i \int_{-V}^{-S} S_{if}(R,t)dE_f \quad , \quad R \leq R_s$$

$$\equiv - \nu(R) \; n(\underset{\sim}{R},t) \tag{5.40b}$$

wherein $\nu(R)$ is introduced as an effective frequency for collisional absorption into block S of C and E pairs with fixed $R \leq R_s$. Integration of (5.40a) yields,

$$\frac{\partial}{\partial t} \int_{R_s}^{\infty} n(\underset{\sim}{R},t)d\underset{\sim}{R} = 4\pi R_s{}^2 \; J \; (\underset{\sim}{R}_s,t) \tag{5.41a}$$

with no flux at infinity . With the aid of (5.8) and (5.13), integration of (5.40b) yields

$$\frac{\partial}{\partial t} \int_{o}^{R_s} n(\underset{\sim}{R},t)d\underset{\sim}{R} + 4\pi R_s{}^2 \; J(\underset{\sim}{R}_s,t) = - \int_{o}^{R_s} d\underset{\sim}{R} \int_{-S}^{\infty} dE_i \int_{-V}^{-S} S_{if}(R,t)dE_f \tag{5.41b}$$

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$$\equiv - \int_{-S}^{\infty} dE_i \int_{-D}^{-S} S_{if}(t)dE_f \qquad (5.41c)$$

$$= - \quad \partial n_s(t)/\partial t \qquad (5.41d)$$

which agrees with (5.15) previously obtained from (E_i, R)-integration. The continuity equations (5.41a) and (5.41d) also follow from (5.6) since $J_s(R_s, t)$ and $n_s(R > R_s, t)$ both vanish. Addition of (5.41a) and (5.41d) yields

$$\frac{\partial}{\partial t} \int_0^{\infty} n(\underset{\sim}{R}, t)d\underset{\sim}{R} + \frac{\partial}{\partial t} \quad n_s(t) = 0 \qquad (5.42)$$

the conservation equation (5.18) appropriate for this closed system.

Define the averaged local rate α_3 ($cm^3 s^{-1}$) for absorption within R_s by

$$\alpha_3 n(R_s, t) = \int_0^{R_s} \nu(R) \ n(\underset{\sim}{R}, t)d\underset{\sim}{R} = \int_{-S}^{\infty} dE_i \int_{-D}^{-S} S_{if}(t)dE_f \qquad (5.43)$$

so that the net rate (5.31) with (5.13) for production of pairs in block S is therefore

$$\frac{\partial}{\partial t} \ n_s(t) = \alpha_3 \ n(R_s, t) = \alpha \ N_A(t) \ N_B(t) \ [1 - \Gamma(t)] \qquad (5.44)$$

under quasi-steady-state (QSS) conditions in block E.

Evaluation of α still involves solution of the phase densities, $n_i{}^S(\underset{\sim}{R}, E_i, L_i{}^2; t)$, in general, or $n_i{}^S(\underset{\sim}{R}, E_i; t)$ for L^2-equilibrium, from the appropriate set (3.7) or (4.6) of coupled equations.

5.3 Approximation and the Debye-Smoluchowski Equation

Assume in addition to QSS in block E where $\partial n_i / \partial t \sim 0$, that those pairs with $R \leqslant R_s$ in the combined blocks C and E are also in steady-state, i.e.,

$$\frac{\partial}{\partial t} \int_0^{R_s} n(R_s, t)d\underset{\sim}{R} = 0 \qquad (5.45)$$

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so that (5.41c) with definition (5.43) reduces to

$$4\pi R_s^2 \, J(R_s,t) = -\alpha_3 \, n(R_s,t) = -\partial n_s(t)/\partial t \qquad (5.46)$$

For $R \geq R_s$ the macroscopic current J can be approximated[1] by (2.76) i.e., by

$$\underset{\sim}{J}(R \geq R_s,t) = \underset{\sim}{J}^d(R \geq R_s,t) = -D\underset{\sim}{\nabla}n - [(K/e)\underset{\sim}{\nabla}V]n \qquad (5.47)$$

since $J_s(R \geq R_s,t)$ and $n_s(R \geq R_s,t)$ both vanish. Provided the local rate α_3 for absorption is regarded as a pre-assigned external parameter, then (5.46) is, in effect, a radiation boundary condition to the solution $n(\underset{\sim}{R},t)$ of the macroscopic continuity equation (5.40a) with J given by (5.47). Since

$$n_s(t) - n_s(0) = \alpha_3 \int_0^t n(R_s,t)dt \qquad (5.48)$$

$\Gamma(t)$ is therefore known from (5.33) so that the required rate of production of S-pairs is determined only by $n(R_s,t)$ via

$$\alpha N_A(t) \, N_B(t) = \alpha_3 \, n(R_s,t) \, [1 - \Gamma(t)]^{-1} \qquad (5.49)$$

Hence under QSS in block E, the steady-state assumption (5.45) and a known local reaction rate α_3, the problem is reduced to one of transport alone. The combination (5.40a) with (5.47) for the current and the boundary condition (5.46) is referred to as the Debye-Smoluchowski Equation (DSE) familiar in the theory of reactions in condensed matter and of coagulation of colloids in solution. Apart from a previous account,[1] DSE has not to the author's knowledge ever been derived from a microscopic basic. If, however, α_3 is not known (as is usual) then the

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present full microscopic treatment based on the coupled transport-collision equations of § 3 and § 4 for $n_i^{s,d}$ is required.

Refs. (24-27) provide preliminary reports[24-26] and a full detailed account[27] of the search for analytical solutions to DSE for general interaction $V(R)$ between A and B.

6. Time Evolution Towards Equilibrium

Relaxation of a plasma,or of any subsystem (A,B,AB) in a bath of systems M,from any initial non-equilibrium distribution is, in principle, a time dependent process which proceeds towards equilibrium under various distinct time scales. A very fast initial transient characterizes Phase I, during which a new distribution in $(\underset{\sim}{R},E,L^2)$ is rapidly established. This is followed by a much slower Phase II, during which recombination, association or dissociation and chemical reactions based on the newly developed distribution of Phase I proceeds towards eventual equilibrium via a dynamic balance of collisional association and dissociation established in Phase III.

During Phase I, the $(\underset{\sim}{R},E,L^2)$-distribution collisionally relaxes within (collisional) time τ_1 to a quasi steady state of excited levels which persist throughout Phase II and is the distribution characteristic of the eventual equilibrium established as $t/\tau_1 \rightarrow \infty$. Phase II is characterized by (reaction) times $\tau_2 \approx \tau_R$, τ_A, or τ_D for recombination, association from non-equilibrium free states or dissociation from non-equilibrium bound levels (whichever pertains to the initial conditions). Since τ_1 is generally of the order of the inverse of the collisional frequency ν_{if}, and since association/dissociation proceeds on a much slower time scale, $\tau_1 << \tau_2$ such that the quasi steady-state distribution attained in Phase I persists throughout Phase II.

The beginning of the third Phase (III) association or dissociation depending on the overall direction as determined by initial densities, has produced a significant population of bound pairs AB or free pairs A + B such that the reverse process (dissociation or association) becomes important with the result that the subsystem relaxes toward eventual equilibrium.

Recognition of Phases I and II facilitated many pioneering and tractable

studies of recombination processes[6-12,17,18] in general, based on the solution of integral equations, and the study[13,14] via a diffusion (weak collision) approximation to association/dissociation processes at low gas densities.

The work of Bates et al.[6-8] and of Flannery[9-11] was concerned with the case of the concentrations $N_{A,B}$ of dissociated (charged) species $\gg N_{AB}$, the concentration of bound systems, such that only Phase II and association were relevant. Also previous work on ion-ion recombination[6-11] dealt with low gas densities N. We are here concerned with theoretical development of both association and dissociation in Phases II and III at all gas densities N, for which the time dependent transport-collisional equations formulated in the previous sections (§2-4) are directly relevant.

6.1 Net Transition Probabilities for Association and Dissociation

As an aid to clarity of presentation, consider first the following analysis of eq.(3.21a) in which explicit dependence on the (R,L^2) variables has been systematically integrated out from the original basic eq. (3.7a). Eq.(3.21a) contains however implicit variation with (R,L^2) as characterized by (3.13) and (2.70) for n_i, and by (3.22) for γ_i. The $(\underset{\sim}{R},E,L_i^2)$ and $(\underset{\sim}{R},E)$ sets (3.7) and (3.12) respectively may then be similarly analyzed without any undue formal difficulty.

The governing equation for the conditional probability density n_i of AB systems per unit dE_i is

$$\frac{\partial}{\partial t} n_i(E_i,t) = \int_{-D}^{\infty} [n_f(t) \nu_{fi} - n_i(t)\nu_{if}]dE_f \equiv - \partial J_i(E_i,t)/\partial E_i \qquad (6.1a)$$

where ν_{if} is the frequency of $i \rightarrow f$ collisional transitions $(E_i \rightarrow E_f)$ and -D is the energy of the lowest bound vibrational level of the AB pair.

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Alternatively,

$$\partial n_i/\partial t = \int_{-D}^{\infty} [\gamma_f(t) - \gamma_i(t)] C_{if} \, dE_f \equiv -\partial J_i/\partial E_i \qquad (6.1b)$$

in terms of C_{if}, the equilibrium collisional rate (3.22), and of γ_i, the normalized distribution (3.23). Since the energy levels of AB be sufficiently close (relative to the thermal energy $k\theta$ of the gas bath M), they form a quasi-continuum and $J_i(E_i,t)$ can then be interpreted as the net upward current (in energy space) across level E_i.

Introduce,

$$A_{fi} = \nu_{fi} - \delta(E_i - E_f) \int_{-D}^{\infty} \nu_{if} \, dE_f , \qquad (6.2)$$

the net probability/sec for $f \to i$ irreversible collisional transitions. Then (6.1a) can be compactly written as,

$$\partial n_i/\partial t = \int_{-D}^{\infty} n_f \, A_{fi} \, dE_f = - \int_{-D}^{\infty} S_{if} \, dE_f \qquad (6.3)$$

where S_{if} is defined by eqs. (5.2) and (5.9).

Since the AB-subsystem is closed, curve crossing and quantum tunnelling AB $\not\gtrless$ A+B being precluded at present,

$$\int_{-D}^{\infty} (\partial n_i/\partial t) dE_i = (\partial/\partial t) \int_{-D}^{\infty} n_i \, dE_i = 0 \qquad (6.4)$$

When relaxation in L_i^2 and R is much faster that E_i- relaxation, assume by the end of Phase I that collisions have been sufficiently rapid to establish a Maxwell-Boltzmann distribution $f(E_i)$ in the energy $E_i \geq 0$ of the dissociated (A,B) species. The continuum distribution is then

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$$\gamma_C(t) = [N_A(t)N_B(t) \ f(E_i)]/[\tilde{N}_A\tilde{N}_B \ f(E_i)] \xrightarrow{t\to\infty} 1, \quad E_i \geq 0 \tag{6.5}$$

where $N_{A,B}(t)$ are the time-dependent concentrations of the dissociated species (A and B) or free ions (X^+ and Y^-), which approach their constant equilibrium values $\tilde{N}_{A,B}$ as $t \to \infty$ in this closed system. The normalized distribution (6.5) is time-dependent but energy-independent. As association develops during phase II the pair concentration of the lowest bound levels, within the range $-S \geq E_i \geq -D$ defining energy-block S, grows. Within S, energy-equilibrium is maintained via collisions so that the S-block distribution, assumed to be

$$\gamma_S(t) = n_i(E_i,t)/\tilde{n}_i(E_i) = \int_{-D}^{-S} n_i \ dE_i / \int_{-D}^{-S} \tilde{n}_i \ dE_i$$

$$\equiv n_S(t)/\tilde{n}_S \to 1, \quad -S \geq E_i \geq -D \quad , \tag{6.6}$$

is only time-dependent. In this closed system, let the E-block be coupled to the time-variations of C and S according to the ansatz,

$$\gamma_i(E_i,t) = P_i^D(E_i) \ \gamma_C(t) + P_i^A(E_i) \ \gamma_S(t) \xrightarrow{t\to\infty} 1 \tag{6.7}$$

where the coupling coefficients P_i^D and P_i^A which depend only on the energy will be later identified as being the _net_ probabilities that bound AB pairs of energy E_i will be collisional dissociated into C or will be fully associated by collision into S. From the asymptotic conditions (6.5) - (6.7), the net probabilities satisfy the conservation of probability

$$P_i^D + P_i^A = 1 \tag{6.8}$$

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as expected, since the complete subsystem is closed to mechanisms other than collisional association/dissociation.

Distributions (6.5) and (6.6) can be also incorporated within (6.7) since C and S are naturally characterized by unit net probability P_i^D ($E_i \geq 0$) for dissociation, and unit net probability P_i^A ($E_i \leq -S$) for association, respectively. Thus, (6.1b) yields,

$$\partial n_i/\partial t = -[\gamma_C(t) - \gamma_S(t)] \int_{-D}^{\infty} (P_f^A - P_i^A) C_{if}\, dE_f \qquad (6.9a)$$

$$= [\gamma_C(t) - \gamma_S(t)] \int_{-D}^{\infty} (P_f^D - P_i^D) C_{if}\, dE_f \qquad (6.9b)$$

which is separable in both time t and energy E_i, a natural result of the assumed form (6.7) subject to the asymptotic constraints (6.5) and (6.6).

The rate of change in the probability densities of pairs in each of the blocks C, E and S is respectively,

$$\partial n_i/\partial t = -[\gamma_C(t) - \gamma_S(t)][\int_{-D}^{0} P_f^A\, C_{fi}\, dE_f]\ ;\ E_i \geq 0; \qquad (6.10a)$$

for block C in a form natural when association ($\gamma_C > \gamma_S$) prevails,

$$\partial n_i/\partial t = [\gamma_C(t) - \gamma_S(t)][\int_{-S}^{\infty} P_f^D\, C_{fi}\, dE_f - P_i^D \int_{-D}^{\infty} C_{if}\, dE_f]\ ;\ 0 \geq E_i \geq -S \qquad (6.10b)$$

for block E and

$$\partial n_i/\partial t = -[\gamma_S(t) - \gamma_C(t)][\int_{-S}^{\infty} P_f^D\, C_{fi}\, dE_f]\quad -S \geq E_i \geq -D \qquad (6.10c)$$

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for block S, in a form natural for dissociation controlled processes $(\gamma_s > \gamma_c)$. Thus, the energy distribution P_i^D once established at the end of Phase I is then preserved at all future times in Phases II and III. Relaxation then proceeds in time at a rate determined by the established $P_i^{D,A}$ and $\gamma_i(t)$ towards eventual equilibrium when $\gamma_c \to \gamma_s \to 1$.

The upward current across any arbitrary level E is

$$J(E_i,t) = \int_{E_i}^{\infty} (\partial n_i/\partial t)dE_i = -\int_{-D}^{E} (\partial n_i/\partial t)dE_i \qquad (6.11)$$

since conservation (6.4) applies to the system, closed between -D and ∞, so that the currents $J(-D)$ and $J(\infty)$ across the end points both vanish.

Thus, the net current across a level E in block C is

$$J(E \geq 0,t) = -[\gamma_c(t) - \gamma_s(t)] \int_{E}^{\infty} dE_i \int_{-D}^{0} P_f^A C_{fi} \, dE_f \qquad (6.12a)$$

and the net current across a level E in block S is

$$J(-S \geq E \geq -D,t) = [\gamma_s(t) - \gamma_c(t)] \int_{-D}^{E} dE_i \int_{-S}^{\infty} P_f^D C_{fi} \, dE_f \qquad (6.12b)$$

which are directed down or up the energy ladder according as $\gamma_c > \gamma_s$ or $\gamma_c < \gamma_s$, respectively. Thus, the overall direction of the relaxation is determined by the inequality

$$\frac{N_A(t)N_B(t)}{\hat{N}_A \hat{N}_B} \gtrless \frac{n_s(t)}{\tilde{n}_s} \qquad (6.13)$$

which is originally established by the initial condition.

The net rate of growth of S-pairs or the downward current $-J(S,t)$ into the S-block is

$$\partial n_s(t)/\partial t = \int_{-D}^{-S} (\partial n_i/\partial t)dE_i \equiv -J(-S,t)$$

$$= [\gamma_c(t) - \gamma_s(t)]\alpha_s \hat{N}_A \hat{N}_B \qquad (6.14a)$$

which, with (6.5) and (6.6) for $\gamma_{c,s}$, yields

$$\partial n_s(t)/\partial t \equiv \alpha_s N_A(t)N_B(t) - k_s n_s(t) \qquad (6.14b)$$

The (time independent) rate α_s $(cm^3 \ s^{-1})$ of association and the frequency k_s (s^{-1}) of dissociation in (6.14b) are hence given by,

$$\alpha_s \hat{N}_A \hat{N}_B = k_s \tilde{n}_s = \int_{-D}^{-S} \tilde{n}_i \ dE_i \int_{-S}^{\infty} P_f^D \ \nu_{if} \ dE_f \qquad (6.15)$$

and therefore satisfy (macroscopic) detailed balance. Characterization of P_f^D in (6.7) as the net probability of dissociation of level f once accessed by collision from level i is therefore appropriate, in keeping with (6.15). When conditions are such that $\gamma_c = N_A(t)N_B(t)/\hat{N}_A\hat{N}_B \gg n([S],t)/\tilde{n}([S]) = \gamma_s$ ≈ 0, association is dominant, and γ_c decreases in time from a quantity $\gg 1$ to unity at equilibrium, while γ_s increases essentially from zero to unity. In the reverse limit, $\gamma_s \gg \gamma_c \approx 0$, for the case of a shock wave moving through a molecular gas, then dissociation prevails until equilibrium when $\gamma_{s,c} \approx 1$ and

the currents (6.14) vanish. The evolution toward equilibrium is described by (6.14b).

The net rate of growth of the C-pairs in (6.10a) or the upward current $J(0,t)$, (6.12a), entering block C is

$$\partial n_C(t)/\partial t = \int_0^\infty (\partial n_i/\partial t)dE_i \equiv J(0,t)$$

$$= [\gamma_s(t) - \gamma_C(t)] k_C \tilde{n}_s \qquad (6.16a)$$

which, with (6.5) and (6.6) for $\gamma_{C,s}$, yields

$$\partial n_C(t)/\partial t \equiv -\alpha_C N_A(t)N_B(t) + k_C n_s(t) \qquad (6.16b)$$

where (time-independent) rate α_C $(cm^3 s^{-1})$ of association from the continuum and the frequency k_C (s^{-1}) of dissociation are given by

$$\alpha_C \tilde{N}_A \tilde{N}_B = k_C \tilde{n}_s = \int_0^\infty \tilde{n}_i \, dE_i \int_{-D}^0 P_f^A \nu_{if} \, dE_f \qquad (6.17)$$

which satisfies detailed balance. Thus, P_f^A in (6.7) is uniquely identified in (6.17) as being the net probability of association of pairs in bound level f once collisionally accessed from the continuum C.

The above expressions (6.15) and (6.17) for the rate of change of free (fully dissociated) C-pairs, and of fully associated S-pairs, respectively, are exact, irrespective of any approximation used to determine the probabilities $P_i^{A,D}$ in the E-block ($0 \geq E_i \geq -S$).

In the quasi-steady-state (QSS) approximation, pioneered and used extensively by Bates and associates in many studies[6-8,16-20] of various types of recombination,

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$$\frac{\partial n_i}{\partial t} = 0 \quad ; \quad \text{block } E \ (0 \geq E_i \geq -S) \tag{6.18}$$

since the frequencies of collisional production and destruction of a system i of energy E_i in block E are very large relative to the low frequency of explicit time decay of these excited levels i. The time-independent probabilities in (6.9) are therefore solutions to the integral equation

$$P_i^D \int_{-D}^{\infty} C_{if} dE_f = \int_{-S}^{\infty} P_f^D \, C_{if} dE_f \tag{6.19}$$

subject to the constraints $P_i^D(E_i \geq 0) = 1$ and $P_i^D(E_i \leq -S) = 0$. Since the system is closed, (6.4) applies i.e.,

$$\partial n_c(t)/\partial t + \partial n_s(t)/\partial t = -\partial n_e(t)/\partial t = J(0,t) - J(-S,t) \tag{6.20}$$

In the QSS-approximation, (6.15) and (6.17) are therefore equivalent, the upward current $J(-S,t)$ leaving block S being equal to the upward current $J(0,t)$ entering the block C.

On invoking the null effect of collisions (cf. eq. (5.24))

$$0 = \int_{-E}^{\infty} dE_i \int_{-E}^{\infty} n_f \, \nu_{fi} \, dE_f - \int_{-E}^{\infty} n_i \, dE_i \int_{-E}^{\infty} \nu_{if} \, dE_f \equiv \int_{-E}^{\infty} dE_i \int_{-E}^{\infty} [\gamma_f(t) - \gamma_i(t)] C_{if} \, dE_f \tag{6.21}$$

for an arbitrary bound level of energy $-E$ within block E, the net upward current (6.11) across $-E$ is

$$J(-E,t) = -\alpha_e \ N_A(t) N_B(t) + k_e \, n_s(t) \tag{6.22}$$

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where both

$$\alpha_e = (\tilde{N}_A \tilde{N}_B)^{-1} \int_{-E}^{\infty} dE_i \int_{-D}^{-E} (P_i^{\ D} - P_f^{\ D}) C_{if} \ dE_f \qquad (6.23)$$

and k_e satisfy the detailed balance relation

$$\tilde{N}_A \tilde{N}_B \ \alpha_e = \tilde{n}_s \ k_e \qquad (6.24)$$

From (6.11),

$$J(0,t) = J(-E,t) + \int_{-E}^{0} (\partial n_i / \partial t) dE_i \qquad (6.25)$$

$$J(-S,t) = J(-E,t) - \int_{-S}^{-E} (\partial n_i / \partial t) dE_i \qquad (6.26)$$

which correspond to (5.25) and (5.26) the set (α_e, k_e) is identical to the exact set (α_s, k_s) appropriate to the current $J(-S,t)$ of (6.14) out of S and to (α_c, k_c) for the current $J(0,t)$ of (6.16) into C, <u>only</u> under quasi-steady-state conditions $(\partial n_i / \partial t) = 0$ in block E.

When initial conditions are such that

$$\gamma_c(t) = N_A(t) N_B(t) / \tilde{N}_A \tilde{N}_B \gg 1 \gg n_s(t)/\tilde{n}_s = \gamma_s(t) \approx 0, \qquad (6.27)$$

then, the dissociation rate $k \ n_s(t)$ in (6.14b) and (6.16b), can only be neglected for times t (in Phase II) much shorter than the time required for the establishment of equilibrium when $\gamma_c = \gamma_s = 1$.

When Phase II is dominated by association ($\gamma_c \gg \gamma_s$) the solution of (6.16b) is then,

$$\frac{1}{N_{A,B}(t)} = \frac{1}{N_{A,B}(0)} + \alpha_c t \tag{6.28}$$

the familiar macroscopic law of recombination[16] where time t is measured from the beginning of Phase II when it is assumed that the densities $N_A(0)$ and $N_B(0)$ of dissociated species are equal. Also the densities $n_s(t)$ of S-pairs are given by the solution of (6.14b) which yields,

$$n_s(t) + N_{A,B}(t) = n_s(0) + N_{A,B}(0) \tag{6.29}$$

when $\alpha_c = \alpha_s = \alpha$ i.e., the total number of pairs in blocks C and S are conserved under QSS-conditions in block E.

As t increases, $\gamma_c(t)$ decreases rapidly from a very large quantity, as

$$\gamma_c(t) = [N_{A,B}(0)/\tilde{N}_{A,B}] \, [1 + \alpha N_{A,B}(0)t]^{-1} \tag{6.30}$$

while γ_s increases slowly, essentially from zero as,

$$\gamma_s(t) = \left[\frac{\alpha N_{A,B}(0)t}{1+\alpha N_{A,B}(0)t}\right] \frac{N_{A,B}(0)}{\tilde{n}_s} + \left[\frac{n_s(0)}{\tilde{n}_s}\right] \tag{6.31}$$

The excited state distribution under (6.27) is

$$\gamma_i(t) \approx P_i^D \gamma_c(t) + \gamma_s(t) \approx P_i^D \gamma_c(t) \qquad (6.32)$$

and is such that $\gamma_i \sim P_i^D \gamma_c$ only for those highly excited levels i at time t when $\gamma_s(t) \ll P_i^D \gamma_c$, as in Phase II.

All of the previous studies of recombination were concerned only with Phase II and dissociation was neglected. When dealing, however, with evolution towards eventual equilibrium (in Phase III) or with the enhancement of mutual neutralization (or curve crossings) by three body collisions the full distribution (6.7), rather than (6.32) is appropriate.

The solutions (6.30) and (6.31) which correspond to condition (6.27) are valid until a substantial fraction of associated pairs relative to their equilibrium concentration have been created, and dissociation becomes important.

When initial conditions and times are such that

$$\gamma_s(t) \gg 1 \gg \gamma_c(t) \approx 0 \qquad (6.33)$$

then the net process is dominated by dissociation. The solution of (6.14b) yields for Phase II,

$$n_s(t) = n_s(0) \exp(-k_s t) \qquad (6.34)$$

the familiar macroscopic law of dissociation, and the solution of (6.16b) yields the conservation requirement (6.27) when k_s and k_c are equal. As Phase III progresses, γ_c increases, association becomes important and equilibrium is achieved.

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6.2 Multivariable Separation

The above strategy (6.7) for separation of the variables E_i and t can be easily generalized to cover multivariable separation. Define, for example

$$\gamma_i^{\pm}(\underset{\sim}{R}, E_i ; t) = P_i^{\pm}(R, E_i) \gamma_c(t) + [1 - P_i^{\pm}(R, E_i)] \gamma_s(t) \tag{6.35}$$

where $P_i^{\pm}$ is the net probability for eventual dissociation of an expanding (+) or contracting (-) pair with internal energy E_i and internal separation R. The set (4.6) therefore separates as

$$\frac{\partial}{\partial t} n_i^s + (\gamma_c - \gamma_s) \frac{1}{R^2} \frac{\partial}{\partial R} [\frac{1}{2} R^2 P_i^d(R) \underset{\sim}{\tilde{j}}_i(R)] = (\gamma_c - \gamma_s) \int_{-V}^{\alpha} dE_f [P_f^s(R) - P_i^s(R)] C_{if} \tag{6.36a}$$

and

$$\frac{\partial}{\partial t} n_i^d + (\gamma_c - \gamma_s) \{ \frac{1}{R^2} \frac{\partial}{\partial R} [\frac{1}{2} R^2 P_i^s(R) \tilde{j}_i(R)] - (P_i^s \mp P_i^d) \frac{1}{R^2} \frac{\partial}{\partial R} (\frac{1}{2} R^2 \tilde{j}_i) \}$$

$$= (\gamma_c - \gamma_s) \int^{\infty} dE_f [P_f^d(R) - P_i^d(R)] C_{if} \tag{6.36b}$$

to be solved for the functions

$$P_i^s(R) = \frac{1}{2} [P_i^+(R, E_i) + P_i^-(R, E_i)] \tag{6.37a}$$

and

$$P_i^d(R) = \frac{1}{2} [P_i^+(R, E_i) - P_i^-(R, E_i)] \tag{6.37b}$$

In blocks C and S, respectively, $P_i^{\pm}$ is unity and zero, P_i^s is unity and zero and P_i^d is zero. If the quasi-steady condition (6.18a) is assumed in block E, (6.36a,b) can be solved independently of the functions $\gamma_{c,s}(t)$. The set (3.7) in R, E_i, L_i^2 and t may be similarly separated.
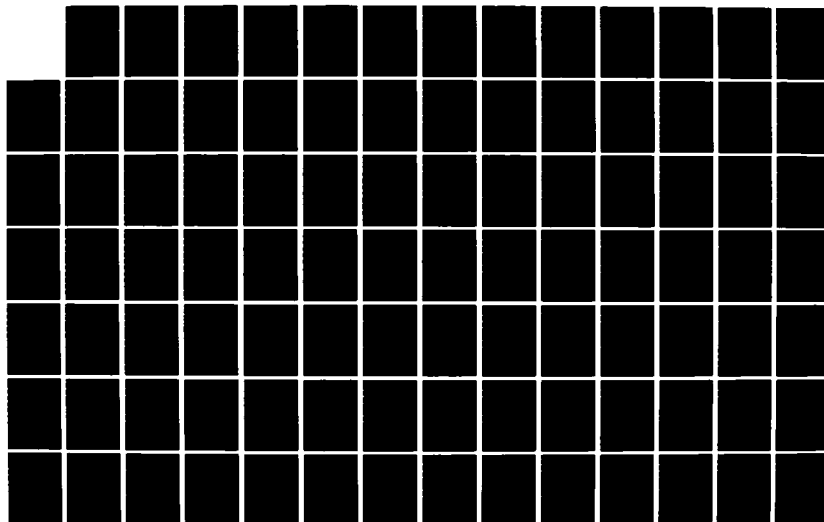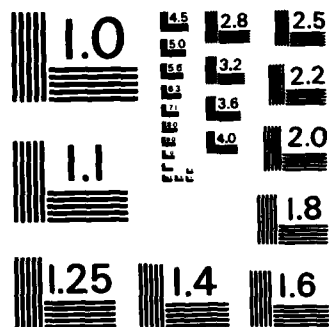
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7. Variational Principles

7.1 Association/Dissociation Rates for non-QSS (Quasi-Steady-State) and for QSS.

Upon identification of $P_i^{A,D}$ in (6.7) as the net probabilities for association/dissociation of one AB-pair of energy E_i, the overall net probabilities/sec for association/dissociation are therefore

$$R^{A,D}(t) = \frac{\partial}{\partial t} \int_{-D}^{\infty} P_i^{A,D}(E_i)\, n_i(t) dE_i = \int_{-D}^{\infty} J_i(E_i,t)(\partial P_i^{A,D}/\partial E_i)\, dE_i \qquad (7.1a)$$

with the aid of (6.1b) and of integration by parts, since the current J_i vanishes at the end points to $E_i = (-D, \infty)$. Equivalent rates, obtained from (6.9) for $\partial n_i/\partial t$, are

$$R^A(t) = \frac{\partial}{\partial t} \int_{-D}^{\infty} P_i^A n_i(t) dE_i = \int_{-D}^{\infty} P_i^A dE_i \int_{-D}^{\infty} S_{fi}(t) dE_f$$

$$= [\gamma_c(t) - \gamma_s(t)] \int_{-D}^{\infty} P_i^A(E_i) dE_i \int_{-D}^{\infty} (P_i^A - P_f^A) C_{if} dE_f \qquad (7.1b)$$

for association where $S_{if}(t)$ is given by (5.9) in terms of (5.2) and

$$R^D(t) = \frac{\partial}{\partial t} \int_{-D}^{\infty} P_i^D n_i(t) dE_i = \int_{-D}^{\infty} P_i^D dE_i \int_{-D}^{\infty} S_{fi}(t) dE_f$$

$$= -[\gamma_c(t) - \gamma_s(t)] \int_{-D}^{\infty} P_i^D(E_i) dE_i \int_{-D}^{\infty} (P_i^D - P_f^D) C_{if} dE_f \qquad (7.1c)$$

for dissociation. In accord with probability conservation (6.8) then for the closed system (6.4),

$$R^A(t) + R^D(t) = 0 \qquad (7.2)$$

at all times, as expected. Subject to the constraints

$$P_i^D = 1 \quad ; \quad P_i^A = 0 \quad ; \quad C\text{-block } (E_i \geq 0) \; ; \tag{7.3a}$$

$$P_i^D = 0 \quad ; \quad P_i^A = 1 \quad ; \quad S\text{-block } (-S \geq E_i \geq -D) \; ; \tag{7.3b}$$

implicit in (6.5) and (6.6), assume that the probabilities $P_i^{A,D}$ are so distributed in energy space that the net rates $R^{A,D}(t)$ are extrema at all times.

From the calculus of variations[22] a necessary condition for the integral

$$I = \int f(y, \dot{y}; x) dx \quad , \quad \dot{y} = dy/dx \tag{7.4}$$

to be an extremum is the Euler-Lagrange equation[22]

$$\frac{d}{dx} \left(\frac{\partial f}{\partial \dot{y}} \right) - \frac{\partial f}{\partial y} = 0 \quad , \tag{7.5}$$

the solution of which determines $y(x)$.

Since $P_i^{A,D}$ remain constant in blocks C and S, then with $x = E_i$, $y = P_i^{A,D}$, and $f(\dot{y}; x) = J(E_i) \, \dot{P}_i^{A,D}$ in (7.5), $R_i^{A,D}$ of (7.1a) is an extremum provided

$$\frac{\partial}{\partial E_i} J_i (E_i, t) = 0 = -\frac{\partial n_i}{\partial t} \quad ; \quad E\text{-block } (0 \geq E_i \geq -S) \tag{7.6}$$

in block E i.e., the quasi-steady-state condition (6.18) of constant-in-energy current $J_i = J_e(t)$ in block E. The equation (6.9) with (7.3) and (7.6) therefore reduces to

$$P_i^A \int_{-D}^{\infty} C_{if} \, dE_f = \int_{-D}^{\infty} P_f^A \, C_{if} \, dE_f \quad ; \quad \text{block } E \tag{7.7a}$$

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for P_i^A and to

$$P_i^D \int_{-D}^{\infty} C_{if} dE_f = \int_{-S}^{\infty} P_f^D C_{if} dE_f \quad ; \quad \text{block} \quad (7.7b)$$

for P_i^d. Since $(\partial P_i/\partial E_i)$ vanishes in blocks C and S and since the current is constant J_e in block E - self consistent conditions (6.3) and (6.6) for an extremum - the extrema of (6.1a) are therefore,

$$R_*^{A,D}(t) = \mp J_e(t) = \pm[\gamma_C(t) - \gamma_S(t) \int_{-E}^{\infty} dE_i \int_{-D}^{-E} (P_f^{A,D} - P_i^{A,D}) C_{if} dE_f \quad (7.8a)$$

the constant-in-energy current J_e past any level E_i in block E; $-J_e$ directed down the energy ladder for association and $+J_e$ upward for dissociation. The extremum to (7.1b) for association is therefore,

$$R_*^A(t) = \frac{\partial}{\partial t} \int_{-D}^{-S} n_i dE_i = [\gamma_C(t) - \gamma_S(t)] \int_{-D}^{-S} dE_i \int_{-D}^{\infty} P_f^D C_{if} dE_f$$

$$\equiv \alpha N_A(t) N_B(t) - k\, n_s(t) \quad (7.8b)$$

where

$$\alpha \tilde{N}_A \tilde{N}_B = \int_{-D}^{-S} dE_i \int_{-D}^{\infty} P_f^D C_{if} dE_f = k \tilde{n}_s$$

The extremum to (7.1c) for dissociation is

$$R_*^D(t) = \frac{\partial}{\partial t} \int_0^{\infty} n_i dE_i = -[\gamma_C(t) - \gamma_S(t)] \int_0^{\infty} dE_i \int_{-D}^{\infty} P_f^A C_{if} dE_f \quad (7.8c)$$

$$\equiv -\alpha N_A(t) N_B(t) + k n_s(t) \quad (7.8d)$$

where

$$\alpha \tilde{N}_A \tilde{N}_B = \int_0^{\infty} dE_i \int_{-D}^{\infty} P_f^A C_{if} dE_f = k \tilde{n}_s \quad (7.8e)$$

and where $P_i^{D,A}$ in block E are solutions of (7.7). The nature of the extrema is determined by performing independent variations δP_i^A to P_i^A for each bound level in block E under the constraint (6.3) of constant $P^{A,D}$ in blocks C and S. The resulting change to (7.1) is

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$$\delta R^A = -\delta R^D = 2[\gamma_c(t) - \gamma_s(t)][\int_{-S}^{0} dE_i \; \delta P_i^A \int_{-D}^{\infty} (P_i^A - P_f^A) \; C_{if} \; dE_f$$

$$+ \; 1/4 \int_{-D}^{\infty} dE_i \int_{-D}^{\infty} (\delta P_i^A - \delta P_f^A)^2 \; C_{if} \; dE_f] \tag{7.9}$$

to second order in δP_i^A. Since δP_i^A are independent of one another, the change in R^A to first order in δP^A vanishes for an extremum and condition (7.7a) is recovered from (7.9), as expected. The change in R^A to second order is wholly determined by the sign of $(\gamma_c - \gamma_s)$. When $\gamma_c > \gamma_s$ and the overall direction according to (6.8) is association, then $R_*^A(t)$ is minimum- and $R_*^D(t)$ is maximum. When the overall direction is dissociation, then $\gamma_s > \gamma_c$ and $R_*^D(t)$ is maximum and $R_*^A(t)$ is minimum.

The proposed Variational Principle is such that the rate corresponding to the overall direction always adjusts itself therefore to a minimum i.e., there is a tendency to counteract the change and the evolution towards equilibrium is impeded.

Rather than solving the integral equations (7.7), an alternative procedure is therefore to explore the variation of $R^{A,D}$ with $P_i^{A,D}$ and to seek a minimum to that rate via (7.1b) for R^A and (7.1c) for R^D, whichever corresponds to the net direction of the process.

Expressions (7.1) pertain to association/dissociation under all conditions, including non-QSS (Quasi-Steady-State), while expressions (7.8) are valid only for QSS-conditions (7.7).

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7.2 General Rate Expression and Application of Variational Principle

Since $\partial P_i^D/\partial E_i$ tends to zero as E_i tends both to zero and to $-D$ ($\approx -\infty$), a possible trial function is,

$$\partial P^D(\lambda;\lambda_\star)/\partial\lambda = a\lambda e^{-d\lambda} \; ; \; d = 1/\lambda_\star \qquad (7.10)$$

where a is a normalization parameter, where λ is the internal energy ($-E_i/k\theta$) in units of $k\theta$ of the gas M, and where d is the one variational parameter which can be expressed as $(1/\lambda_\star)$, in terms of the location at $\lambda = \lambda_\star$ of the minimum to (7.10).

Under the constraints that $P^D(\lambda=0)$ is unity and that $P^D(\lambda \rightarrow \infty)$ tends to zero then the normalization parameter a is $(-1/\lambda_\star)$, and integration of (7.10) then yields,

$$P^D(\lambda;\lambda^\star) = e^{-x}(1+x) \qquad , x = \lambda/\lambda_\star \qquad (7.11)$$

and

$$P^A(\lambda;\lambda^\star) \equiv 1 - P^D = 1 - e^{-x}(1+x) \qquad (7.12)$$

which are simple one-parameter variational functions for the dissociation/ association probabilities $P^{D,A}(\lambda)$. The variational association rate (7.14) in terms of the time-independent rate α (cm^2s^{-1}) of association in (7.8b) and of $\Gamma(t)$ of (5.33) is

$$R^A(t) = \alpha N_A N_B[1-\Gamma(t)] = [\gamma_c(t)-\gamma_s(t)]\int_{-D}^{\infty} P_i^A dE_i \int_{-D}^{\infty} (P_i^A - P_f^A)C_{if}dE_f \qquad (7.13)$$

$$= \frac{1}{2} [\gamma_c(t) - \gamma_s(t)] \int_{-D}^{\infty} dE_i \int_{-D}^{\infty} (P_i^A - P_f^A)^2 C_{if} aE_\gamma \qquad (7.13b)$$

Consider, as an example, ion-ion recombination $(X^+ + X^- + X \rightarrow X_2 + X)$ between equal-mass species. The relevant one-way equilibrium collision kernels C_{if} to be used in (7.13) are given by expression (B39), (B40), (B44), (B51), (B52) and (B54) of Appendix B.

When (7.12) is inserted into (7.13) and when $\lambda*$ is varied, the long-dashed curve in Fig. 2 is obtained for the ratio $R(\lambda*,t)/R_*^A(t)$. The exact rate $R_*^A(t)$ is determined by inserting the solution of the integral eqn. (7.7a), the QSS condition, in (7.13), so that it is simply the downward (E-constant) current, $-J_e$, given by

$$R_*^A(t) = -J_e(t) = [\gamma_c(t) - \gamma_s(t)] \int_{-E}^{\infty} dE_i \int_{-D}^{-E} (P_i^A - P_f^A) C_{if} aE_f \qquad (7.14)$$

which is of course identical to (5-34a-c) and to (7.8a). Not only does the variational parameter $\lambda_* = 1.25$ provide a minimum but it yields its exact result!

Introduction of a three-parameter (λ_*,b,c) trial function

$$\partial P^D(\lambda;\lambda_*,b,c)/\partial\lambda = a\lambda(1 + b\lambda + c\lambda^2)e^{-d\lambda} \qquad (7.15)$$

where d can be expressed in terms of the location at λ_* of the minimum to (7.15) by

$$\Lambda_* = 1/d = \lambda_*(1 + b\lambda_* + c\lambda_*^2)/(1+2b\lambda_* + 3c\lambda_*^2) \qquad (7.16)$$

Upon integration, the association probability is therefore,

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$$P^A(\lambda;\lambda_*,b,c) = 1 - e^{-x}[1 + x + x^2\Lambda_*(b + 3c\Lambda_* + c\Lambda_* x)/(1+2b\Lambda_*+6c\Lambda_*^2)] \qquad (7.17)$$

where

$$x = \lambda/\Lambda_* \qquad (7.18)$$

and its derivative is,

$$dP^A(\lambda;\lambda_*,b,c)/\partial\lambda = e^{-x}(x+b\Lambda_* x^2+c\Lambda_*^2 x^3)/(1+2b\Lambda_*+6c\Lambda_*^2) \qquad (7.19)$$

Fig. 2 illustrates that a minimum at $\lambda_* = 1.25$ is again obtained for the combinations ($b = 0.20$, $c = 0$) and ($b = 0.20$, $c = -0.006$) and that this minimum is the exact QSS-result. Comparison of the corresponding probabilities for all three variational cases with the exact numerical solution of (7.7) is shown in Fig. 3. The agreement is excellent for such simple variational functions. A more sensitive test is provided in Fig. 4 by the corresponding comparison of the derivatives. All these curves including the exact solution display a maximum at the same location $\lambda = 1.25 = \lambda_*$ which is perhaps key to the overall success obtained.

In conclusion, the present Variational Principle appears to be very powerful. Also, when approximate probabilities are derived then (7.13) is the basic expression to be used for the association rates, rather than (7.14) which is approriate only for exact QSS-solutions in block E. Under exact QSS, (7.13) of course reduces to (7.14). If, for example, probabilities based on the diffusion equation are adopted, then (7.13) provides highly accurate rates.[28]

7.3 Tellegen's Theorem and the Principle of Least Dissipation

The set of equations (6.1b) for $\partial n_i/\partial t$ for the blocks C, E and S involves the energy E_i as a continuous variable since the spacing between the bound levels are much smaller than the thermal energy $k\Theta$ of the gas. The discrete representation of (6.1b) can be written as

$$I_i \equiv \frac{\partial n_i}{\partial t} = \sum_f \frac{\partial n_{if}}{\partial t} \equiv \sum_f I_{if} \tag{7.20}$$

where

$$\frac{\partial}{\partial t} n_{if} = [\gamma_f(t) - \gamma_i(t)]C_{if} \equiv (V_f - V_i)/R_{if} \equiv I_{if} \tag{7.21}$$

As Bates[29] has pointed out, the formal structure of (7.20) is identical to an electrical network where the current I_{if} in the line segment e_{if} (edges, element) between nodes (vertices), i and f, of the network is equivalent to the voltage drop V_{fi} ($= V_f - V_i \equiv \gamma_f - \gamma_i$) times the conductivity C_{if} of the element e_{if} (with resistance R_{if}) i.e., (7.21) is simply Ohm's Law for each element.

The quasi-equilibrium condition ($\partial n_i/\partial t = 0$ in block E) is equivalent to Kirchhoff's Current Law (KCL),

$$I_i(t) = \sum_f I_{if}(t) = 0 \tag{7.22}$$

i.e., the net instantaneous current entering and leaving each node i in block E is zero, which expresses the conservation of current.

Since $\gamma_i(t)$ varies continuously and monotonically with E_i between γ_c (constant over all energies in block C) and γ_s (constant over all energies in

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block S),

$$\sum_{e_{if}} V_{fi} = \sum \left[\gamma_f(t) - \gamma_i(t) \right] = 0 \qquad (7.23)$$

where the sum is over each segment e_{if} within a <u>closed</u> loop ($C \not\subset E \not\subset S$). Eq. 7.23) is analogous to Kirchhoff's Voltage Law (KVL) i.e., the sum of voltage changes V_{fi} around a closed loop is zero, and expresses the uniqueness of potential or of γ_i.

Just as KCL and KVL deal with an equilibrium distribution of current and voltage, an equally powerful relationship for equilibrium of power in a network which satisfies Kirchhoff's Laws was first enunciated in 1952 by Tellegen.[30] Tellegen's Theorem (TT) for KCL and KVL network states that the sum of instantaneous powers p_i delivered to all elements e_{if} is zero[30-32] i.e.,

$$\sum_i p_i(t) = \sum_i \sum_{e_{if}} I_{if}(t) V_{if}(t) = - \sum_i^{E\,(C,E,S)} \sum_{e_{if}} \left[\gamma_f(t) - \gamma_i(t) \right]^2 C_{if} = 0 \qquad (7.24)$$

for all elements e_{if} with all nodes i only in the block E which only obeys KCL (since $\partial n_i/\partial t = 0$) and KVL, and with nodes f in any of the blocks C, E and S. Since the equilibrium rate C_{if} is symmetric, the rate (7.1a) with (7.2) may be expressed as,

$$R^{A,D}(t) = \pm 1/2 [\gamma_C(t) - \gamma_S(t)] \int_{-D}^{\infty} dE_i \int_{-D}^{\infty} (P_i^A - P_f^A)^2 C_{if}\, dE_f \qquad (7.25)$$

where (+) and (−) are associated with R^A and R^D, respectively.

The contribution to (7.1) which originates from the block E is

$$R^{A,D}(E;t) = \frac{\partial}{\partial t} \int_{-S}^{0} P_i^{A,D}\, n_i(t)\, dE_i = 0 \qquad (7.26)$$

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under the quasi-equilibrium condition ($\partial n_i/\partial t = 0$ in block E). Hence

$$R^{A,D}(E,t) = \pm\ 1/2\ [\gamma_c(t) - \gamma_s(t)]\int_{-S}^{0} dE_i \int_{-D}^{\infty} (P_i^A - P_f^A)^2 C_{if}\ dE_f = 0 \qquad (7.27)$$

which is the continuum analogy of Tellegen's Network Theorem (7.24)

Since p_i is the time rate of change in total energy ($n_i E_i$) of all pairs n_i of energy E_i,

$$p_i(t) = \frac{\partial}{\partial t}\ (n_i E_i) \qquad (7.28)$$

then Tellegen's Theorem implies

$$\sum_i p_i(t) = \frac{\partial}{\partial t}\sum_i (n_i E_i) \equiv \frac{\partial}{\partial t}\ [\int_{-S}^{0} n_i E_i\ dE_i] = 0 \qquad (7.29)$$

such that the total energy of all pairs in block E therefore remains constant in time and total energy of all pairs in block E is then conserved. This is a remarkable result! But the principle of energy conservation is already inherent to Kirchhoff's Laws and therefore need not be separately stipulated as implied in (7.29) via TT. The three laws are equally powerful in that any two of KCL, KVL and TT imply the third. The greater significance of Tellegen's Theorem, however, lies not in the confirmation of this fundamental law to one network, which in itself is no surprise, but in its general application to two topologically equivalent networks which obey Kirchhoff's Laws via the basic result

$$\sum_i \sum_{e_{if}} I_{if}(t)\ v_{if}(t) = \sum_i \sum_{e_{if}} i_{if}(t)\ V_{if}(t) = 0 \qquad (7.30)$$

where (I_{if}, V_{if}) and (i_{if}, v_{if}) are associated with each of two equivalent networks respectively and satisfy Kirchhoff's Laws for each network.

The Voltage Minimax Theorem[31] i.e., the maximum and minimum potentials in nonlinear resistor networks are at external nodes (i.e., within the C and S blocks external to block E), is applicable here and can be deduced[31] from Tellegen's Theorem.

In the full electrical network composed of blocks C, E and S, KCL is of course not satisfied in the C and S blocks (since $\partial n_i/\partial t$ is non-zero except in the $t \to \infty$ limit of thermodynamic equilibrium), and neither is TT. With the aid of (7.24) and (7.25) the total power absorbed by the complete network (C, E and S),

$$\sum_{C,E,S} p_i(t) = \frac{\partial}{\partial t} [\int_{-D}^{\infty} E_i n_i(t) dE_i] = -[\gamma_c(t) - \gamma_s(t)]^2 \int_{-D}^{\infty} dE_i \int_{-D}^{\infty} (P_i^A - P_f^A)^2 C_{if} dE_f$$

$$= \begin{cases} -2[\gamma_c(t) - \gamma_s(t)]R^A(t) \leqslant 0 \\ +2[\gamma_c(t) - \gamma_s(t)]R^D(t) \leqslant 0 \end{cases} \tag{7.31}$$

is always negative i.e., energy is always dissipated. The equality only holds at thermodynamic equilibrium when $\gamma_c \to \gamma_s \to 1$. When the net direction is associa-tion, $\gamma_c > \gamma_s$ and R^A is positive and minimum. The Variational Principle (§ 7.1) of minimum R^A then implies via (7.31) that the energy dissipated to the gas bath is least. When the net direction is dissociation, $\gamma_s > \gamma_c$, R^D is positive and minimum and the Variational Principle (§ 7.1) also implies via (7.31) least energy of dissipation. An alternative form of the present Variational Principle is that the probabilities are so distributed among the energy levels not only to yield extremum rates $R^{A,D}(t)$, as in § 7.1, but also to provide least rate (7.31) of energy dissipation. This Principle of Least Dissipation is of great significance

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in many fields e.g., thermodynamics,[33] heat conduction, fluid mechanics, etc. Onsager,[15] for example, derived the Principle explicitly for heat conduction. Joule's Law for a net current entering into a KVL and a KCL electrical network (block E) via all connecting elements in the block C and to all existing modes in the block S, states that the currents are so distributed within the network that the summed rate of dissipation of energy in the combined C, E and S blocks is a minimum. _We have here derived the Principle explicitly from (7.22) via extrema (§7.1) to the rates of association/dissociation processes._ Bates,[29] by analogy with Joule's Law, postulated that a measure S of the restoration rate of thermodynamic equilibrium by recombination for highly non-equilibrium systems (i.e., $\gamma_c \gg \gamma_s$ such that explicit time-dependence can be ignored) be a minimum, a Principle which resulted[34] for recombination alone in the quasi-steady-state condition (7.6) of block E. From eq. (7.1) and (7.31) it follows that this unnormalized time-independent measure S can now be identified with the rate $2\alpha\tilde{N}_A\tilde{N}_B$. We have also generalized the situation by asserting that association/dissociation in general proceeds such that the _rates $R^{A,D}(t)$ of (7.1) are extrema at all times_ such that $R^{A,D}(t \to \infty)$ tends naturally to zero when thermodynamic equilibrium is established (in contrast to S). The Principle of Least Dissipation is then satisfied, irrespective of the QSS-condition (7.6). Under the added constraints (7.3), the condition for extrema in $R^{A,D}$ yields the QSS-condition (7.5) quite naturally. We have also shown that the QSS-condition is equivalent to Tellengen's Theorem (7.29) such that the total power (7.31) in the Principle of Least Dissipation reduces to the sum of powers dissipated only in blocks C and S.

In conclusion, an alternative procedure to solution of coupled integro-differential equations derived in §4 is the direct search for extrema to the rates (7.1). These extrema are the actual rates of the process and the system satisfies the Principle of Least Dissipation. The procedure is, in general, irrespective of the quasi-steady-state condition (7.5) which necessarily follows only when the further constraints (7.3) are imposed. Direct application of the Variational Principle yields excellent results (cf Fig. 2-4).

8. Summary

Sets of transport-collisional Master Equations required for a comprehensive description of the two-particle non-equilibrium microscopic distribution n of subsystems (A-B) in a thermal gas bath M have been derived in §2 and §3 for various physical representations. Each set is appropriate to the variation of gas density N between its low and high density limits. Assumption of equilibrium in one or more of the dynamical physical quantities (R, E, L_i^2, T_i) in §4 helps reduce the complexity and dimensionality of the solution n for the corresponding Master Equation for the distribution of subsystems. Even in the limit of low gas density N, the procedure, not only of course yields the appropriate input-out Master Equation (4.12a), the subject of many previous studies[6-14], but also uncovers an additional eqn, (4.12b) or (4.17b) which helps complete the full description of association/dissociation processes at low N. The various Master Equations furnish complete details of n as N is varied.

In §5, expressions for association/dissociation rates $R^{A,D}(t)$ are formulated in terms of two-particle distribution function under conditions both of quasi-steady-state (QSS) of block E and of non-QSS, when the appropriate rates are given by (3.34) and by (5.36), respectively. By operating at a more basic microscopic level, the present approach has also exposed in §5.3 the key assumptions inherent to the Debye-Smoluchowski Equation used frequently for chemical reactions in condensed matter. The present treatment therefore provides a unified account of reactions in both gas and condensed matter phase.

In §6, the evolution from a non-equilibrium situation to full thermodynamic equilibrium with the gas M is provided by introduction of the probabilities $P_i^{A,D}$ for association or dissociation of level i of the A-B

pair. Here, the ansatz (6.7) permits separation of time t from the remaining physical variables as $(E_i, L_i^2, \underset{\sim}{R})$, and automatically permits the QSS-condition to be maintained at all times towards eventual equilibrium. The non-QSS rates $R^{A,D}(t)$ are now given by (7.1) and (7.13) and the QSS-rates by (7.8) or (7.14). The former expressions are valuable[28] when approximate probabilities $P_i^{A,D}$, such as those given by the diffusion approach,[28] are used, whereas the latter QSS-rates are inappropriate[28] when approximate $P_i^{A,D}$ are used.

A new Variational Principle for general association/dissociation rates $R^{A,D}(t)$ of eq. (7.1) is proposed in §7.1. The Principle asserts that the actual rates $R^{A,D}(t)$ are extrema at all times i.e. the rate $R^A(t)$ or $R^D(t)$, whichever corresponds to the overall direction of the process, always adjusts itself to a minimum. If conditions are such that the overall direction is association then, at all times t, $R^A(t)$ is minimum and $R^D(t)$ is maximum; and vice-versa when dissociation is the overall direction. There is therefore a tendency to counteract the change and evolution towards equilibrium is impeded. Provided P_i^A is zero and unity in blocks C and S, respectively, a consequence is the QSS-condition (7.6), or the integral eq. (7.7b), so that QSS-rates $R_*^{A,D}(t)$, which can now be derived directly from the current, are extrema, and are exact.

Direct application of the Principle in §7.2 shows that use of simple analytical variational functions for $P_i^{A,D}$ in the new general expressions (7.1) or (7.13) for $R^{A,D}(t)$ under non-QSS yields a minimum (for ion-ion recombination) which reproduces the exact QSS-rates.[10] The general expression (7.1) is valuable when approximate probabilities $P_i^{A,D}$ are used, in contrast to the QSS-expression (7.8).

In §7.3, contact is established between the present Principle and (a) with Tellegen's Theorem[30-32] for theory of electrical networks i.e. the

total energy in QSS-block E remains constant in time, and (b) with the Principle of Least Dissipation (of Onsager[15,33] for heat conduction) wherein the total energy dissipated by the (A-B) pairs in combined blocks C, E and S is always least and (c) with Bates' Postulate[29] for highly non-equilibrium systems ($\gamma_C \gg \gamma_S$) that, by analogy with Joule's Law[29], an unnormalized measure S of the total rate of restoration of thermodynamic equilibrium is a minimum, which results[34] in the QSS-condition. The general principle here is that the net time-dependent rates $R^{A,D}(t)$ are extrema at all times t, and it naturally follows that $R^{A,D}(t \to \infty)$ tends to zero, as it should, when thermodynamic equilibrium is established.

Various components of the present theory e.g. reduction of the collisional terms via a Fokker-Planck analysis to obtain a diffusional treatment which is highly accurate for all systems and interactions, and the search for (exact) time-dependent analytical solutions of the Debye-Smoluchowski Equation (§5.4) for general interactions are considered in future papers.[27,28]

Acknowledgment

Appendix A: Equilibrium Distributions and Related Properties

Here we summarize and derive various classical equilibrium distributions and properties relevant   to the present theory. Bates and McKibbin[35] have already discussed several important aspects of classical distribution functions. The probability distribution of AB pairs with internal separation $\underset{\sim}{R}$ and internal momentum $\underset{\sim}{p}$ in the phase interval $d\underset{\sim}{R}d\underset{\sim}{p}$ under thermodynamic equilibrium at temperature T with dissociated species A and B is[36]

$$n(\underset{\sim}{R},\underset{\sim}{p})d\underset{\sim}{R}d\underset{\sim}{p} \equiv \frac{n_{AB}(\underset{\sim}{R},\underset{\sim}{p})d\underset{\sim}{R}d\underset{\sim}{p}}{N_A N_B} = \frac{\omega_{AB}}{\omega_A \omega_B} \frac{h^3}{(2\pi mkT)^{3/2}} \left(\frac{d\underset{\sim}{p}d\underset{\sim}{R}}{h^3} \right) exp(-E/kT) \qquad (A1)$$

where the combined electronic and nuclear degeneracy factors are ω_{AB} for the AB pair with phase density n_{AB}, with reduced mass m and internal energy $E \leqslant 0$, and are ω_A and ω_B for each of the dissociated species of equilibrium concentration (cm^{-3}) N_A and N_B, respectively. The ratio of the corresponding translational partition functions (number of quantum states available to "move" at temperature T) is $h^3/(2\pi mkT)^{3/2}$, and $d\underset{\sim}{p}d\underset{\sim}{R}/h^3$ is the number of internal AB states (relative energy E and angular momentum L) in the element $d\underset{\sim}{p}d\underset{\sim}{R}$ of phase space. The exponential term is the canonical distribution for the species of energy E< 0 interacting with a heat reservoir (gas) at temperature T. The equilibrium constant $K_{eq}(\underset{\sim}{R},\underset{\sim}{p})d\underset{\sim}{R}d\underset{\sim}{p} = (\alpha/k)d\underset{\sim}{R}d\underset{\sim}{p}$ for $A + B \underset{k}{\overset{\alpha}{\rightleftarrows}} AB$, with forward association rate $\alpha(cm^3 s^{-1})$ and dissociation frequency $k(s^{-1})$, is also given by (A1) since $\alpha N_A N_B = kn_{AB}$.

Implicit to (A1), the internal energy,

$$E = T_i + V(R) = p^2/2m + V(R) \qquad (A2)$$

where V(R) is the potential energy between A and B at separation R and where T_i is the relative kinetic energy $p^2/2m$, and the internal angular momentum

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squared of the AB pair,

$$L^2 = R^2 p^2 \sin^2\theta \qquad (A3)$$

where θ is the angle between $\hat{R}$ and $\hat{p}$, are both conserved in time. For structureless particles $\omega_{AB} = \omega_A \omega_B$.

The equilibrium distribution $n(R,p)$ is independent of the directions (θ,ϕ) and (θ_R, ϕ_R) of $\hat{p}$ and $\hat{R}$, respectively, and depends only on p and R via (A2) for E. Since $p^2 dp\, d(\cos\theta) = (m\, p\, dE)dL^2/(2R^2p^2 \cos\theta)$, then

$$n(R,E,\theta) = \frac{\exp(-E/kT)}{(2\pi mkT)^{3/2}} \, (2\pi mp) \qquad , \qquad (A4)$$

the probability density (per unit $dRdEd(\cos\theta)$) of (R,E,θ) pairs is independent of θ. Since L^2 varies from $0 \to L^2_{max}(=R^2p^2) \to 0$ as θ varies from $0 \to \frac{\pi}{2} \to \pi$, then

$$n(R,E,L^2) = \frac{\exp(-E/kT)}{(2\pi mkT)^{3/2}} \left[\frac{2\pi m}{R^2(p^2-L^2/R^2)^{1/2}} \right] \qquad (A5)$$

is the probability density (per unit $dR\, dE\, dL^2$) of pairs with (R,E,L^2). Also the probability density is

$$n(R,E) = \int_0^{R^2p^2} n(R,E,L^2)dL^2 = \frac{\exp(-E/kT)}{(2\pi mkT)^{3/2}} \left[4\pi mp \right] \qquad (A6)$$

per unit $dRdE$ and is the Maxwell-Boltzmann distribution

$$n(R,T) = \frac{2}{\sqrt{\pi}} \frac{T_i^{1/2}\exp(-T_i/kT)}{(kT)^{3/2}} \exp(-V/kT) \qquad (A7)$$

per unit $dRdT$. The distribution per unit $dE\, dL^2$ is

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$$n(E,L^2) = \int_{R_1}^{R_2} n(\underset{\sim}{R},E,L^2)d\underset{\sim}{R} = \frac{\exp(-E/kT)}{(2\pi mkT)^{3/2}} \left[4\pi^2 \tau_R(E,L^2) \right] \qquad \text{(A8)}$$

where τ_R is the radial period i.e., time dR/v_R for completion of a round trip between the turning points $R_1(E,L^2) \rightarrow R_2(E,L^2) \rightarrow R_1(E,L^2)$ given by the zeros of the radial speed v_R i.e., of

$$\frac{1}{2} mv_R^2 = p^2/2m - L^2/2mR^2 = E - [V(R) + L^2/2mR^2] \qquad \text{(A9)}$$

The probability that (E,L^2)-pairs have separation $\underset{\sim}{R}$ in the interval $d\underset{\sim}{R}$ about $\underset{\sim}{R}$ is then

$$\frac{n(\underset{\sim}{R},E,L^2)d\underset{\sim}{R}}{n(E,L^2)} = \frac{2dR}{\tau_R v_R} = \frac{dT}{T} \qquad \text{(A10)}$$

where T is half the radial period. This is expected since L^2-conservation implies constant areal speed.

The radial period for a Coulomb field $(V = -e^2/R)$ is

$$\left. \begin{aligned} \tau_R^{(c)}(E,L^2) &= (m/2|E|)^{1/2} \int_{R_1}^{R_2} \left[(R_2-R)(R-R_1) \right]^{-1/2} dR^2 \\ &= 2\pi(e^2/2|E|)^{3/2}(m/e^2)^{1/2} \equiv 2\pi a^{3/2}(m/e^2)^{1/2} \end{aligned} \right\} \qquad \text{(A11)}$$

is independent of L^2, and is proportional to the cube-root of the semimajor axis a $(\equiv e^2/2|E|)$ for elliptical motion (Kepler's Law). Since the radial and angular periods are the same for Coulomb attraction τ_R, is also the time τ_c for completion of the closed elliptical orbit,

$$R = 2R_1R_2[(R_1+R_2) + (R_2-R_1)\cos\theta]^{-1} \qquad \text{(A12)}$$

which is the distance from the focus (force-center) and θ is measured from the eccentricity vector joining the focus to the periapsis.

For the three dimensional harmonic oscillator ($V = \frac{1}{2} k R^2$), the radial period is

$$\tau_R^{(0)}(E,L^2) = (m/k)^{1/2} \int_{R_1^2}^{R_2^2} \left[(R_2^2-R^2)(R^2-R_1^2)\right]^{-1/2} dR^2 = \pi(m/k)^{1/2} \equiv \pi/\omega = \frac{1}{2} \tau_c \quad (A13)$$

is independent of both E and L^2, and is one half the angular period or the time $2\pi/\omega$ for completion of the associated closed elliptical orbit

$$R^2 = 2R_1^2 R_2^2 \left[(R_1^2+R_2^2) + (R_2^2-R_1^2)\cos 2\theta\right]^{-1} \quad (A14)$$

with the force center at the center of the ellipse. While circular orbits are possible for certain combinations of E and L^2 for other interactions V, closed orbits for all E < 0 and L^2 are only possible for the above Coulombic (C) and oscillator (O) interactions which, in addition to conservation of E and L appropriate to all radial V(R), yield a futher (time) conserved quantity associated with a further dynamical symmetry; for C, the direction of the Runge-Lenz vector[37] which joins the foci and periapsis is constant in time; for O, each component energy E_x and E_y for individual motion in the X and Y directions of the orbit plane are conserved, as is $E = E_x + E_y$, the total energy.

The energy distribution for all states with L^2 in a specified range $0 \leq L^2 \leq L_x^2$ of L^2 is therefore with the aid of (A11) and (A13) in (A8) given by

$$n(E,L^2 \leq L_x^2) = \frac{\exp(-E/kT)}{(2\pi mkT)^{3/2}} \left[4\pi^2 \tau_R L_x^2\right] \quad (A15)$$

for both Coulomb and Oscillator interactions. The probability density (per unit energy interval) of orbits with a given energy E which therefore intersect a sphere of radius R_x is given therefore by (A15) with $L_x^2 = p_x^2 R_x^2$

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$= 2m\ R_x^2\ [E-V(R_x)]$ where p_x is the momentum at R_x associated with the orbit which just touches the R_x-sphere.

The distribution per unit dE is

$$n(E) = \int_o^{R_E} n(\underset{\sim}{R},E)d\underset{\sim}{R} = \int_o^{L_o^2} n\ (E,L^2)dL^2 \qquad (A16)$$

where R_E is the classical turning point given by $|V(R_E)| = |E|$ and where L_o is the maximum angular momentum associated with a given energy E.

For Coulombic attraction, $L_o^2 = 2m\ E\ a^2$ so that

$$n_c(E) = \frac{4\pi^2\ \exp(-E/kT)}{(2\pi mkT)^{3/2}}\ \tau_R(E)L_o^2 = \frac{\exp(-E/kT)}{(2\pi mkT)^{3/2}} \left[\frac{2^{1/2}m^{3/2}\pi^3 e^6}{|E|^{5/2}} \right] \qquad (A17)$$

the Saha-Boltzmann formula for ionization equilibrium. For the three-dimensional oscillator, $L_o = (m/k)^{1/2}\ E = E/\omega$, the equilibrium energy distribution is,

$$n_o(E) = \frac{\exp(-E/kT)}{(2\pi mkT)^{3/2}} \left[4\pi^3(m/k)^{3/2}\ E^2 \right] \qquad (A18)$$

The fraction of the total number of bound orbits of energy E which <u>cross</u> a sphere of radius R_x, i.e., those with $L^2 \le L_x^2 = 2m\ R_x^2[E-V(R_x)]$, is therefore,

$$f_x(E) = L_x^2/L_o^2 = \begin{cases} (R_x/a)^2[E-V(R_x)]/|E| \ , & \text{Coulomb} \\ \\ 2m(\omega R_x/E)^2[E-V(R_x)], & \text{Oscillator} \end{cases} \qquad (A19)$$

Thus $f_x(E)\ n(E)dE$ is the number of classical orbits with energy between E and $E + dE$ that cross a sphere of radius R_x centered at the origin. As R_x increases from zero, the number of crossing Coulombic orbits increases as R_x, reaches a maximum at $R_x = a = e^2/2|E|$, and then decreases to zero as R_x tends to

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$e^2/|E| = 2a$, the classical turning point for the $L = 0$ orbit; because high L-orbits fully encompass the R_x-sphere for small $R_x < a$ and are fully encompassed by the R_x-sphere when $a < R_x < 2a$.

The fractional contribution to the overall Coulombic density distribution (A17) that arises within the R_x-sphere is

$$g_x(E) = \frac{n(E, R \leq R_x)}{n(E)} = \frac{2}{\pi}\left[\theta_x - \frac{1}{4}\sin 2\theta_x - \frac{1}{4}\sin 4\theta_x + \frac{1}{12}\sin 6\theta_x\right] \qquad (A20)$$

where $\theta_x = \sin^{-1}(R_x/R_E)$ in terms of the turning point $R_E = e^2/|E|$ where $g_x \to 1$.

Thus $g_x(E)n(E)dE$ is the equilibrium number of pairs with internal separation $R \leq R_x$ and with internal energy between E and $E + dE$.

The density of bound AB-pairs with internal separation $\underset{\sim}{R}$ is

$$n(\underset{\sim}{R}) = \int_{-V(R)}^{0} n(\underset{\sim}{R}, E)dE = \int_{0}^{T_0} n(\underset{\sim}{R}, T_i)dT_i \qquad (A21)$$

where T_0 is the maximum kinetic energy $(-V)$ of relative motion at R. With respect to the distribution $\exp(-V/kT)$ over R of all levels (bound and continuous) the normalized fraction

$$f(R) = n(\underset{\sim}{R})/\exp(-V/kT) = [\text{erf}(-V/kT)^{1/2} - \frac{2}{\sqrt{\pi}}|V/kT|^{1/2}\exp(V/kT)] \qquad (A22)$$

of bound levels varies from 0 to 1 as R decreases from infinity to zero. For Coulombic attraction, f is 0.20, 0.43, 0.73 and 0.996 at $R = 2R_e$, R_e, 0.5 R_e and 0.15 R_e, respectively, where R_e is the natural (Onsager) radius e^2/kT where $V = kT$.

The conditional equilibrium probability or the equilibrium constants $K_{eq} = \alpha/k$ per unit $dr_1\, dr_2$ ... for $A + B \overset{\alpha}{\underset{k}{\rightleftharpoons}} AB$ can in general be written as,

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$$n(\Gamma_1,\Gamma_2,..,\Gamma_s) = \frac{h^3 \exp(-E/kT)}{(2\pi mkT)^{3/2}} \rho_c(\Gamma_1,\Gamma_2,...,\Gamma_s) \equiv K_{eq}(\Gamma_1,\Gamma_2,..,\Gamma_s) \qquad (A23)$$

where ρ_c is the classical density or statistical weights of internal states.
The corresponding statistical volumes, $h^3\rho_c$ are given directly by the square-
bracket terms in (A4) - (A8) for each of the five sets $(\underset{\sim}{R},E,\theta)$, $(\underset{\sim}{R},E,L^2)$,
$(\underset{\sim}{R},E)$, $(\underset{\sim}{R},T)$ and (E,L^2) of variables and in (A17) and (A18) for the particular
energy distributions appropriate to Coulombic and oscillator attractions.

Finally, it is worth noting that equilibrium with respect to a given
variable Γ_j alone implies that the fractional distribution $n(\Gamma_1,\Gamma_2, ..., \Gamma_s)/\int$
$n \, d\Gamma_j$ is given simply by the corresponding equilibrium fraction.

Classical-Quantal Correspondences. Since the three-dimensional Coulomb (C)
and oscillator (O) interactions are unique in having closed bounded orbits
for all values of $E < 0$ and L^2, new and interesting classical-quantal correspondences
may be derived. Under appropriate quantization, $n_\phi h$ and $(n_{R,\theta}+1/2)h$ when $n_{R,\theta,\phi}$
$= 0, 1, ...$, of the actions associated with (ϕ) and libration (R,θ) generalized
coordinates, and generalized momenta (p_R,p_θ,p_ϕ) respectively, the full classical
action for Coulombic attraction

$$J = \oint p_R dR + \oint p_\phi d\phi + \oint p_\theta d\theta = (2m)^{1/2}\, \pi\, e^2\, |E|^{-1/2} = (n_r + n_\theta + n_\phi + 1)h \qquad (A24)$$

being quantized to integral $(n \geq 1)h$, yields, as is well known, the exact
quantal energies. For the isotropic oscillator, the quantized classical action

$$J = \oint p_x dx + \int p_y dy + \int p_z dz = 2\pi(m/k)^{1/2}\, E = (n+3/2)h \quad , \quad n = 0, 1, ... \qquad (A25)$$

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yields the correct quantal energies[38]

$$E_n = (n + 3/2)\hbar\omega \quad ; \quad \omega = (k/m)^{1/2} \qquad (A26)$$

with degeneracy $\frac{1}{2}(n+1)(n+2)$. The number of internal states $\rho_Q(E)$ per unit energy interval dE is therefore given by

$$\rho_Q(E)dE = \frac{1}{2}(n+1)(n+2)dn = \frac{1}{2}(n+1)(n+2)dE_n/\hbar\omega \qquad (A27)$$

which in the limit of high $\dot{n} \gg 1$ agrees with the classical density $\rho_c(E) = 4\pi^3 E^2/(h^3\omega^3)$ obtained from (A18) and (A23). Since even ℓ are associated with even n, and odd ℓ are associated with odd n, then in the classical limit of continuous ℓ,

$$\rho_Q(E_n,L^2)dE_n\ dL^2 = \frac{1}{2}(2\ell+1)dn\ d\ell = \frac{1}{2}dE_n\ dL^2/\hbar^3\omega \qquad (A28)$$

with $L^2 = \ell(\ell+1)\hbar^2$. This quantal density ρ_Q agrees exactly with the classical density $\rho_c(E,L^2) = 4\pi^2\ \tau_R/h^3$ obtained from (A8) and (A13). Corresponding identities

$$\rho_Q(E,L^2) = n^3/(me^4) = 4\pi^2\ \tau_c/h^3 = \rho_c(E,L^2) \qquad (A29)$$

and

$$\rho_Q(E) = n^5/(e^2/a_0) = 4\pi^2\ \tau\ L_0^2/h^3 = \rho_c(E) \qquad (A30)$$

for Coulombic attraction have already been shown.[35] These identities support the use of classical distributions for these interactions in heavy-particle systems.

The classical average of R^S for bound orbits with $E < 0$ and all accessible L^2, is

$$\langle R^S(E) \rangle = \int_0^{R_E} R^S \, n(\underset{\sim}{R}, E) d\underset{\sim}{R} \Big/ \int_0^{R_E} n(\underset{\sim}{R}, E) d\underset{\sim}{R} \qquad (A31)$$

which, for the Coulomb case, yields

$$\langle R^S(E) \rangle = R_E^S \, B(\tfrac{3}{2}, \tfrac{5}{2} + s)/B(\tfrac{3}{2}, \tfrac{5}{2}) \qquad (A32)$$

where R_E is the turning point $e^2/|E|$ and where the Beta function $B(x,y)$ is $\Gamma(x) \, \Gamma(y)/\Gamma(x+y)$ in terms of the Gamma function Γ. Hence,

$$\langle R(E_n) \rangle = \left(\tfrac{5}{4}\right) a \qquad ; \qquad a = e^2/2|E_n| \equiv n^2 a_0 \qquad (A33)$$

whch agrees at high $n \gg 1$ with the quantal expectation value[39]

$$\langle R_n \rangle = \frac{1}{n^2} \sum_{\ell=0}^{n-1} (2\ell+1) \langle R_{n\ell} \rangle = \frac{5}{4} (1 + 1/5n^2) n^2 a_0 \qquad (A34)$$

Moreover, the classical average of R over a given bound (E, L^2)-orbit is

$$\langle R(E, L^2) \rangle = \int_{R_1}^{R_2} R \, n(\underset{\sim}{R}, E, L^2) d\underset{\sim}{R} \Big/ \int_{R_1}^{R_2} n(\underset{\sim}{R}, E, L^2) d\underset{\sim}{R}$$

$$= \frac{3}{2} a - L^2/2me^2 \qquad (A35)$$

and agrees exactly with the quantal value $\frac{1}{2} a_0 [3n^2 - \ell(\ell+1)]$.[39] If the ℓ-summation in (A34) is replaced by L^2-integration between 0 and $L^2_{max} = 2m|E|a^2$, then the quantal result (A34) yields the classical result (A33) exactly.

The averaged value of R for these orbits of energy E that cross a sphere of radius R_x is therefore

$$\langle R(E,L_x^2)\rangle = \int_0^{L_x^2} dL^2 \int_{R_1}^{R_2} R\, n(R,E,L^2)dR \bigg/ \int_0^{L_x^2} dL^2 \int_{R_1}^{R_2} n(R,E,L^2)dR$$

$$= \frac{3}{2} a - L_x^2/4me^2 \tag{A36}$$

$$= \frac{3}{2} a - \frac{1}{2e^2} R_x^2 [E - V(R_x)] \tag{A37}$$

which for Coulomb attraction tends to $\frac{3}{2} a$ in the limit of small radii $R_x \ll a$ when only the $L = 0$ orbit crosses. When R_x equals a, all L^2-orbits cross and (A37) tends to $\left(\frac{5}{4}\right)$ a, in agreement with (A33).

Apart from the intrinsic interest and considerable insight gained from noting that the classical equilibrium probability distribution and the quantal probability $|\psi_{n\ell m}|^2$ have much in common, all of the distributions (A4)-(A8), (A15)-(A22) over physical variables (R,E,L^2) and their associated properties (A32)-(A37), are directly relevant towards implementation of the theory and solution of the Master Equations developed in the main text for association/ dissociation processes in dense gases.

Appendix B: Equilibrium Energy-Change Collisional Rates for Various Subsystem AB-Bath M Interactions.

Theoretical Equilibrium Rates: In this section the collisional term (2.1b) of the "Boltzmann" equation (2.1) is transformed so as to yield equilibrium rates $C_{if}(R)$ for $i \to f$ transitions in the internal energy E_i of the AB pair with internal separation R via collision with the Maxwellian bath of gas particles M. Explicit expressions for C_{if} appropriate to various interactions (Coulomb, Polarization, Hard-Sphere, Charge-Transfer) of A and B with M are summarized for use as a comprehensive package in the theory provided in the main text.

Denote A, B and M by $i = 1$, 2 and 3, respectively, their masses and reduced masses by M_i and M_{ij}, respectively, and their pre- and post-collision velocities and momenta by χ_i, R_i and χ', R_i' taken all relative to the (1-2) center of mass before the (1-3) collision. The (1-3) relative velocities before and after the collision are g and g' with orientation (ψ, ϕ) with respect to polar axis along $\hat{g}$. The changes $\varepsilon(\equiv E_f - E_i)$ and P in the internal energy and internal momentum of the pair AB are $\frac{1}{2} M_{12}[(\chi' - \chi_2)^2 - (\chi_1 - \chi_2)]^2$ and $M_{12}(g' - g)$, respectively.

The rate C_{if} is the sum $C_{if}^{(1)} + C_{if}^{(2)}$ of the individual contributions $C_{if}^{(j)}$ arising from (j-3) scattering alone. Expressions for the averaged rates

$$k_{if}(E_i, E_f) = \int F(u) \, k_{if}(u) du \qquad (B1)$$

arising from elastic (j-3) scattering by general,[7] hard-sphere[11] and polarization[8] interactions and from charge-transfer collisions[10] for general masses have been determined previously[7,11] by integrating the partial rates $k_{if}(u)$ for a fixed (1-2) relative speed u over the normalized speed

distribution $F(u)$. Since the emphasis here is on the non-equilibrium R distributions of Boltzmann's equation at higher gas densities, the more relevant quantity is the energy change kernel $C_{if}(R)$ which is related to the previous quantity (B1) via

$$k_{if}(E_i,E_f) = [\tilde{n}_i(E_i)]^{-1} \int_0^{R_{if}} \tilde{n}_i(R,E_i)\, k_{if}(R)\, dR \equiv [\tilde{n}_i(E_i)]^{-1} \int_0^{R_{if}} C_{if}(R)\, dR \qquad (B2)$$

where R_{if} is the minimum of the outermost turning points R_i and R_f associated with E_i and E_f respectively. The isolated kernels $C_{if}(R)$ for the various interactions are extracted from the previous work[7,8,10,11] as follows.

The Jacobians J in the following transformations

$$d\hat{g}'(\psi,\phi)\, d\hat{\rho}_3(\theta_3\phi_3) \equiv J_2\, d\epsilon\, d(\cos\psi)\, dg\, d\phi_3 = J_3\, d\epsilon\, dP\, dg\, d\phi_3 \qquad (B3)$$

valuable to the collisional term in Boltzmann's Equation (2.1b) have already been determined[7,9,40-42] as has[42] also J_5 in

$$d\rho_1'\, d\hat{\rho}_3' = J_5\, d\epsilon\, dP\, d\rho_1 \qquad (B4)$$

valuable to transformation between quantal and semiquantal treatments[42]. The orientation (θ_3,ϕ_3) of $\hat{\rho}_3$ is taken with respect to the polar axis along $\hat{\rho}_1$. Evaluation of J_2 in (B3) yields (from ref. 7 for elastic A-M collisions and refs. 41 and 42 for inelastic A-M collisions),

$$\frac{1}{2}\, d(\cos\theta_3)d\phi\, d(\cos\psi) \equiv \frac{g\, dg}{v_1 v_3}\, \frac{d\epsilon}{gS(v_1,v_3,g)}\, \frac{d(\cos\psi)}{[(\cos\psi^+ - \cos\psi)(\cos\psi - \cos\psi^-)]^{1/2}} \qquad (B5)$$

where

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$$S(v_1,v_3,g) = \frac{M_{13}}{(1+a)} \left[(1+a)(v_1^2+av_3^2) - ag^2\right]^{1/2} = S(v_1',v_3',g') \qquad \text{(B6)}$$

is symmetric with respect to pre- and post-speeds. The limits[7,41,42] $\psi^{\pm}(v_1,v_3,g;)$ in (B5) to the scattering angle ψ for fixed v_1, v_3, g and ε need not be reproduced here. The limits $g^{\pm}(v_1,v_3;\varepsilon)$ to the relative speed g in (B5) are[7,41,42]

$$g^{-}(v_1,v_3;\varepsilon) = \max[|v_1-v_3| \, , \, |v_1'-v_3'|] \left.\vphantom{\begin{array}{c}1\\1\\1\\1\end{array}}\right\} \qquad \text{(B7)}$$

$$g^{+}(v_1,v_3;\varepsilon) = \min[v_1+v_3, \, v_1'+v_3']$$

and $g^+ \geq g^-$.

Determination of J_3 in (B3) yields[9,40-42] the alternative expression,

$$\frac{1}{2} d(\cos\theta_3)d\phi \; d(\cos\psi) \equiv \frac{g \; dg}{v_1 v_3} \frac{2g \; d\varepsilon}{P[(g_+^2-g^2)(g^2-g_-^2)]^{1/2}} \; \frac{P \; dP}{M_{13}^2 g^2} \qquad \text{(B8)}$$

where the limits $g_{\pm}(v_1,v_3;P,\varepsilon)$ to the relative speed g for fixed v_1, v_3, P and ε also need not be reproduced here. The limits $P^{\pm}(v_1,v_3;\varepsilon)$ to the momentum change P are

$$P^{-}(v_1,v_3;\varepsilon) = \max[M|v_1'-v_1|, \, M_s|v_3'-v_3|] \left.\vphantom{\begin{array}{c}1\\1\\1\\1\end{array}}\right\} \qquad \text{(B9)}$$

$$P^{+}(v_1,v_3;) = \min[M(v_1'+v_1) \, , \, M_s(v_3'+v_3)]$$

where

$$M = M_1(1 + M_1/M_2) \qquad \text{(B10)}$$

the effective mass of the AB pair in the (1-3) collision, and where

$$M_S = (M_1+M_2)M_3/(M_1+M_1+M_3) = aM = (1+a)M_{13} \quad , \qquad (B11)$$

the reduced mass of the full pair-gas system, can be expressed in terms of a mass-ratio parameter[7]

$$a = M_2M_3/M_1(M_1+M_2+M_3) \qquad (B12)$$

for (1-3) collisions.

Under thermodynamic equilibrium at temperature T,

$$\frac{\tilde{n}_i(\underset{\sim}{R},E_i)}{\tilde{N}_A\tilde{N}_B} = \frac{\exp(-E_i/kT)}{(2\pi M_{12}kT)^{3/2}} \; 4\pi M_{12}(M_1 v_1) \qquad (B13)$$

then the equilibrium rate for energy-change collisions at frequency ν_{if} is

$$C_{if}(R)dE_f = \tilde{n}_i(\underset{\sim}{R},E_i)\nu_{if}(R) \; dE_f \qquad (B14a)$$

$$\equiv \tilde{n}_i(\underset{\sim}{R},E_i)dE_f \int \; N_o(\underset{\sim}{P}_3)d\underset{\sim}{P}_3 g\sigma(g,\psi) \; d(\cos\psi)(d\phi/d\epsilon) \qquad (B14b)$$

which is, in general, a four-dimensional integral. The transformation (B5) is appropriate to the cases of general differential cross sections $\sigma(g,\psi)$ or of isotropic cross sections $\sigma(g)$, and (B8) is appropriate for $\sigma(P,g)$ or $\sigma(P)$. For isotropic gas distributions $N_o(P_3)$, $C_{if}(R)$ is therefore a triple integral for general scattering of the AB pairs by M. Considerable reduction to a double or single integral or to an algebraic expression occurs for the following specific interactions.

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CASE (1), $\sigma(P)$: For Coulombic attraction $(-e^2/R)$ between 1 and 3, the differential cross section per unit solid angle is

$$\sigma(P) = 4\,e^4\,M_{13}^{\ 2}/P^4 \qquad (B15)$$

a function only of momentum-change P. With (B8) in (B14b), the g-integration involves the integral $\int_{x^-}^{x^+}(x^+-x)(x-x^-)^{-1/2}\,dx = \pi$ so that the equilibrium rate is (B14a) with the frequency (per unit dE_f) given by

$$\nu_{if}^{(1)}(R) = (\pi/M_{13}^2 v_1)N \int_{v_o}^{\infty} v_3^{-1}\,G(v_3)dv_3 \int_{P^-}^{P^+}\sigma(P)dP \qquad (B16)$$

for general $\sigma(P)$. The limit v_o arises from reality of $P^{\pm}$ in (B8) and satisfies $\frac{1}{2}M_s\,v_o^{\,2} = \max(0, E_f - E_i)$, which asserts that the kinetic energy of AB-M relative motion be sufficient for excitation $(E_f > E_i)$ or be at least zero for de-excitation $(E_f < E_i)$. The R-dependence of ν_{if} at fixed E_i occurs via v_1 in $E_i = \frac{1}{2}M\,v_1^2 + V(R)$. The distribution G in speeds v_3 of the bath particles 3 of density N (cm^{-3}) is orientation independent and may for example be taken as the Maxwellian

$$\int_{4\pi} N_o(\underline{R}_3)d\underline{R}_3 = N\,G(v_3)dv_3 = \frac{2N}{\sqrt{\pi}}\left(\frac{1}{2}M_s\,v_3^{\,2}/kT\right)^{1/2}$$

$$\exp\left(-\frac{1}{2}M_s\,v_3^{\,2}/kT\right)d\left(\frac{1}{2}M_s\,v_3^{\,2}/kT\right) \qquad (B17)$$

appropriate to thermodynamic equilibrium between 3 and the (1-2) center-of-mass. Hence,

$$\exp(-E_i/kT)v_3^{-1}\,G(v_3)dv_3 = \frac{2}{\sqrt{\pi}}\left(\frac{1}{2}M_s/kT\right)^{1/2}\exp(-E/kT)d(E/kT) \qquad (B18)$$

where the total (conserved) energy of the system is

$$E = \frac{1}{2} M_s v_3^2 + E_i = \frac{1}{2} M_s v_3'^2 + E_f \qquad (B19)$$

From (B13) and (B15),

$$\frac{\tilde{n}_i(\underset{\sim}{R}, E_i)}{\hat{N}_A \hat{N}_B} \frac{G(v_3) dv_3}{v_1 v_3} = \frac{2}{\pi} \frac{a^{1/2} M}{(kT)^2} \exp(-E/kT) \, d(E/kT) \qquad (B20)$$

so that the equilibrium collisional $(E_i \rightarrow E_f)$ rate (B14) for general $\sigma(P)$ is

$$C_{if}^{(1)}(R) = \frac{2a^{1/2} MN}{M_{13}^2 (kT)^2} \int_{E_o}^{\infty} \exp(-E/kT) \, d(E/kT) \int_{P^-}^{P^+} \sigma(P) dp \qquad (B21)$$

where E_o is $\max(E_i, E_f)$. Since $P_{\pm}$ of (B9) is symmetric with respect to pre and
post collision speeds, C_{if} is also symmetric thereby satisfying required
detailed balance. For hard-sphere scattering, $\sigma(P) = \sigma_o/4\pi$, and the inner
integral in (B21) is simply $(P^+ - P^-)\sigma_o/4\pi$; and (B21) then agrees with Eq. (32)
of ref. (11), for Coulomb scattering (B15), the inner integrand of (B21) is
$\frac{4}{3} e^4 M_{13}^2 (P^{-3} - P^{-3})$.

The frequencies ν_{if} and rates C_{if} are pure functions only of the initial
and final kinetic energies $T_i = \frac{1}{2} Mv_1^2$ and $T_f = \frac{1}{2} Mv_1'^2$; and the R-dependence
in (B21) arises via the (1-2) interaction $V(R)$ in $T_i = E_i - V(R)$ and $T_f = E_f - V(R)$ for fixed E_i and E_f.

CASE (2); $\sigma(g)$: When the (1-3) differential cross section is taken as the
orbiting cross section,

$$\sigma(g) = (\alpha e^2 / 4M_{13} g^2)^{1/2} \equiv B/g \qquad (B22)$$

appropriate to polarization attraction $(-\alpha e^2/2R^4)$ followed by core repulsion then, on
integrating (B5) over ψ,

$$v_{if}^{(2)}(R) = (\pi/v_1)N \int_{v_o}^{\infty} v^{-1} G(v_3)dv_3 \int_{g^-}^{g^+} g\sigma(g)dg/S(v_1,v_3,g) \tag{B23}$$

for isotropic (1-3) cross sections $\sigma(g)$, in general.

On adopting the Maxwellian distribution (B17) for G, the equilibrium collisional rate (B14) for this second case is therefore

$$c^{(2)}(R) = [2a^{1/2}MN/(kT)^2] \int_{E_o}^{\infty} \exp(-E/kT)d(E/kT) \int_{g^-}^{g^+} g\sigma(g)dg/S(v_1,v_3,g) \tag{B24}$$

For polarization attraction (B22), the inner integral yields

$$B \int_{g^-}^{g^+} dg/S = \frac{B(1+a)}{M_{13}a^{1/2}} [\sin^{-1}(g^+/A) - \sin^{-1}(g^-/A)] \tag{B25}$$

where

$$A^2(v_1,v_3) = (1+a)(v_1^2 + av_3^2)/a \tag{B26}$$

Since

$$2 \sin^{-1} x^{1/2} = \frac{1}{2}\pi - \sin^{-1}(1-2x), \tag{B27}$$

the result of Bates and Mendas[8] for k_{if}, the averaged energy-change rate (B2) per AB-pair, is recovered.

CASE (3); Charge-Transfer: On assuming that the cross section σ^X for symmetrical resonance charge transfer

$$X^+ + X \rightarrow X + X^+ \tag{B28}$$

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is independent of the speed g of relative motion as at low energies, then the angular integrations of (B14) yield simply,

$$\frac{d(\cos\theta_3)}{4\pi} \int\limits_{(\psi,\phi,\phi_3)} [g\sigma^X(g,\psi)d(\cos\psi)d\phi]d\phi_3 = \frac{1}{2} (v_1^2+v_3^2-2v_1v_3\cos\theta_3)^{1/2} Q^X d(\cos\theta_3)$$

$$= \left(\frac{1+c}{c}\right)^{3/2} [v_3^2-(v_1^2+2\epsilon/M_1)]^{1/2} Q^X dE_f/(2M_1v_1v_3) \qquad (B29)$$

where Q^X is the integral cross section for charge transfer, where

$$c = M_1/M_2 \qquad (B30)$$

for (1-3) collisions and where $\epsilon = E_f - E_i$ is the energy change. The frequency of $i \rightarrow f$ collisional transitions at (1-2) separation $\underset{\sim}{R}$ is therefore,

$$\nu_{if}^{(3)}(R) = \left(\frac{1+c}{c}\right)^{3/2}\left(\frac{NQ^X}{2M_1v_1}\right) \int\limits_{v^-}^{v^+} v_3^{-1} \, G(v_3) \, [v_3^2-(v_1^2+2\epsilon/M_1)]^{1/2} \qquad (B31)$$

where the limits to v_3 for a specified energy change ϵ at given speed v_1 are[10]

$$v^{\pm}(v_1;\epsilon) = (1+c) \, [v_1 + 2 \, /M_1(1+c)]^{1/2} \pm c \, v_1 \qquad (B32)$$

and originate from the assumption that the (1-3) collision (B28) simply interchanges $\underset{\sim}{v}_1$ and $\underset{\sim}{v}_3$. On adopting the Maxwellian distribution, (B31) can be rewritten as

$$\nu_{if}^{(3)}(R) = \left(\frac{1+c}{c}\right)^{3/2}\left(\frac{NQ^X}{2M_1v_1}\right) \exp(E_i/kT) \, I_{if}(v_1;E_i,E_f) \qquad (B33)$$

where

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$$I_{if}(v_1;E_i,E_f) = \left[\exp -\left(\frac{1+c}{1+2c}\right)\left(\frac{E_i+E_f}{kT}\right)\right] \exp\left[-V(R)/(2c+1)kT\right] \int_{E^-}^{E^+} G(E)dE \qquad (B34)$$

is symmetrical in E_i and E_f. The fraction of Maxwell particles with energies E in the range $E^- \le E \le E^+$ is

$$G(E)dE = \left[\text{erf}(E/kT)^{1/2} - \frac{2}{\sqrt{\pi}}(E/kT)^{1/2}\exp(-E/kT)\right]_{E_-}^{E^+} \qquad (B35)$$

where for this case,

$$E^{\pm} = [c(1+c)/(1+2c)][\{E_i-V(R)\}^{1/2} \pm \{E_f - V(R)\}^{1/2}]^2 \qquad (B36)$$

Hence the equilibrium rate for $i \to f$ charge-transfer collisional transitions is

$$C^x_{if}(R) = \frac{[(1+c)/c]^{3/2}}{(2\pi M_{12})^{1/2}} \frac{N \, Q^x}{(kT)^{3/2}} I_{if}(v_1;E_i,E_f) \qquad (B37)$$

an algebraic expression which satisfies detailed balance and which yields the rate (in ref. 9) for k_{if}, the averaged rate (B2) per AB-pair.

Computational Equilibrium Rates: All of these equilibrium rates for the above three cases may be conveniently expressed for computational purposes in terms of dimensionless units,

$$\lambda = -E_i/kT, \qquad \mu = -E_f/kT, \qquad v(r) = -V(R)/kT$$

$$\qquad (B38)$$

$$r = R/R_e, \qquad R_e = e^2/kT$$

as

as

$$4\pi \, C_{if}(R)R^2 dR |dE_i||dE_f| = \Gamma \, \alpha_T \, F(\lambda,\mu;r) r^2 \, dr \, d\lambda \, du, \; (\text{cm}^3 \, \text{s}^{-1}) \tag{B39}$$

in terms of specified mass factors Γ and the Thomson (low density) rates (see, for example, ref. 10).

$$\alpha_T = \frac{4}{3} \, \pi (R_e/\beta)^3 (3kT/M_{12})^{1/2} \, \sigma_0 N \; , \quad \beta = 3/2 \tag{B40}$$

where σ_0 is the integral cross section for (1-3) collisions at relative energy $\frac{3}{2}$ kT. The appropriate mass factors Γ in (B39) and cross sections σ_0 in (B40) are

$$\Gamma^H = \left(\frac{3}{2}\right)^{1/2}\left(\frac{\beta^3}{\pi}\right) \frac{(1+a)^2}{a^{3/2}} \left(\frac{M_{12}}{M_1}\right) \; ; \quad \sigma_0 = \sigma_0^H \tag{B41}$$

for hard-sphere (1-3) collisions with integral cross section σ_0^H,

$$\Gamma^C = \frac{3a}{\pi(1+a)} \; \Gamma^H \qquad ; \quad \sigma_0 = \sigma_0^C = \frac{1}{9} \, \pi R_e^2 \tag{B42}$$

for Coulomb (1-3) collisions with integral cross section σ_0^C which corresponds to Coulomb scattering by angles $\psi \geq \pi/2$, and to energy transfers $\epsilon \geq (3/2)kT$ for equal mass species. For (1-3) polarization attraction/core repulsion;

$$\Gamma^P = \left(\frac{3}{2}\right)\left(\frac{\beta^3}{\pi}\right) \frac{(1+a)^{5/2}}{a^{3/2}} \left(\frac{M_{12}}{M_1}\right) \; ; \quad \sigma_0 = \sigma_0^P = 2\pi(\alpha R_e/3)^{1/2} \tag{B43}$$

and σ_0^P adopted in Thomson's rate (B40) is the corresponding integral (elastic or momentum transfer) collisional cross section at (3/2)kT relative energy. For (1-3) charge-transfer collisions,

$$\Gamma^X = \left(\frac{3}{2}\right)^{1/2}\left(\frac{\beta^3}{\pi}\right) \left(\frac{1+c}{c}\right)^{3/2} \; ; \quad \sigma_0 = 2Q^X \tag{B44}$$

where σ_0 in (B46) is the corresponding momentum-transfer cross section, taken as twice the cross section Q^X for charge transfer.[43]

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The corresponding dimensionless functions F in (B39) are symmetric in λ and μ and are

$$F^H(\lambda,\mu;r) = \int_{Y_o}^{\infty} \exp(-Y)dY \ [\tilde{P}_+ - \tilde{P}_-]; \quad Y_o = \max(-\lambda,-\mu) \tag{B45}$$

for hard-sphere (1-3) collisions with (dimensionless) momentum-change limits $\tilde{P}_+ \geq \tilde{P}_-$, given by

$$\tilde{P}_-(\lambda,\mu;r) = \max \left[[v(r) - \lambda]^{1/2} - [v(r)-\mu]^{1/2} \ ; \ a^{1/2}[(Y+\lambda)^{1/2}-(Y+\mu)^{1/2}] \right]$$

and

$$\tilde{P}_+(\lambda,\mu;r) = \min \left[[v(r) - \lambda]^{1/2} + [v(r)-\mu]^{1/2} \ ; \ a^{1/2} [(Y+\lambda)^{1/2} + (Y+\mu)^{1/2}] \right] \tag{B46}$$

Also

$$F^C(\lambda,\mu;r) = \int_{Y_o}^{\infty} \exp(-Y)dY \ [\tilde{P}_-^{-3} - \tilde{P}_+^{-3}] \tag{B47}$$

for Coulomb (1-3) collisions.

For polarization (1-3) collisions,

$$F^P(\lambda,\mu;r) = \int_{Y_o}^{\infty} \exp(-Y)dY \ [\sin^{-1}(G_2/A) - \sin^{-1}(G_1/A)] \tag{B48}$$

where

$$G_1(\lambda,\mu;r) = \max \left[|(Y+\lambda)^{1/2} - a^{1/2}[v(r)-\lambda]^{1/2}| \ ; |(Y+\mu)^{1/2} - a^{1/2}[v(r)-\mu]^{1/2}| \right]$$

$$G_2(\lambda,\mu;r) = \min \left[(Y+\lambda)^{1/2} + a^{1/2}[v(r)-\lambda]^{1/2}; \ (Y+\mu)^{1/2} + a^{1/2}[v(r)-\mu]^{1/2} \right] \tag{B49}$$

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and

$$A = (1+a)^{1/2} [v(r) + Y]^{1/2} \tag{B50}$$

For charge-transfer (1-3) collisions

$$F^X(\lambda,\mu;r) = \exp\left(\frac{1+c}{1+2c}\right) (\lambda+\mu) \left[\frac{\sqrt{\pi}}{2} \text{ erf } g - g \exp(-g^2)\right]_{g_-}^{g_+} \tag{B51}$$

where

$$g_\pm^2(\lambda,\mu;r) = \frac{c(1+c)}{(1+2c)} \left[[v(r)-\lambda]^{1/2} \pm [v(r)-\mu]^{1/2} \right]^2 \tag{B52}$$

The universal expression (B39) is also valuable in that the one-way equilibrium rate across an arbitrary bound level $\nu = - E/kT$ is simply

$$\alpha_{eq} = \Gamma \, \alpha_T \int_{-\infty}^{\nu} d\lambda \int_{\nu}^{\omega} F(\lambda,\mu) d\mu \tag{B53}$$

where $\omega = - D/kT$ is the maximum binding energy in units of (kT) and where

$$F(\lambda,\mu) = \int_0^{r_m} F(\lambda,\mu;r) r^2 \, dr \, , \, r_m = 1/\max(\lambda,\mu) \tag{B54}$$

This equilibrium collisional rate displays[10,11] a minimum at $\nu^* = (1-3)kT$, the location of a bottleneck.[28]

Moreover, the non-equilibrium association/dissociation rate (6.3) reduces simply to

$$\alpha_A = \Gamma \, \alpha_T \int_{-\infty}^{\nu} d\lambda \int_{\nu}^{\omega} [P^D(\lambda) - P^D(\mu)] \, F(\lambda,\mu) d\mu \tag{B55}$$

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where $P^D(\lambda)$ is the net probability of collisional dissociation of pairs with energy $(-\lambda kT)$. Eq. (B55) with $\nu = 0$ provides the loss rate (6.17) from the continuum (Block C); and provides, with $\nu = -S/kT = \varepsilon$, the growth rate (6.15) of block S, and with arbitrary ν in the block E, $(0 < \nu < \varepsilon)$, provides the association rate (6.23) under quasi-steady-state conditions in block E.

Also various energy-change moments,

$$D_i^{(m)}(E_i) = \frac{1}{m!} \int_{-D}^{\infty} (E_f - E_i)^m C_{if} dE_f \qquad (B56)$$

useful in a Fokker-Planck analysis[43] of the collision term (2.1b) of the main text and expressed simply as

$$D_i^{\ m}(E_i) = \Gamma\alpha(kT)^{m-1}(-1)^m \mathcal{D}_i^{(m)}(\lambda) \qquad (B57)$$

where the dimensionless moments

$$\mathcal{D}_i^{(m)}(\lambda) = \frac{1}{m!} \int_{-\infty}^{\omega} (\mu-\lambda)^m F(\lambda,\mu) d\mu \qquad (B58)$$

are easily determined[28] on using the relevant expression, (B45), (B47), (B48) or (B51), appropriate to the chosen interaction between AB and the gas species.

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Figure Captions

Fig. 1. Assignment of the fully dissociated block C of free $A + B$ pairs, of the fully-associated block S of bound (A-B) pairs and the block E of pairs in highly excited bound levels.

Fig. 2. Ratio of the association rate $R^A(\lambda^*,b,c)$, eq. (7.13) to the exact QSS-rate, eq. (7.14) over variational parameters λ^*, b and c.

Fig. 3. Association and Dissociation Probabilities $P^{A,D}(\lambda)$ as a function of depth into the energy well. For $E_i \sim 10$ kθ, where θ is gas temperature, P^A is almost unity and P^D is negligible. ——— EXACT QSS; $- - - -$, $----$, $.....$ Variational Functions with $\lambda_* = 1.25$ and with the set (b,c) equal to (0,0), (0.20,0) and (0.20,-0.006) respectively.

Fig. 4. First Derivative $(dP^A/d\lambda)$ of association probabilities, corresponding to curves of Fig. 3. The minima of the exact QSS and Variational functions result in identical locations.

FULLY DISSOCIATED PAIRS

$p^D = 1$; $p^A = 0$

p^D , p^A TO BE DETERMINED

$p^A = 1$; $p^D = 0$
FULLY ASSOCIATED PAIRS

INTERNAL ENERGY OF (A-B) PAIR

(A-B) SEPARATION R
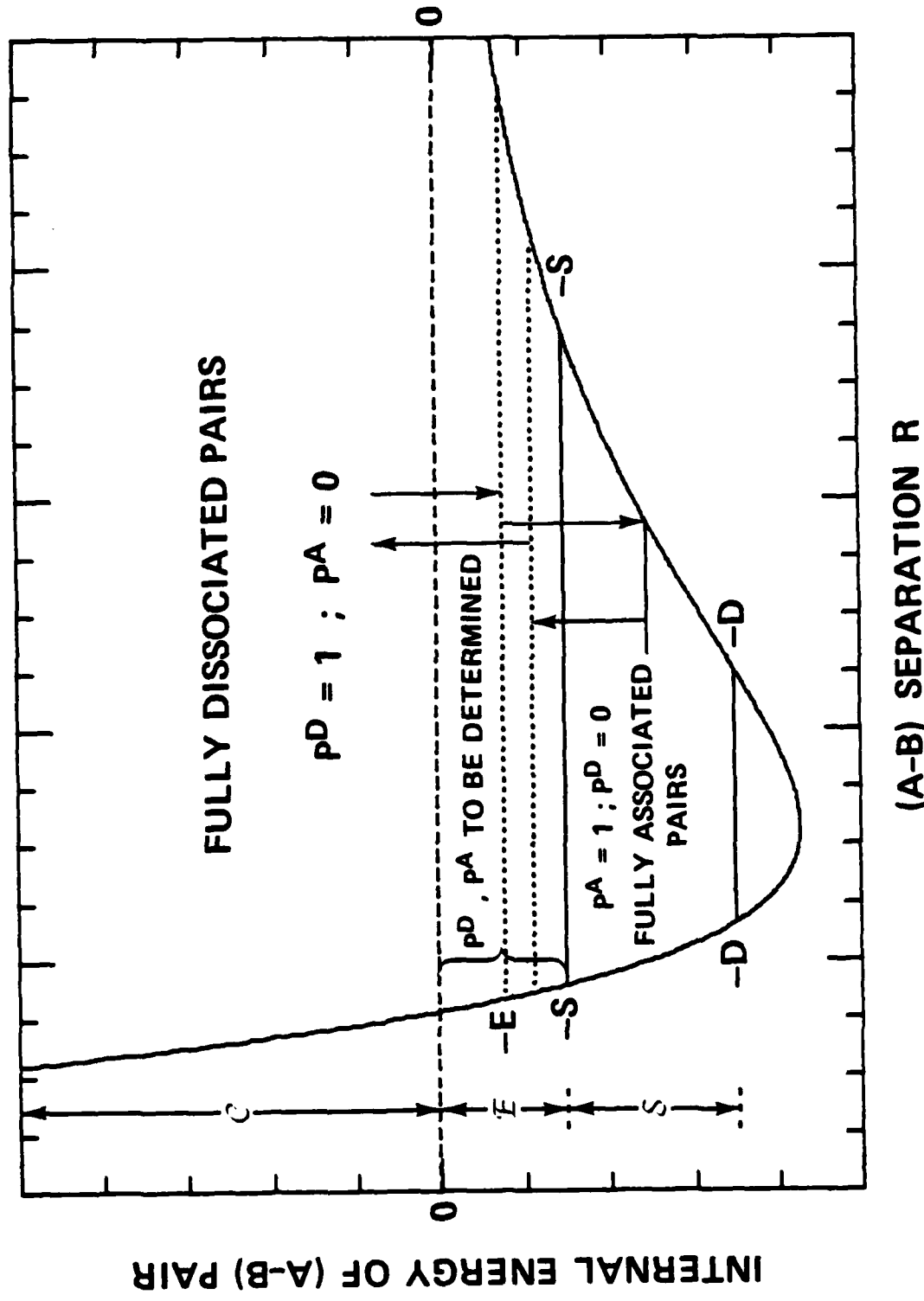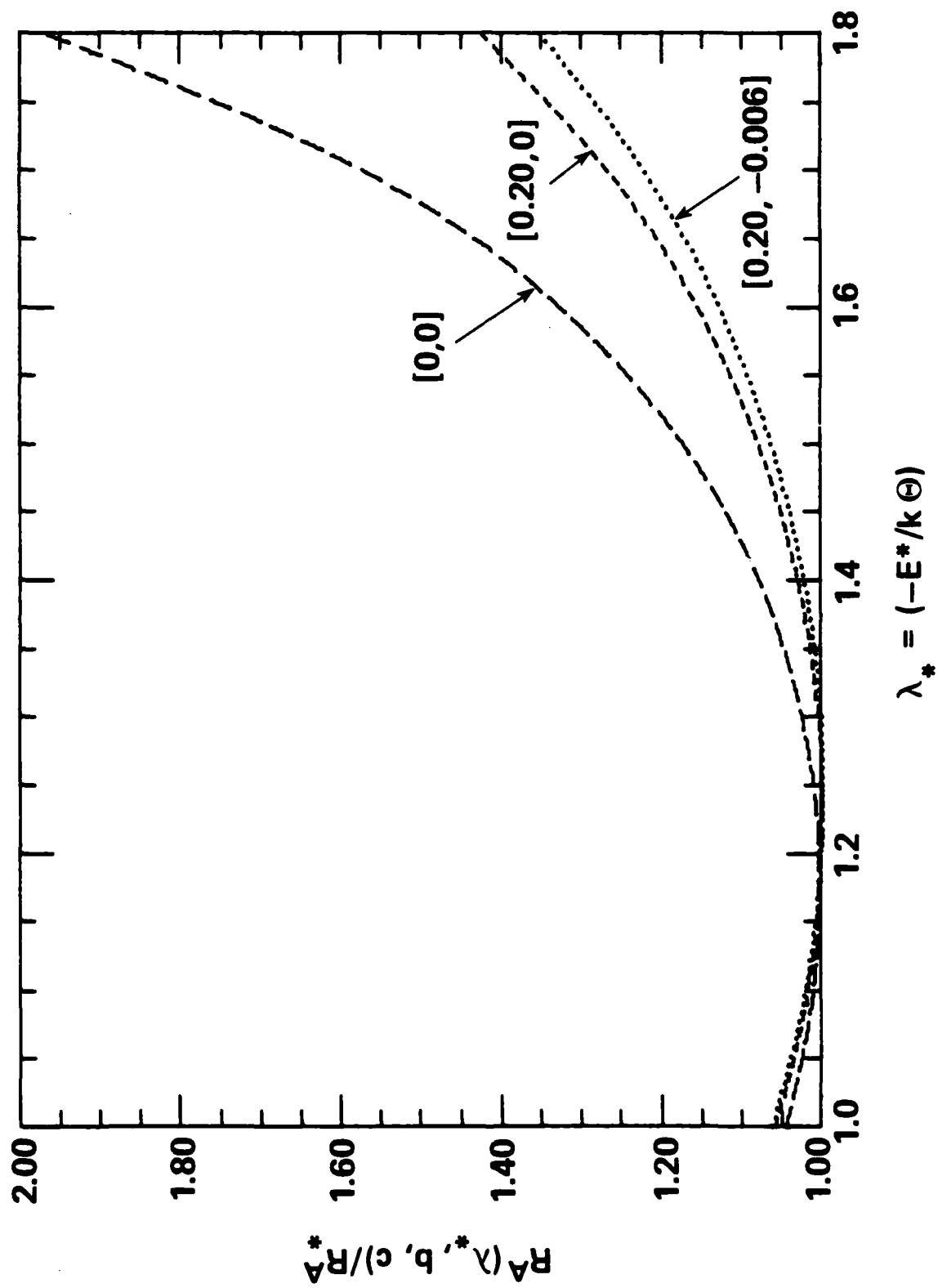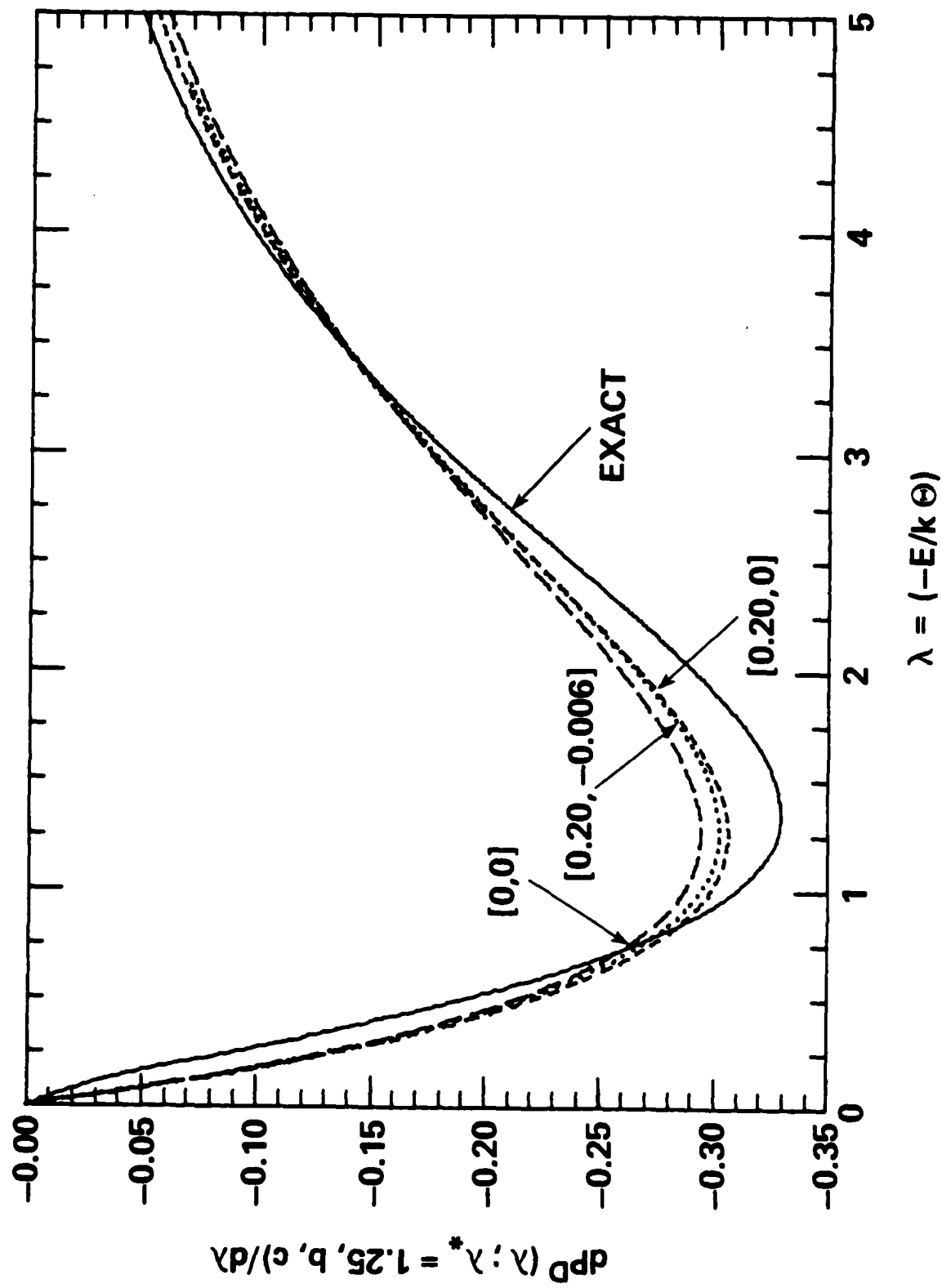
Figure 1
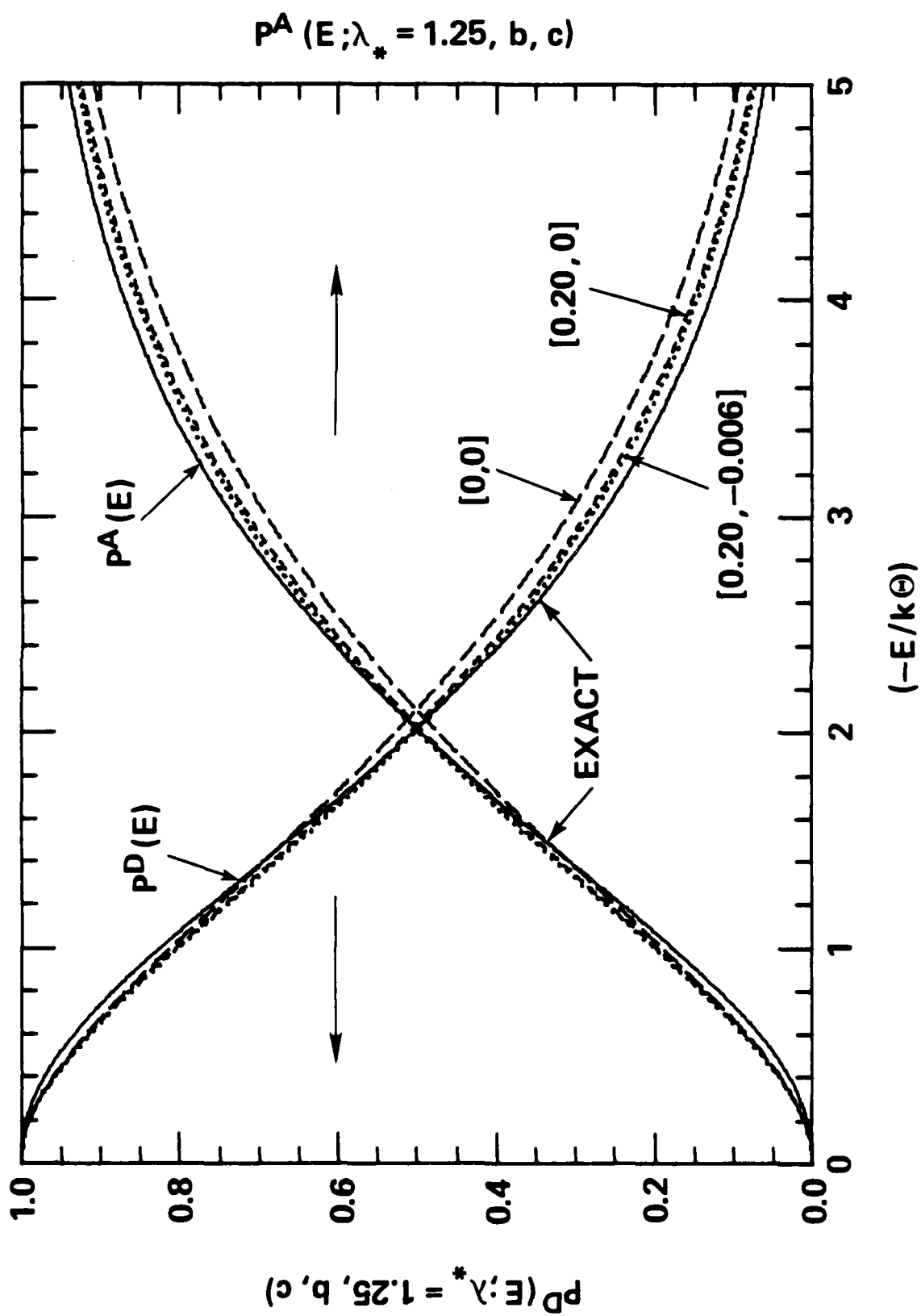
Figure 2

Figure 3

Figure 4

Appendix B

Diffusional Theory of Association/Dissociation

Non-Equilibrium Processes for General Systems

Diffusional Theory of Association/Dissociation Non-Equilibrium Processes for General Systems

M. R. Flannery,
School of Physics,
Georgia Institute of Technology
Atlanta, Georgia, 30332, U.S.A.

Abstract: Upon re-examination of the foundations of the diffusional treatment of association/dissociation processes involving a non-equilibrium distribution of (A-B) pairs in a gas M, it is shown that highly accurate results may be obtained for general mass systems provided a new and more basic expression for the time-dependent association/dissociation rates $R^{A,D}(t)$ is introduced. These rates $R^{A,D}(t)$ are derived here in terms of the probability $P_i^{A,D}(E_i)$ that (A-B) pairs with internal energy E_i has associative/dissociative character and are obtained without appeal to the quasi-steady-state (QSS) condition for highly excited levels E_i. Then association and dissociation can be treated in a unified way and evolution towards equilibrium with the gas is naturally achieved. Comparison is made between the exact probabilities $P_i^{A,D}$ obtained from the QSS-condition to the Exact input-output Master Equation and those obtained from the derived diffusional equation. $R^{A,D}(t)$ reduces to the constant-in-energy current $J(t)$ through the excited levels only for exact QSS of the Master Equation. When approximate probabilities are adopted, identificiation of $R^{A,D}(t)$ with $J(t)$ is not justified. The basic expression introduced here for $R^{A,D}(t)$ is appropriate for both exact and approximate (diffusional) probabilities and yields excellent results for ion-ion recombination in a dilute gas over the full range of masses of the species involved and over various classes of ion-neutral interaction (polarization, hard-sphere and charge-transfer).

Contents

1. Introduction

The picture of recombination and of association/dissociation processes
involving subsystems (A-B) in a thermal bath of dilute gas M as occurring via
diffusion in energy-space has stimulated[1-7] a great deal of interest, in
principle valuable to elucidation of many examples of laser-induced plasmas,
decay, of reaction processes in flames, of shock wave propagation etc. In a
classic paper, Pitaevskii[1] derived a rather elegant analytical result, which
because of its inherent simplicity over more sophisticated and therefore time-
consuming procedures based on a collisional input-output Master Equation[8-10],
has been applied to situations[3-5], other than to electron-ion recombination[1,7]
for which it was originally intended. Bates[11] has pointed out that of the
several different classical diffusion models of _electron-ion_ recombination,
the correct model is that of Pitaevskii.[1] Moreover, the formula of Pitaevskii
can be reproduced[12] exactly by Thomson-style arguments. In spite of its
attractive features, the diffusion picture as formulated[1-6] achieved
remarkably disappointing results for _heavy-particle_ ion-ion recombination[3-6],
or for any atom-atom association process, in a gas.

Apart from recognition that diffusion methods (based on a Fokker-Planck
reduction of the input-output collisional integral) are likely to be valid
only when the collisional energy changes are small, the basic intrinsic defect
for application of the Pitaevskii expression to general mass systems remains
undetected. Moreover, that a much less sophisticated "bottleneck" model[13]
achieved much closer agreement[10] with the exact results of the Master
Equation[8-10] for ion-ion recombination presents a puzzle.

On examination in this paper of the foundation of the diffusion approach
in a new light, the basic defect in the treatment becomes apparent. In §2,
probabilities $P_i^{A,D}$ for association/dissociation of pairs (A-B) with internal

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energy E_i are introduced and an expression for the time-dependent current $J_i(E_i,t)$ is developed. In §3.1, a Fokker-Planck (FP) analysis of the collision integral and current J_i is performed consistently to fourth-order and useful relationships between the various energy-change moments are established. In §3.2, the diffusion approach, based on a second-order FP-analysis, is shown to provide accurate probabilities $P_i^{A,D}$ for general systems but inaccurate heavy-particle currents from which previous rates were obtained.[2-6] A new expression for the time-dependent rates $R^{A,D}(t)$ under all conditions is developed in §4 in terms of $P_i^{A,D}$. These rates obtained with diffusional $P_i^{A,D}$ will then be compared with exact rates[10,15] for the benchmark case of ion-ion recombination in a gas for various masses and ion-gas interactions.

As initiated in ref (14), the analysis here so describes the time evolution from a non-equilibrium distribution of (A-B) pairs with a thermal bath of gas M towards full thermodynamic equilibrium that association and dissociation are treated in a unified way and that general expressions for the rates of association/dissociation are obtained without appeal to the quasi-steady-state condition[1-10] for highly excited levels of the (A-B) pair.

2. Master Equation and Quasi-Steady-State Rates

The collisional input-output Master Equation[2,4,8-10] that governs the distribution $n_i(E_i,t)dE_i$ for the density (cm^{-3}) of subsystems AB with internal energy E_i in the interval dE_i about E_i can be written as,[14]

$$\frac{\partial}{\partial t} n_i(E_i,t) = -\int_{-D}^{\infty} S_{if}(t)dE_f \equiv -\frac{\partial}{\partial E_i} J_i(E_i,t) \qquad (2.1)$$

where the net two level input-output collisional rate of depletion of energy level E_i is

$$S_{if}(t) = n_i(E_i,t)\nu_{if}(E_i,E_f) - n_f(E_f,t)\nu_{fi}(E_f,E_i) = -S_{fi}(t) \qquad (2.2)$$

in terms of $\nu_{if}dE_f$, the frequency (s^{-1}) for $i \to f$ transitions which change the energy E_i to between E_f and $E_f + dE_f$ by collision of the (A-B) pair with the gas M. The energy of the lowest bound level of the AB pair is -D with respect to the dissociation limit, taken as zero energy. The separation between the energy levels of AB is sufficiently small in comparison to the thermal energy (kT) of the bath species M that the levels form a quasi-continuum. Thus J_i in (2.1) is the net upward current (in energy space) past energy level E_i. Since J_i vanishes as $E_i \to \infty$ and -D, it is therefore determined either by the integral expression,

$$J_i(E_i,t) = \int_{E_i}^{\infty} dE_i \int_{-D}^{\infty} S_{fi}(t)dE_f = \int_{E_i}^{\infty} dE_i \int_{-D}^{E_i} S_{fi}(t)dE_f \qquad (2.3)$$

with the aid of the null effect, $S_{if} + S_{fi} = 0$, of collisions, or by the equivalent expression,

$$J_i(E_i,t) = \int_{-D}^{E_i} dE_i \int_{-D}^{\infty} S_{if}(t)dE_f = \int_{-D}^{E_i} dE_i \int_{E_i}^{\infty} S_{if}(t)dE_f \qquad (2.4)$$

since the currents past the end points (-D, ∞) vanish.

Subdivide the range (-D $\to$ ∞) of internal energy into three blocks[14]; the continuum block C in which the pairs (A+B) are fully dissociated, the intermediate block E of highly excited bound levels of (A-B) between the dissociation limit at zero energy and a lower bound level -S, and the lowest (sink) block S composed of tightly bound levels between -S and -D where the pairs AB are fully associated. The level -S is sufficiently deep that the net

probability of <u>direct dissociation</u> by collision with the thermal bath is negligible. In practice, level $-S$ arises quite naturally from the collisional mechanics via the cut-off effect of the Maxwellian distribution of the gas bath at temperature T and generally lies $\sim$ 10 kT below the dissociation limit (cf. Fig 3 of §3).

The net rate of depletion of dissociated species (A+B) with density (cm^{-3}),

$$n_c(t) = \int_0^\infty n_i(E_i,t)dE_i \qquad (2.5)$$

in block C $(0 < E_i < \infty)$ is simply

$$R_c(t) = -\frac{\partial n_c(t)}{\partial t} = -J(0,t) = \int_0^\infty dE_i \int_{-D}^0 S_{if}(t)dE_f \qquad (2.6)$$

the downward current past the dissociation neck. The net rate of increase in the density (cm^{-3})

$$n_s(t) = \int_{-D}^{-S} n_i(E_i,t)dE_i \qquad (2.7)$$

of pairs considered to be fully associated in block S with energy E_i in the range, $-S < E_i < -D$ is

$$R_s(t) = \frac{\partial n_s(t)}{\partial t} = -J(-S,t) = \int_{-S}^\infty dE_{if} \int_{-D}^\infty S_{if}(t)dE_f \qquad (2.8)$$

the net downward current past level $-S$.

Since the system is considered to be closed

$$R_c(t) = R_s(t) + \int_{-S}^{o} (\frac{\partial n_i}{\partial t}) dE_i \qquad (2.9)$$

Introduce, as in ref. 14, the time-independent probability $P_i^A(E_i)$ that (A-B) pairs with energy E_i are considered as associated, then the overall rate for association is

$$R^A(t) = \int_{-D}^{\infty} P_i^A(E_i)(\frac{\partial n_i}{\partial t}) dE_i = R_s(t) + \int_{-S}^{o} P_i^A (\frac{\partial n_i}{\partial t}) dE_i \qquad (2.10)$$

since P_i^A is unity in block S and is zero in block C. The overall rate for dissociation is similarly,

$$R^D(t) = \int_{-D}^{\infty} P_i^D(E_i)(\frac{\partial n_i}{\partial t}) dE_i = - R_c(t) + \int_{-S}^{o} P_i^D(\frac{\partial n_i}{\partial t}) dE_i \qquad (2.11)$$

where $P_i^D(E_i)$, the probability that (A-B) pairs with energy E_i are considered as dissociated, is unity in block C and zero in block S.

In terms of the one-way equilibrium rate

$$C_{if} = \tilde{n}_i \nu_{if} = C_{fi} \qquad (2.12)$$

where $\tilde{n}_i dE_i$ is the (time independent) equilibrium number density of AB pairs in the energy interval dE_i about E_i, and of the normalized distribution,

$$\gamma_i(E_i,t) = n_i(E_i,t)/\tilde{n}_i(E_i) \qquad (2.13)$$

then (2.2) yields

$$S_{if}(t) = [\gamma_i(t) - \gamma_f(t)]C_{if} = -S_{fi}(t) \qquad (2.14)$$

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with the aid of detailed balance (2.12). The Master Equation (2.1) is then

$$\frac{\partial n_i}{\partial t} = \int_{-D}^{\infty} [\gamma_f(t) - \gamma_i(t)] C_{if} dE_f = - \frac{\partial J_i}{\partial E_i} \qquad (2.15)$$

Assume that the energy distribution of pairs in the Continuum block C and the Sink block S is Maxwellian i.e.

$$\gamma_i(E_i,t) = \begin{cases} \gamma_C(t) & , E_i > 0 \\ \gamma_S(t) & , -S > E_i > -D \end{cases} \qquad (2.16)$$

are pure functions of time t which tend to unity as $t \to \infty$.

The non-equilibrium energy distribution of pairs in the intermediate block E of excited levels is therefore separable in energy and time according to the ansatz[14],

$$\gamma_i(E_i,t) = P_i^D(E_i)\gamma_C(t) + P_i^A(E_i)\gamma_S(t) \xrightarrow{\ t \to \infty\ } 1 \qquad (2.17)$$

where P_i^D is the probability that state i is coupled to the continuum i.e. P_i^D is the probability of dissociation, and where P_i^A is the probability that state i is coupled to the sink i.e. P_i^A is the probability of association. Thus $(P_i^A + P_i^D)$ is unity at all times since $\gamma_{C,S}(t \to \infty)$ and $\gamma_i(t \to \infty)$ all tend to unity when full thermodynamic equilibrium with the gas M is established. Hence (2.15) can be conveniently separated in E_i and t according to

$$\frac{\partial n_i(E_i,t)}{\partial t} = - [\gamma_C(t) - \gamma_S(t)] \int_{-D}^{\infty} (P_f^A - P_i^A)C_{if} dE_f \qquad (2.18a)$$

$$= [\gamma_C(t) - \gamma_S(t)] \int_{-D}^{\infty} (P_f^D - P_i^D)C_{if} dE_f \qquad (2.18b)$$

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and the time-dependent current (2.3) or (2.4) separates as

$$J_i(E_i,t) = [\gamma_c(t) - \gamma_s(t)]j_i(E_i) \qquad (2.19)$$

where the time-independent fraction of the current down the energy ladder is

$$-j_i(E_i) = \int\limits_{E_i}^{\infty} dE_i \int\limits_{-D}^{E_i} (P_f^A - P_i^A)C_{if}dE_f = \int\limits_{-D}^{E_i} dE_i \int\limits_{E_i}^{\infty} (P_f^D - P_i^D)C_{if}dE_f \qquad (2.20)$$

Hence

$$\frac{\partial n_i}{\partial t} = [\gamma_c(t) - \gamma_s(t)](\frac{\partial j_i}{\partial E_i}) \qquad (2.21)$$

2.1 Quasi-steady-state (QSS) Rates

As has previously been shown[14], the association/dissociation rates $R^{A,D}(t)$ achieve extrema $R_*^{A,D}(t)$ when the number densities n_i in block E are in quasi-steady-state (QSS) i.e. $\partial n_i/\partial t \approx 0$ in E. The rate R_*^A is a minimum[14] when the net direction is association (as in relaxation of a fully dissociated plasma). The minimum association rate in terms of the effective two-body (constant) rate α (cm^3s^{-1}) for association between A and B with densities $N_{A,B}(t)$ at time t and of the frequency $k(s^{-1})$ of dissociation of S-pairs with density $n_s(t)$ is

$$R_*^A(t) = \alpha N_A(t)N_B(t) - kn_s(t) = R_s(t) = R_c(t) \qquad (2.22)$$

which, by (2.10), is therefore equal to the rate $R_s(t)$ for production of S-pairs or the rate $R_c(t)$ for loss of C-pairs. Hence the required coefficient α is determined from either

$$\alpha N_A(t)N_B(t)[1-r(t)] = \int\limits_{-S}^{\infty} dE_i \int\limits_{-D}^{-S} S_{if}(t)dE_f = -J(-S,t) \qquad (2.23a)$$

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with the aid of (2.3), or from

$$\alpha N_A(t) N_B(t) [1 - \Gamma(t)] = \int_0^\infty dE_i \int_{-D}^0 S_{if}(t) dE_f = -J(0,t) \qquad (2.23b)$$

where a measure of the departure of the densities $N_{A,B}$ and n_s from their corresponding values $\tilde{N}_{A,B}$ and $\tilde{n}_s$ for full thermodynamic equilibrium with the gas M is provided by the factor,

$$\Gamma(t) = [\tilde{N}_A \tilde{N}_B / N_A(t) N_B(t)] [n_s(t) / \tilde{n}_s] \qquad (2.24)$$

The dissociation frequency constant k in (2.22) automatically satisfies the detailed balance relation

$$k \tilde{n}_s = \alpha \tilde{N}_A \tilde{N}_B \qquad (2.25)$$

which satisfies (2.22) when equilibrium ($\Gamma = 1$) is established so that the net rate $R_*^A(t)$ vanishes.

Under the ansatz (2.17), (2.23) and (2.25) with the aid of (2.20) yield the constants

$$\alpha \tilde{N}_A \tilde{N}_B = [\int_0^0 dE_i \int_{-D}^0 P_f^A C_{if} dE_f] = -j(0) \qquad (2.26)$$

which uniquely identifies P_f^A as the association probability, and

$$k \tilde{n}_s = [\int_{-D}^{-S} dE_i \int_{-S}^\infty P_f^D C_{if} dE_f] = -j(-S) \qquad (2.27)$$

which similarly identifies P_f^D as the dissociation probability. Under QSS for

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level E_i in block E, (2.21) shows that

$$\alpha \tilde{N}_A \tilde{N}_B = - j(0) = - j_i(E_i) = -j(-S) = k\tilde{n}_s \qquad (2.28)$$

so that the constants α and k are simply determined by the current (2.20) past arbitary level E_i in block E. Under QSS of block E, the probabilities $P_i^{A,D}$ in the currents (2.20), (2.26) and (2.27) must satisfy the integral equation

$$P_i^{A,D} \int_{-D}^{\infty} C_{if} dE_f = \int_{-S}^{\infty} P_f^{A,D} C_{if} dE_f , \qquad (2.29)$$

the QSS-condition, obtained from (2.18) and solved subject to the constraints that P_i^A is zero in block C ($0 < E_i < \infty$), and is unity in block S ($-S > E_i > -D$). Also P_i^D is unity and zero in C and S, respectively.

It is now the aim to find simple analytical _approximate_ expressions for both $P_i^{A,D}$ and j_i by converting in §3 from an integral representation as (2.1) or (2.18) to a differential representation, and then to raise and resolve the question (in §4) whether or not (2.28) is the correct expression which has always been assumed[1-6] when _approximate_ probabilities $P_i^{A,D}$ are involved, rather than the exact solutions of the integral equation (2.29) - the exact QSS condition which yields (2.28) exactly.

3. Fokker-Planck Reduction

The conversion of the integral operator in (2.18) into a differential operator is achieved by a Fokker-Planck analysis[1] useful when the collision kernel C_{if} favors small energy changes. Here the current J_i in (2.18) is determined to fourth-order, rather than to the customary second order[2].

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3.1 Fokker-Planck Current to Fourth-Order in Enery-Change Moments

On introduction of an arbitary but well-behaved function $\phi_i(E_i)$ whose derivatives vanish at the end-points $[\infty, -D]$, then, with the aid of (2.18),

$$\int_{-D}^{\infty} \phi_i \frac{\partial n_i}{\partial t} dE_i = \int_{-D}^{\infty} \gamma_i dE_i \int_{-D}^{\infty} (\phi_f - \phi_i) C_{if} dE_f \tag{3.1}$$

On expanding the difference

$$\phi_f - \phi_i = \sum_{n=1}^{\infty} \frac{1}{n!} (E_f - E_i)^n [\frac{\partial^n \phi_i}{\partial E_i^n}] \tag{3.2}$$

as a function of energy change $(E_f - E_i)$, assumed small, and upon integration by parts under the explicit recognition that $(\partial^n \phi_i / \partial E_i^n) \to 0$ for $n > 1$ as $E_i \to [\infty, -D]$, then (3.1) can be expressed as

$$\int_{-D}^{\infty} \phi_i \frac{\partial n_i}{\partial t} dE_i = [J_i \phi_i]_{-D}^{\infty} - \int_{-D}^{\infty} \phi_i \frac{\partial J_i}{\partial E_i} dE_i \tag{3.3}$$

to give the following expression for the current,

$$J_i(E_i, t) = \sum_{n=0}^{\infty} (-1)^n \frac{\partial^n (\gamma_i D_i^{(n+1)})}{\partial E_i^n} \tag{3.4}$$

where the energy change moments[2-4] of the collision kernel C_{if} for one-way $(i \to f)$ equilibrium collision rates (2.2) are

$$D_i^{(m)}(E_i) = \frac{1}{m!} \int_{-D}^{\infty} (E_f - E_i)^m C_{if} dE_f \tag{3.5}$$

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Evaluation of these moments can be facilitated by adopting the expressions for C_{if} which corresponds to various A-M and B-M binary interactions (symmetrical resonance charge-transfer[8-10], hard-sphere[10], polarization[15], coulombic[14]) which are presented in universal form in Appendix B of ref. 14. These moments are normalized[14] to the quantity $(-1)^m \Gamma \alpha_T (kT)^{m-1}$ where α_T is the Thomson rate[14], where Γ is a mass factor[14] which depends on the interaction involved (see Appendix B, ref. 14), and where T is the temperature of the gas bath.

The frequency of all collisions for an equilibrium distribution of E_i-pairs is $D_i^{(0)}$; $D_i^{(1)}/D_i^{(0)}$ and $2D_i^{(2)}/D_i^{(0)}$ are respectively the averaged energy-change $\langle \Delta E_i \rangle$ and the average energy change squared $\langle \Delta E_i^2 \rangle$ __per collision__ with the gas. Figs. 1(a,b) illustrate the general trend of these moments calculated here for the specific case[8,10] where internal-energy changes in an ion pair $(X^+ - X^-)$ are due to symmetrical resonance charge-transfer $(X^+ - X)$ collisions. In this case, the velocity vectors of the (fast) ion X^+ and the (thermal) neutral X are interchanged. Large transfers of energy are therefore involved, as is confirmed by $D_i^{(2)}$, the averaged energy-change squared $\langle \Delta E_i^2 \rangle$ __per second__ shown in Fig. 1(a). This case will therefore provide a most stringent test for the weak-collision (diffusion) procedures studied here.

As the binding $\lambda = -E_i/kT$, in units of the thermal energy kT of the gas, increases from the dissociation limit (at zero), the equilibrium number[10] ($\sim \lambda^{-5/2} \exp \lambda d\lambda$) of levels in the range $d\lambda$ about λ decreases from a large value, reaches a minimum at $\lambda^* = 2.5$ and then increases exponentially. Since the energy change frequency ν_{if} for each pair decreases rapidly with increase of binding, the overall shapes of the equilibrium moments $D_i^{(m)}$ in Figs. 1a,b can therefore be explained. Note that the equilibrium collisional frequency $D_i^{(0)}$ is relatively constant in the range (1.8-4) kT of binding. Also the

frequency $D_i^{(0)}$ of energy-change is negative for binding energies

$\lambda = (-E_i/kT) < 1.4 = \lambda^*$, i.e. these pairs become less tightly bound upon

collision and pairs with binding $\lambda > 1.4$ kT become more tightly bound upon

collision (when $D_i^{(1)} > 0$). This critical binding energy specifies the

location at λ^* of a bottleneck, which separates the region $\lambda < \lambda^*$ where

excitation dominates from the region $\lambda > \lambda^*$ where de-excitation is prevalent.

Note also that the even moments $D_i^{(m)}$ display minima which become sharper with

increase of m, as expected, and that the minimum in $D_i^{(2)}$ coincides with the

zero of $D_i^{(1)}$ at λ^*, as clearly shown in Fig. 1b. As we go deeper into the

well, D_1/D_0, the averaged energy-change per collision and D_2/D_0, the averaged

energy-change squared per collision tend to increase linearly with energy

depth (Fig. 1b). These features are quite general for the various ion-neutral

interactions and can be exploited here.

Figs. (2a,b) illustrate the variation of inverses of the even moments

$D_i^{(2)}$ and $D_i^{(4)}$ for different interactions[14] of A and B with M (charge-transfer

CX, hard-spahere HS, and polarization POL). The bottleneck to $D_i^{(2)}$ occurs

roughly in the same location (~ 1.25 kT) for all the interactions, and the

energy-change squared per sec is greatest for the charge-transfer interaction

and weakest for the polarization attraction, as expected. The

moment $D_i^{(4)}$ exhibits similar but more amplified behavior.

Since C_{if} is symmetrical in i and f - the detailed-balance relation

(2.12) - then C_{if}, when expressed as a function of the energy-mean

$\bar{E} = \frac{1}{2}(E_f + E_i)$ and the energy-change $\Delta = E_f - E_i$, is such that[2] $C_{if} =$

$C_{if}(\bar{E}, |\Delta|)$. On expanding C_{if} about E_i in terms of the expansion parameter

Δ, which is assumed small, then

$$C_{if}(\bar{E} = E_i + \frac{1}{2}\Delta, |\Delta|) = \sum_{n=0}^{\infty} \frac{1}{n!}\left(\frac{\Delta}{2}\right)^n \left(\frac{\partial^n C_i}{\partial E_i^n}\right) \qquad (3.6)$$

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where C_i is $C_{if}(\bar{E} = E_i, |\Delta|)$. The moments (3.5) are therefore determined from,

$$m! D_i^{(m)}(E_i) = \sum_{n=1,3,5,}^{\text{odd}} (2^n n!)^{-1} \left[\frac{\partial^n F_i^{(m+n)}}{\partial E_i^n}\right] \; ; \; m \text{ odd}, \qquad (3.7a)$$

$$= \sum_{n=0,2,4,}^{\text{even}} (2^n n!)^{-1} \left[\frac{\partial^n F_i^{(m+n)}}{\partial E_i^n}\right] \; ; \; m \text{ even}, \qquad (3.7b)$$

which involves only the terms

$$F_i^{(s)}(E_i) = \int_{-D}^{\infty} \Delta^s C_i(E_i, |\Delta|) dE_f \qquad (3.8)$$

with s-even, since -D is effectively infinite (~ 5 eV) for the excited states i in the range $0 > E_i > (10-20)kT$ of interest (cf. Fig. 3a, below).

In equilibrium, γ_i in (3.4) is unity and the current can then be expressed, with the aid of (3.7), as

$$\mathcal{J}_i = \sum_{n=0}^{\infty} (-1)^n \left[\frac{\partial^n D_i^{(n+1)}}{\partial E_i^n}\right] = \sum_{n=0,2,}^{\text{even}} \sum_{j=0,2}^{\text{even}} (n-2j)[2^{j+1}(n+2)!(j+1)!]^{-1}$$

$$\frac{\partial^{j+n+1} F_i^{(j+n+2)}}{\partial_i E^{j+n+1}} \qquad (3.9)$$

This new form clearly shows that the coefficient of its first term $\partial F_i^{(2)}/\partial E_i$, which arises from the leading term of the expansion (3.7) for both

$D_i^{(1)}$ and $\partial D_i^{(2)}/\partial E_i$, is identically zero. The coefficient of the second term $\partial^3 F_i^{(4)}/\partial E_i^3$, which is the net balance of the second term in the expansion (3.7) for both $D_i^{(1)}$ and $\partial D_i^{(2)}/\partial E_i$ and of the leading term in the expansion (3.7) for both $\partial^2 D_i^{(3)}/\partial E_i^2$ and $\partial^3 D_i^{(4)}/\partial E_i^3$, is also zero. The leading non-vanishing contribution to (3.9) is $[-\frac{1}{576} \partial^5 F_i^{(6)}/\partial E_i^5]$ which is the net balance of the third terms in the expansion (3.7) for both $D_i^{(1)}$ and $\partial D_i^{(2)}/\partial E_i$ and of the second terms in the expansion (3.7) for both $\partial^2 D_i^{(3)}/\partial E_i^2$ and $\partial^3 D_i^{(4)}/\partial E_i^4$. The consistent neglect of $\partial^4 D_i^{(5)}/\partial E_i^4 \sim \partial^5 F_i^{(6)}/\partial E_i^5$ and higher-order derivatives demands both the neglect in (3.4) of terms with $n > 4$ and the neglect in (3.7a) and (3.7b) of terms with $n > 5$ and $n > 4$, respectively. Hence, the equilibrium current

$$\mathfrak{J}_i \approx D_i^{(1)} - \partial D_i^{(2)}/\partial E_i + \partial^2 D_i^{(3)}/\partial E_i^2 - \partial D_i^{(4)}/\partial E_i^3 \equiv 0 \qquad (3.10)$$

is exact to fourth-order in the moments and is identically zero! Relationships between even and odd moments can be obtained from (3.7) by neglecting $F_i^{(6)}$ and higher terms, i.e. $D_i^{(5)}$ and higher moments, to give

$$D_i^{(1)} = \frac{\partial}{\partial E_i} \left[D_i^{(2)} - \frac{\partial^2 D_i^{(4)}}{\partial E_i^2} \right] \qquad (3.11a)$$

$$D_i^{(3)} = 2 \frac{\partial}{\partial E_i} D_i^{(4)} \qquad (3.11b)$$

which also ensure zero equilibrium current. In view of (3.11) note that equilibrium ($\mathfrak{J}_i = 0$) is obtained only when the current (3.4) is expanded to even order.

With the aid of (3.10), the non-equilibrium current (3.4) to fourth order in moments $D_i^{(m)}$ is

$$J_i^{(4)}(E_i,t) = - [D_i^{(2)} - 2\frac{\partial D_i^{(3)}}{\partial E_i} + 3\frac{\partial^2 D_i^{(4)}}{\partial E_i^2}](\frac{\partial \gamma_i}{\partial E_i}) + [D_i^{(3)} - 3\frac{\partial D_i^{(4)}}{\partial E_i}](\frac{\partial^2 \gamma_i}{\partial E_i^2})$$

$$- D_i^{(4)}(\frac{\partial^3 \gamma_i}{\partial E_i^3}) \qquad (3.12)$$

which is the differential representation (up to and including the fourth-order moment $D_i^{(4)}$) of the double integral

$$J_i(E_i,t) = \int_{E_i}^{\infty} dE_i \int_{-D}^{E_i} [\gamma_f(t) - \gamma_i(t)]C_{if}dE_f \qquad (3.13)$$

for the exact current (2.3). The differential form (3.12) can be called the Fokker-Planck current to fourth-order since the general Fokker-Planck expansion can be employed for any variable whose changes are small in comparison with averaged characteristic values e.g. the collisional energy change Δ here is assumed small relative to the thermal energy kT of the gas bath. Changes in vector momentum $\underline{p}$ are in general very large here so that the usual Fokker-Planck analysis[1] in vector $\underline{p}$-space would not be valid.

Upon use of the approximations (3.11), which are internally consistent to neglect of moments higher than $D_i^{(4)}$, (3.12) reduces to

$$J_i^{(4)}(E_i,t) = - [D_i^{(2)} - \frac{\partial^2 D_i^{(4)}}{\partial E_i^2}](\frac{\partial \gamma_i}{\partial E_i}) - \frac{1}{2}D_i^{(3)}(\frac{\partial^2 \gamma_i}{\partial E_i^2}) - D_i^{(4)}(\frac{\partial^3 \gamma_i}{\partial E_i^3}) \quad (3.14)$$

Inserting the ansatz (2.17) in (3.12), then (2.15) with (3.12) yields

$$\frac{\partial n_i(E_i,t)}{\partial t} = - [\gamma_c(t) - \gamma_s(t)]\frac{\partial j_i(E_i)}{\partial E_i} \qquad (3.15)$$

where in terms of the probability P_i^D for dissociation, the time independent

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current to fourth-order is,

$$j_i^{(4)}(E_i) \approx - [D_i^{(2)} - 2 \frac{\partial D_i^{(3)}}{\partial E_i} + 3 \frac{\partial^2 D_i^{(4)}}{\partial E_i^2}](\frac{\partial P_i^D}{\partial E_i})$$

$$+ [D_i^{(3)} - 3 \frac{\partial D_i^{(4)}}{\partial E_i}](\frac{\partial^2 P_i^D}{\partial E_i^2}) - D_i^{(4)}(\frac{\partial^3 P_i^D}{\partial E_i^3}) + \ldots \quad (3.16)$$

For quasi-steady-state (QSS) in block , j_i is constant. When third-order and higher derivatives of P_i^D, are ignored, a straightforward exercise in the solution of the resulting second-order differential equation can be performed to provide analytical expressions for P_i^D, if required.

3.2 Diffusion Equation and Current

On ignoring in (3.16) moments $D_i^{(3)}$ and higher, the (diffusional) current is,

$$j_d(E_i) = - D_i^{(2)} \frac{\partial P_i^D}{\partial E_i} = D_i^{(2)} \frac{\partial P_i^A}{\partial E_i} \quad (3.17)$$

so that (3.15) reduces to

$$\frac{\partial n_i(E_i,t)}{\partial t} = [\gamma_c(t) - \gamma_s(t)] \frac{\partial}{\partial E_i} [D_i^{(2)} \frac{\partial P_i^D}{\partial E_i}] \quad (3.18)$$

which is a diffusion equation in energy space. The frequency $D_i^{(2)}$ at which the averaged energy-transferred squared changes under thermodynamic equilibrium conditions is the diffusion coefficient (energy^{2}s^{-1}) in energy space. This kind of streaming equation has been previously derived via other techniques by Pitaevskii[1] for electron-ion recombination under highly non-equilibrium conditions when $\gamma_c \gg \gamma_s$ so that $\gamma_i = P_i^D \gamma_c$ in (2.20), and by Keck and Carrier[2] for heavy-particle association/dissociation. It has been studied

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by Landon and Keck[3], by Mahan[5] and by Bates and Zundi[6] for highly non-equilibrium ($\gamma_c \gg \gamma_0$) ion-ion recombination. By explicitly including here the factor ($\gamma_c - \gamma_s$) via the ansatz (2.17), eqs. (3.15) and (3.18) for all $\gamma_{c,s}$ help to emphasize the complete evolution towards thermodynamic equilibrium attained when $\gamma_c \rightarrow \gamma_s \rightarrow 1$.

Another advantage of the ansatz (2.17) is that the intermediate block of highly excited levels can be taken to be in quasi-steady-state (QSS) i.e. $\partial n_i / \partial t \approx 0$ in either (2.18) or (3.18) for all times. The QSS-diffusional curent (3.17) is constant over E, so that the solution of (3.17) subject to condition

$$P_i^D(-S) = 0, \quad P_i^A(-S) = 1 \tag{3.19}$$

is

$$P_d^D(E_i) = - j_d \left[\int_{-S}^{E_i} dE/D^{(2)}(E) \right] = 1 - P_d^A(E_i) \tag{3.20}$$

where the subscript d denotes quantities associated with the diffusion equation (3.18). Various levels of approximate schemes readily follow.

(A) Since

$$P_i^D(0) = 1, \quad P_i^A(0) = 1 \tag{3.21}$$

then (3.20) yields

$$-j_d^{(p)} = \left[\int_{-S}^{0} dE/D^{(2)}(E) \right] = \alpha_p \tilde{N}_A \tilde{N}_B \tag{3.22}$$

for the downward diffusional current which, when compared with (2.28) provides the recombination rate α_p of Pitaevskii[1] used for ion-ion recombination by

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Landon and Keck[3] and by Mahan.[5] Note that the current (3.22) is proportional to the area under the curves in Fig. 2a, and that the association and dissociation probabilities $P_i^{A,D}$ at energy E_i are proportional to the areas which correspond to the energy-ranges $(0 \rightarrow E_i)$ and $(E_i \rightarrow -S)$ respectively.

(B) Rather than requiring (3.21), j_d in (3.20) can be fixed by inserting (3.20) into (2.26) for $j(0)$ to give

$$-j(0) = \int_{-D}^{0} C_f dE_f + j_d \int_{-D}^{0} dE_f C_f [\int_{-S}^{E_f} dE_i / D_i^{(2)}] \qquad (3.23)$$

where

$$C_f(E_f) = \int_0^\infty C_{if}(E_i, E_f) dE_i \qquad (3.24)$$

is the total one-way equilibrium rate for collisional population of a bound level E_f from the continuum C. On equating the exact current $j(0)$ in (3.23) with the diffusional current j_d, then

$$-j_d^{(k)} = [\int_{-D}^{0} C_f dE_f]\{1 + \int_{-D}^{0} dE_f C_f [\int_{-S}^{E_f} dE / D^{(2)}(E)]\}^{-1} = \alpha_K \tilde{N}_A \tilde{N}_B \qquad (3.25)$$

which yields the expression of Keck[4] for α_k. The term in braces, $\{-\}^{-1}$ is simply the ratio of the downward diffusional current to the one-way equilibrium current across the dissociation neck.

(C) Another possibility in similar vein to (B) is to insert (3.20) into (2.27) for $j(-S)$ to give

$$j_d(-S) = [\int_0^\infty D_f dE_f]\{1 + \int_{-S}^{0} dE_f D_f [\int_{-S}^{E_f} dE / D^{(2)}(E)]\}^{-1} = \alpha \tilde{N}_A \tilde{N}_B \qquad (3.27)$$

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where

$$D_f(E_f) = \int_{-D}^{-S} C_{if}(E_i,E_f)dE_i \qquad (3.28)$$

is the total one way equilibrium rate for collisional excitation out of block S to any level f in blocks E and C. The term in braces, $\{-\}^{-1}$ is simply the ratio of the upward diffusional current across $-S$ to the one-way equilibrium current across $-S$.

The feature common to all the above procedures (A)-(C) is that the required current (3.17) depends on the accuracy of the gradient (dP_i^D/dE_i) which, due to the neglect of higher derivatives in (3.16), is described by the diffusion equation (3.18) less precisely than are the actual diffusion QSS-solutions i.e. (3.18) may furnish accurate P_i^D but relatively inaccurate derivatives. More importantly however is that (2.28), which is valid only under exact QSS-condition (2.29) of the exact Master Equation, (2.1) or (2.18), has been invoked for the diffusional currents $j_d^{(P)}$ of (3.22) and $j_d^{(k)}$ of (3.23) which result from the QSS-condition of the different Master (diffusional) Equation (3.18).

The QSS-solution of (3.18) subject to constraints (3.19) and (3.21) is

$$P_d^A(E_i) = \{\int_{E_i}^{0} dE/D^{(2)}(E)\}\{\int_{-S}^{0} dE/D^{(2)}(E)\}^{-1} \qquad (3.29)$$

for the probability that any level E_i in block E, once accessed by collision, has "associative" character. The probability that level E_i has "dissociative" character is the complementary function

$$P_d^D(E_i) = \{\int_{-S}^{E_i} dE/D^{(2)}(E)\}\{\int_{-S}^{0} dE/D^{(2)}(E)\}^{-1} \qquad (3.30)$$

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Thus both functions are constrained to vary monotonically between zero and unity as does the exact numerical solution to the integral equation (2.29) so that, when compared with the exact numerical values, will involve less error than their corresponding derivatives

$$\frac{\partial P_i^{A,D}}{\partial E_i} = \mp \{D_i^{(2)}(E_i)\}^{-1} j_d^{(p),(k)} \tag{3.31}$$

appropriate to currents (3.22) and (3.25) in schemes (A) and (B) above.

3.3 Calculations

The ion-ion (termolecular) recombination process

$$X^+ + Y^- + M \rightarrow XY + M \tag{3.32}$$

is taken as a benchmark case. The recombination coefficient α has previously been represented[9,16] very accurately by the sum

$$\alpha = \alpha_1 + \alpha_2 \tag{3.33}$$

of coefficients α_i obtained by considering separate contributions from $(X^+ -Z)$ and $(Y^- -Z)$ binary collisions (i = 1 and 2, respectively). The exact numerical rates α_i are obtained from (2.28) by inserting the exact numerical solution of the integral equation (2.29), the QSS-condition into (2.20) for the current $j_i(E_i)$. The rates α_i have been tabulated[9,10,15] as a function of the mass-ratio parameter,

$$a_i = M_j M_3 / M_i (M_1 + M_2 + M_3) \tag{3.34}$$

where M_i are the masses of species X^+, Y^- and M, $i = 1,2$ and 3 respectively and where the set (i,j) is equal to $(1,2)$ or $(2,1)$ depending $(1-3)$ or $(2-3)$ collisions, respectively.

Based on previous analysis[8-10], universal expressions have been presented in Appendix B of ref 14 for the equilibrium rate C_{if} appropriate to the three classes - polarization[15], charge-transfer[8,10] and hard-sphere[10] - of ion-neutral interactions, calculations have been performed here for the exact QSS-rates α_E that rise from $(1-3)$ collisions and for the corresponding diffusional rates, (3.22) for α_p and (3.25) for α_K of Pitaevskii[1] and Keck[4] respectively. The exact rates α_E reproduce the previous calculations[10,15], and there is little discernable difference between α_p and α_K which now be simply called the diffusional rates α_D obtained when the diffusional current (3.17) is inserted in (2.28).

Table I provides present values of the ratio α_D/α_E for the various interactions over the full range of mass parameter a, eq. (3.34) with i=1 and 2. Small a $\approx 10^{-3}$ corresponds to collisional recombination of heavy ions $(M_1 \approx M_2 \gg M_3)$ in a much lighter (electron) gas, intermediate a(= 1/3 for $M_1 = M_2 = M_3$) corresponds to species of equal mass, and large a $\approx 10^3$ for $M_1 \ll M_2 \approx M_3$ corresponds to electron-ion recombination in an ambient gas. The cases of small and large a involve energy transfers which are very much less than the energy kT of the gas so that the diffusional (weak collision) approach is likely to be valid.

As Table I shows, the diffusional rates are reliable, as expected, only for recombination in a vanishingly light gas (a $\approx 10^{-3}$) or for electron-ion recombination (a $\approx 10^3$) in a general gas, the case for which Pitaevskii[1] designed his diffusional treatment. The diffusional rates are higher by

between a factor of 3-6 for intermediate a ~ 1. As the ion-neutral interaction varies from polarization attraction, to hard-sphere repulsion and to charge-transfer interaction, the energy-change in the ion-neutral collision becomes progressively larger (see Fig. 2a,b) so that the diffusional rates (based on weak collisions) become less accurate, as shown directly by the variation of entries in Table 1 for a specified mass parameter a.

Since (3.17) predicts zero current in both the fully dissociated and fully associated blocks, C and S respectively, the diffusional current (3.17) is therefore discontinuous, zero in C, j_d in E and zero in S. The diffusion rates (3.22) of Pitaevskii and (3.25) of Keck are therefore expected to be valid only in the limit of vanishingly small rates α of association. This is true only for the limiting cases in Table 1 of small and large a. Then the actual rates α_E for electron-ion collisional recombination in a gas and for electron-ion recombination in a gas are[7] ~ 10^{-9} cm^3 s^{-1} at STP, which are three orders of magnitude less that the rate[17] α_E ~ 10^{-6}cm^{3}s^{-1} at STP for ion-ion recombination in an equal mass gas.

Another reason for failure of the diffusion approach as previously applied to general-mass cases is also apparent. As Figs. 3(a,b) show, the diffusion equation (3.18) in general furnishes fairly accurate probabilities $P_i^{A,D}$, (3.29) and (3.30), but less reliable gradients $dP_i^{A,D}/dE_i$.

In an effort to distinguish between the requirements of accurate distributions $P_i^{A,D}$ and the integral/differential forms of the collision integral of the Master Equation, assume that the intermediate block E between blocks C and S is absent i.e.

$$P_i^D (E_i) = \begin{cases} 1, & -E < E_i < \infty \\ 0, & -D < E_i < -E \end{cases} \qquad (3.35)$$

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where -E is some bound energy level. The current (2.25) then reduces to

$$-j_{BN}(-E) = \int_{-E}^{\infty} dE_i \int_{-D}^{-E} C_{if} dE_f = \alpha_{BN}(E)\bar{N}_A\bar{N}_B \qquad (3.36)$$

which is the one-way equilibrium downward current across level -E. As -E is varied, this current achieves a minimum[10] at energy -E* ($\approx$ -2kT) which therefore acts as a "bottleneck"[13] to the recombination which proceeds at rate $\alpha_{BN}(E*)$. The ratio of α_{BN} at the bottleneck E* to the exact numerical rate α_E is displayed in Table I for the "intermediate" hard-sphere case[10]. The bottleneck method fails quite markedly for small and large mass parameters a, where by contrast the diffusion current is successful, and becomes much more reliable than the diffusion approach at intemediate a ($\approx$ 1). Since (3.36) assumes the least possible knowledge of the probabilities $P_i^{A,D}$ (subject to the constraints) but an integral form to the input-output collision dynamics, it follows that accurate distributions are essential at small and large a where the collision dynamics is weak, so that the discontinuous integral form (2.25) does reduce indeed to the continuous streaming form (3.17). For intermediate a when the energy-changes are certainly not weak, inclusion of the integral form (2.25) is apparently more important than the use of accurate distributions (which are constrained to vary between unity and zero at the boundaries of block E).

The closeness exhibited in Fig. 3(a) between the diffusional probabilities, (3.29) and (3.30), and the exact numerical probabilities may be exploited in two ways. First, an interative procedure

$$P^{(n+1)}(E_i) \int_{-D}^{\infty} C_{if} dE_f = \int_{-S}^{\infty} P^{(n)}(E_f) C_{if} dE_f \qquad (3.37)$$

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to the solution of the integral equation (2.29) can be developed by using the diffusional analytical probabilities as the starting (n=0) solution. It is found here that convergence to within 1% of the exact solution can be in general achieved after five iterations, so that accurate rates can then be determined from (2.28) and (2.20) since the QSS-condition (2.29) is satisfied.

Since the diffusional probabilities (3.29) and (3.30) are reasonably accurate, a second possibility is to insert them directly into (2.20) to yield the rate α from (2.28). This procedure, at first sight attractive, is however inconsistent, in that the diffusional probabilities while satisfying quasi-steady-state (QSS) of the diffusional equation (3.18) in block E, do not satisfy the condition (2.29) for QSS of the Master Equation (2.18). The resulting current (2.20) will therefore not be a constant in block E. This is demonstrated by Fig. 4 which compares the exact downward current $-j_E(E_i)$ past level E_i obtained from the solution of (2.29) in (2.20) with the approximate downward current $-j_A(E_i)$ obtained by inserting (3.29) in (2.20). Not only is the approximate current past the bound levels far from being constant, but assignment of a bound level E_i for determination of α from (2.28) is uncertain. Moreover the current j_i exhibits a very rapid variation in the neighborhood of the dissociation limit (at zero energy) that use of $j(0)$ in (2.28) cannot be recommended. The exact value of $j(0)$ is $\sim$ 50% higher than the approximate $j(0)$. Some defense can be made by adopting the value of j_A at the bottleneck energy of $\sim$ 2 kT to (3.36). Then $j_A \approx j_E$, but the foundation is not firm.

The basic reason for the inconsistency of this second approach for j_A is not that the diffusional probabilities are not sufficiently accurate for useful application but that the current expression (2.28) for the association

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rate is not valid when approximate probabilities, which do not satisfy the QSS-condition (2.29) to the exact Master Equation, are used. This dilemma is resolved in the following section.

4. Basic Expression for Rates and Results

The expression (2.9) for the time-dependent association (recombination) rate $R^A(t)$ is exact, while expressions for α in §2.1 hold only for QSS ($\partial n_i/\partial t = 0$) of the Master Equation (2.18) for block E. With the aid of (2.1) in (2.9), the rate

$$R^A(t) = \int_{-D}^{\infty} P_i^A dE_i \int_{-D}^{\infty} S_{fi}(t) dE_f \tag{4.1}$$

where S_{fi} is given by (2.2) is also exact. Under the basic ansatz (2.17), then

$$R^A(t) = [\gamma_c(t) - \gamma_s(t)] \int_{-D}^{\infty} P_i^A dE_i \int_{-D}^{\infty} (P_i^A - P_f^A) C_{if} dE_f \tag{4.2a}$$

$$= \frac{1}{2} [\gamma_c(t) - \gamma_s(t)] \int_{-D}^{\infty} dE_i \int_{-D}^{\infty} (P_i^A - P_f^A)^2 C_{if} dE_f \tag{4.2b}$$

$$\equiv \alpha N_A(t) N_B(t) - k n_s(t) \tag{4.3}$$

with the result that the time-independent rate constant α ($cm^3 s^{-1}$) of association is determined by

$$\alpha N_A N_B = \int_{-D}^{\infty} P_i^A dE_i \int_{-D}^{\infty} (P_i^A - P_f^A) C_{if} dE_f \tag{4.4}$$

When the exact QSS condition (2.29) is satisfied by the probabilities $P_i^{A,D}$, then (4.4) reduces to (2.28) with (2.20) for the current j_i. When

$P_i^{A,D}$ are determined via an approximate procedure, as by the diffusional treatment of §3.2, then (4.4) remains the appropriate expression for the rate α. The QSS-condition (2.29) corresponds to a minimum[14] in α and hence any approximate $P_i^{A,D}$ will yield higher rates α (cf. Table 1).

An alternative exact expression which emphasizes the role of the current J_i is obtained by using (2.1) and by integrating (2.10) and (2.11) by parts to give

$$R^{A,D}(t) = - \int_{-D}^{\infty} P_i^{A,D}(E_i)(\frac{\partial J_i}{\partial E_i})dE_i = \int_{-S}^{\infty} J_i(E_i,t)(\partial P_i^{A,D}/\partial E_i)dE_i \qquad (4.5)$$

since J_i vanishes at the end points and since $P_i^{A,D}$ are both constants in blocks C and S. It is <u>only</u> when J_i, given exactly by (2.3) or (2.4) is constant-in-energy (QSS) over block E that it can be taken outside the integral sign to give the minimum

$$R_*^A(t) = R_*^D(t) = [\gamma_c(t)] - \gamma_S(t)]j_i(E_i) \qquad (4.6)$$

in terms of (2.20) for j_i and of P_i determined from the QSS-condition (2.29). Otherwise, the exact expression (4.5) is used.

The exact rates α_E obtained in §3.3 for the various ion-neutral interactions are normalized (cf ref. 10 and Appendix B, ref 14) to the corresponding Thomson rate[10]

$$\alpha_T = \frac{4}{3} \pi (R_e/\beta)^3(3kT/M_{12})^{1/2}\sigma_0 N \quad , \quad \beta = 3/2 \qquad (4.7)$$

where R_e is the natural unit (e^2/kT) for Coulombic attraction between the ions 1 and 2. The integral cross section σ_0 for (1-3) elastic collisions at

relative energy ($\frac{3}{2}$ kT) is taken in (4.5) to be $2Q^X$, $2\pi(pR_e/3)^{1/2}$ and σ_0^H respectively for symmetrical resonance charge-transfer collisions[11] with cross section Q^X, for polarization (orbiting) collisions in terms of the polarizability p of the gas M, and for hard-sphere collisions with cross section σ_0^H. Universal expressions for the normalized ratios (α_E/α_T) have already been presented[14] in a form suitable for direct computation.

Approximate rates α_A can now be determined by inserting the diffusional (approximate) probabilities (3.29) in (4.4). Fig. 5 displays a comparison of the corresponding ratios

$$R_T = (M_1/M_{12})(\alpha/\alpha_T) \tag{4.8}$$

where α is taken as the exact rate α_E or the approximate rate α_A, which arises from (1-3) collisions.

Excellent agreement is obtained over the full range of the mass parameter a, eq (3.34) with i = 1 and j =2 i.e. from a ~ 10^{-3} for association of heavy ions in a light (electron) gas, to intermediate a ~ 1/3 for equal mass species and up to large a ~ 10^3 which corresponds to electron-recombination in a gas. As expected, greatest departures occur for the case of equal masses which involves the largest energy transfer so that the diffusional probabilities would also show their greatest departure from the exact probabilities as in Fig. 3a. For this case (a = 1/3), the diffusional result corresponding to hard-sphere collisions which in turn involve largest energy-transfers (cf. Fig. 2) exhibit the largest of small departures. The present diffusional treatment is also excellent for all of the various classes of (1-3) interaction considered.

5. Summary

On introduction of probabilities $P_i^{A,D}(E_i)$ that pairs (A-B) with internal energy E_i will tend to associate and dissociate in a thermal bath of gas M, and upon use of the ansatz (2.17) for their normalized energy distribution $\gamma_i(t)$ at time t, the basic Master Equation (2.1) and current (2.3) has been transformed into corresponding equations (2.18) and (2.19) which are separable in E_i and t. The diffusional equation (3.18), which is a derived approximation to the Master Equation (2.18), yields, for general systems, accurate probabilities $P_i^{A,D}$ (cf Fig 3) but very inaccurate currents (3.22) or (3.25), cf Table 1. Since previous expressions for association (recombination) rates α rely on a Quasi-Steady-State Condition (QSS) of (2.29) to the original Master Equation (2.18), they were therefore based on the currents (2.20), (2.26) and (2.27) via eq (2.28). Since the diffusional probabilities do not satisfy this original QSS-condition, the corresponding diffusional current is, in general, not appropriate for determination of the rates α. The resulting diffusional rates (3.22), or (3.25), are therefore not reliable[2-6] (Table 1), except for those cases in which the current is relatively small i.e. for collision electron-ion recombination[1] in a gas and for ion-ion recombination in a vanishingly light gas.

A new expression (4.2), derived for the rates, is the correct and more basic expression for use under general conditions, as when QSS is not satisfied. When QSS is satisfied, (4.2) reduces to (2.28) based on the current (2.20) and the QSS-rates are minimum.[14] The rate (4.2) is required for use of approximate probabilities, such as those (3.29) provided either by the diffusional treatment, as here, or by simple analytical variational functions for $P_i^{A,D}$, which do not satisfy the basic QSS-condition (2.29).

The diffusional probabilities can be used in an iterative solution of (2.29) to give highly accurate probabilities (to within 1%) after a few iterations and hence accurate rates (2.28). They can also be used in the basic formula (4.2) to yield excellent agreement with the exact numerical QSS-results for various classes of ion-neutral interactions over the full range of mass parameters for general systems.

In conclusion, application of the diffusional equation (3.18) to general systems is an accurate procedure provided the solutions $P_i^{A,D}$ are inserted in the appropriate and more basic expression (4.2) for the rate, rather than into the derived expressions (3.17) or (2.20) for the diffusional or exact currents, which only follow from the QSS-condition (2.29) to the exact input-output Master Equation (2.18).

Acknowledgment

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Table 1: Variation of the ratio (α_D/α_E) and (α_{BN}/α_E) with mass-ratio parameter a for (1-3) collisions and with the various (1-3) interactions: polarization (POL), hard-sphere (HS) and symmetrical resonance charge-transfer (CX). The exact, diffusional and bottleneck rates are α_E, α_D and α_{BN}, respectively.

	α_D/α_E			α_{BN}/α_E
a	POL	HS	CX*	HS
0.001	0.955	0.969	0.997	50.51
0.01	1.159	1.205	1.295	7.692
0.1	2.000	2.410	2.985	2.950
1/3	2.924	3.891	5.051	2.227
1.0	3.413	4.854	6.329	2.020
10.0	2.000	2.941	-	2.674
100.0	1.156	1.403	-	6.452
1000.0	0.955	1.053	-	32.26

*Here small a implies $M_2 \ll M_1 = M_3$ and a = 1 implies $M_2 \gg M_1 = M_3$.

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<u>Figure Captions</u>

Fig. 1 (a) Normalized energy-change frequency moments $D^{(m)}$ (energy^m s^{-1}), m = 0-4, as a function of internal energy $E_i = -\lambda(kT)$ of the bound ion-pair. (b) Ratios $D^{(m)}/D^{(o)}$ (energy^m per collision), m = 1 and 2, and comparison of $D_i^{(1)}$ with $\partial D_i^{(2)}/\partial\lambda$ which shows that the minimum of $D_i^{(2)}$ has same location as the zero in $D_i^{(1)}$. Equal-mass species and charge-transfer ion-neutral collisions are assumed and moments are normalized to the quantity $(-1)^m\Gamma\alpha_T(kT)^{m-1}$ given in ref. 14.

Fig. 2 Inverses of moments (a) $D^{(2)}(\lambda)$ and (b)$D^{(4)}(\lambda)$ as a function of internal energy $E_i = -\lambda kT$ of the ion-pair for various ion-neutral interactions: POL (polarization), HS (hard-sphere), CX (charge-transfer). Equal-mass species are assumed.

Fig. 3(a). Probabilities $P^{A,D}$ for association and dissociation of an ion-pair bound with energy $E_i = -\lambda kT$. Equal-mass species and charge-transfer ion-neutral collisions are assumed. ——: Exact QSS-solution of eq. (2.29). ----: Diffusional Approximation, eq. (3.29) and (3.30).

Fig. 3(b) Derivatives $(dP^A/d\lambda)$ of probability P^A of Fig. (3a) for association. QSS: from solution of eq (2.29). D: diffusional approximation, eq (3.31).

Fig. 4. Comparison of currents, eq (2.20), past energy level $E_i = -\lambda kT$, obtained (——) from exact solution of eq (2.29) and from (---) diffusion probabilities eq (3.29). Equal-mass species and charge-transfer ion-neutral collisions are assumed. The current is normalized to $(2\alpha_T\tilde{N}_A\tilde{N}_B)$ where α_T is the Thomson rate, eq (4.5).

Fig. 5. Normalized rates R_T, eq (4.6), for ion-ion recombination in a dilute gas as a function of mass parameter a, eq (3.34) for various ion-neutral interactions: HS (hard-sphere), CX (charge-transfer) and POL (polarization). ———: exact rates. □, ○, △: rates obtained with diffusional probabilities, eq (3.29), in basic eq (4.4) for HS, CX and POL interactions.
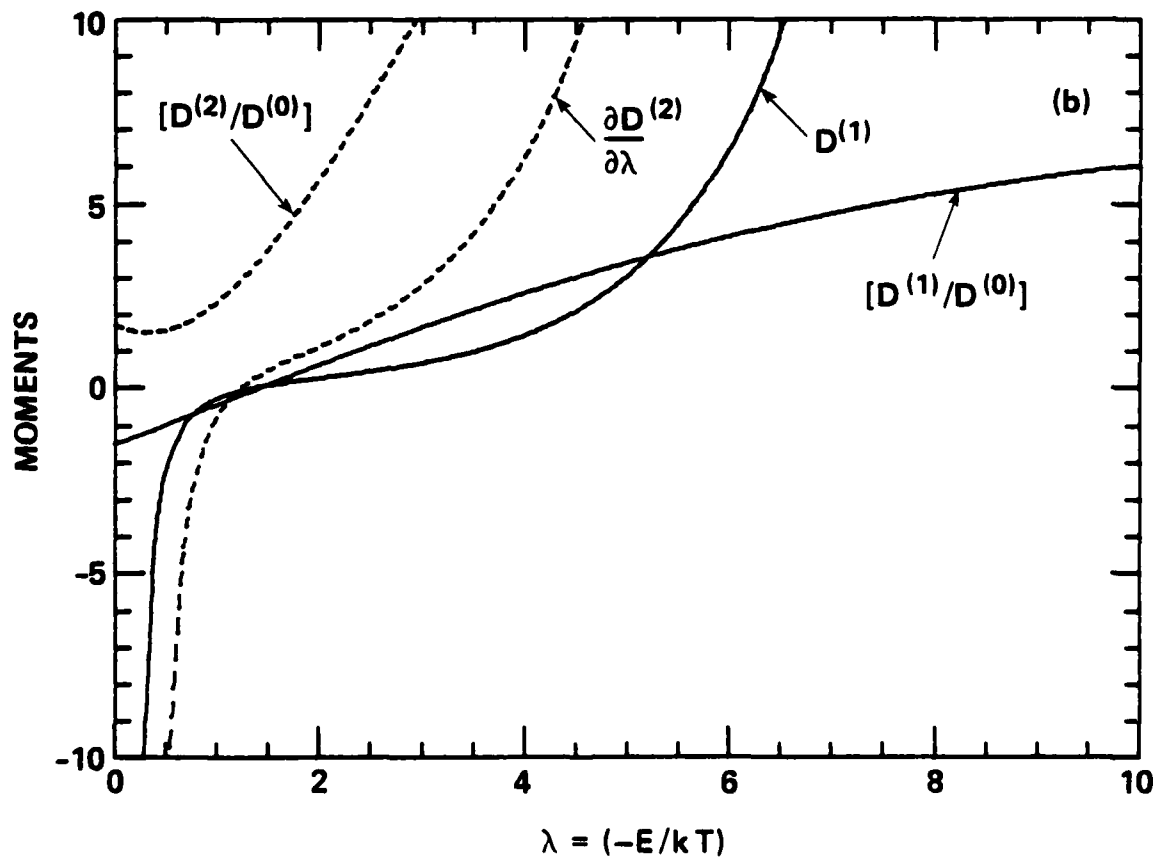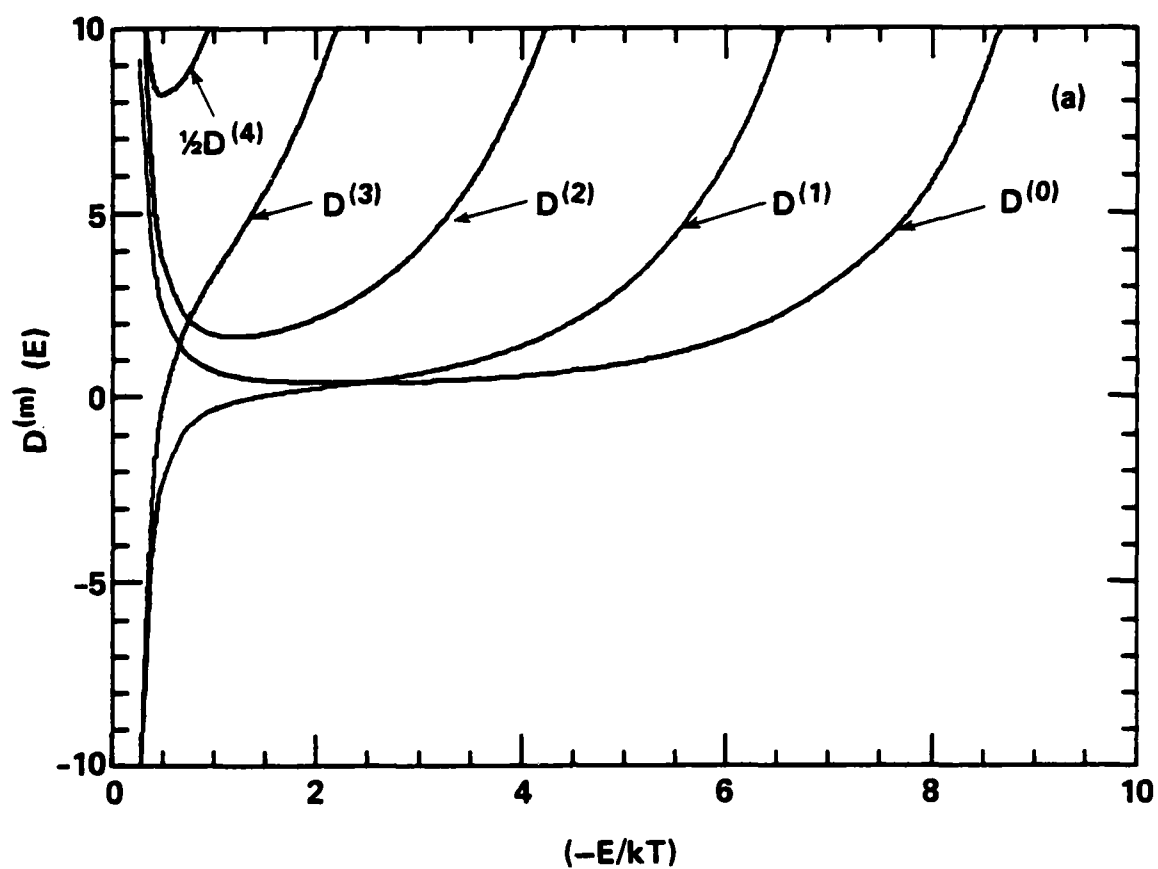
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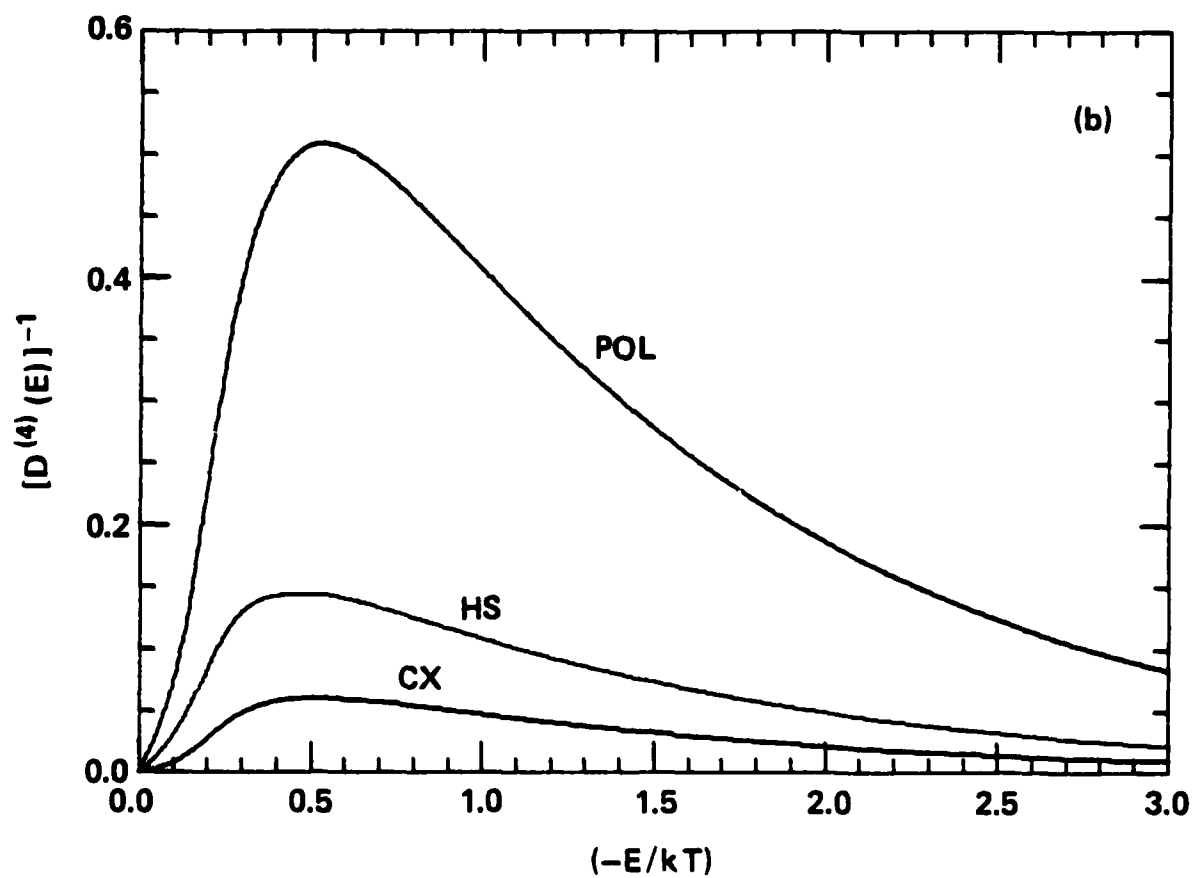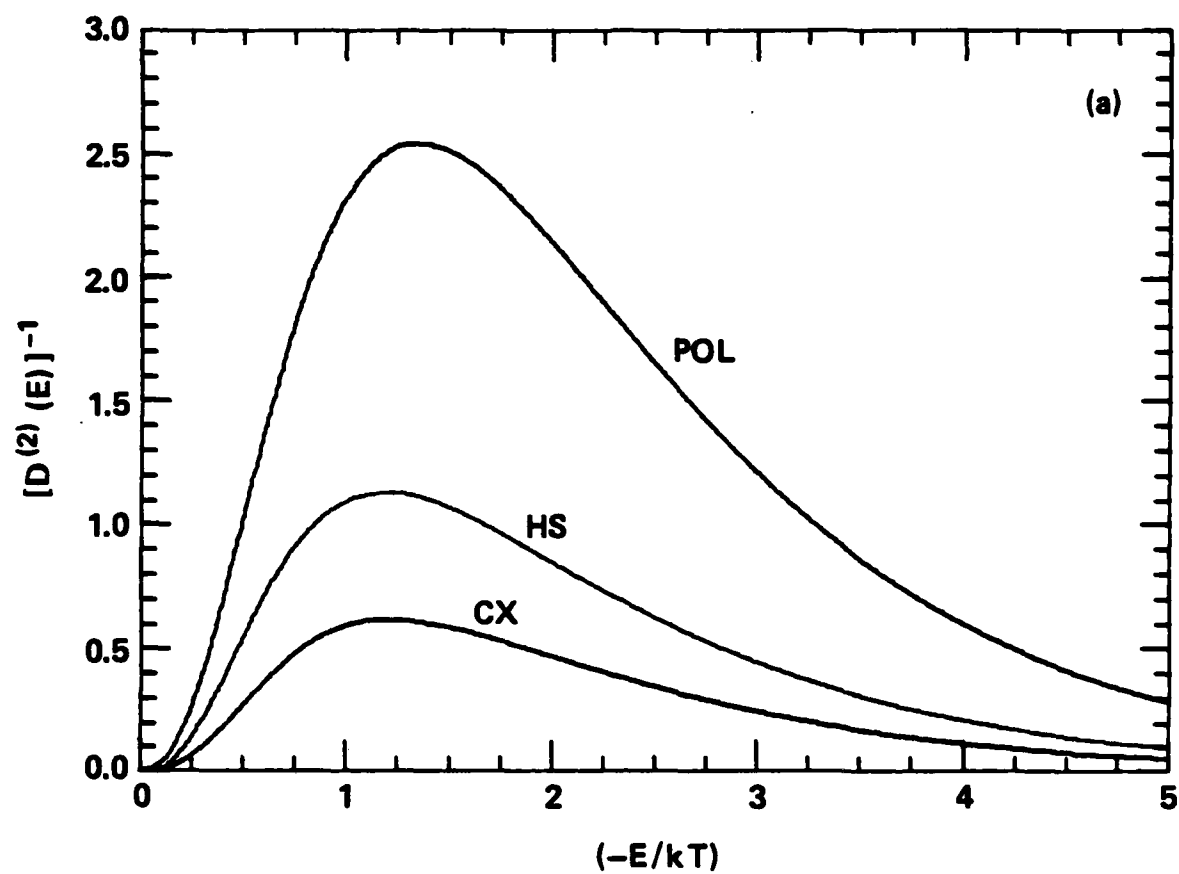
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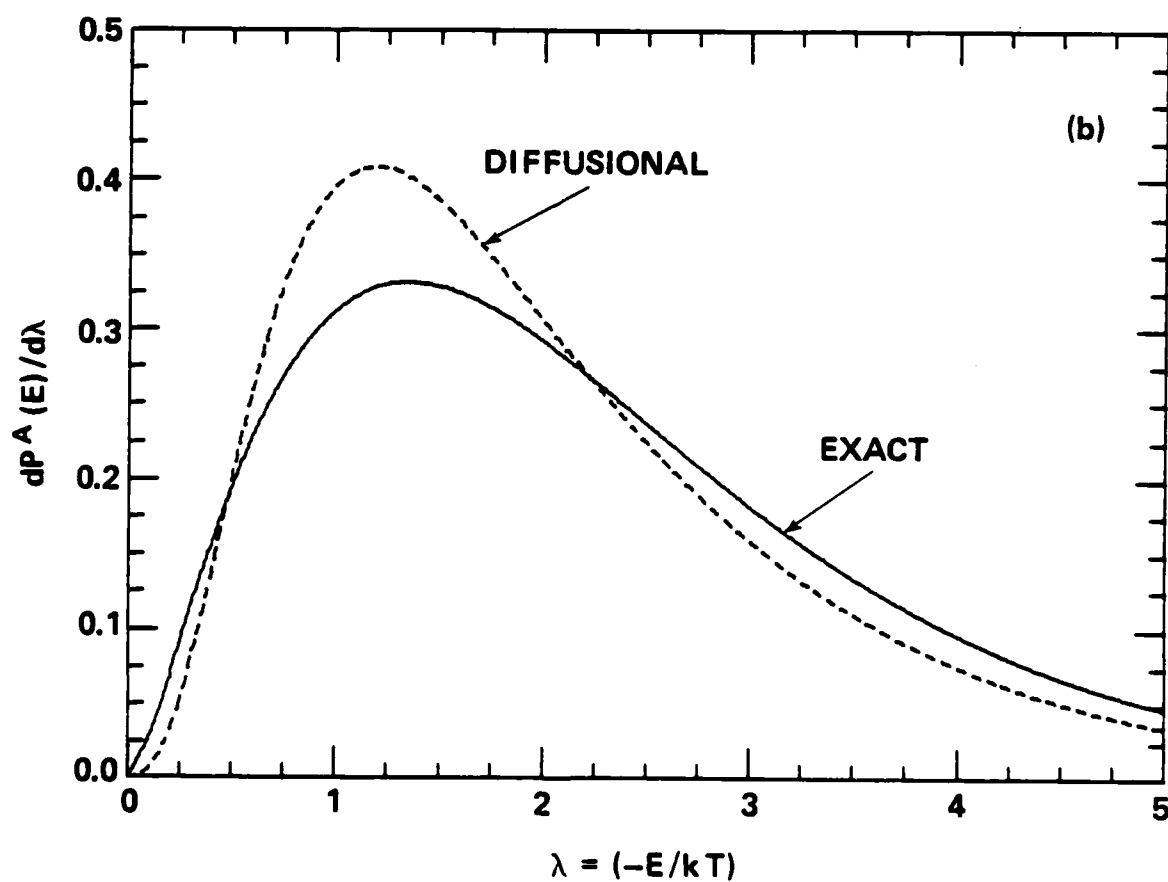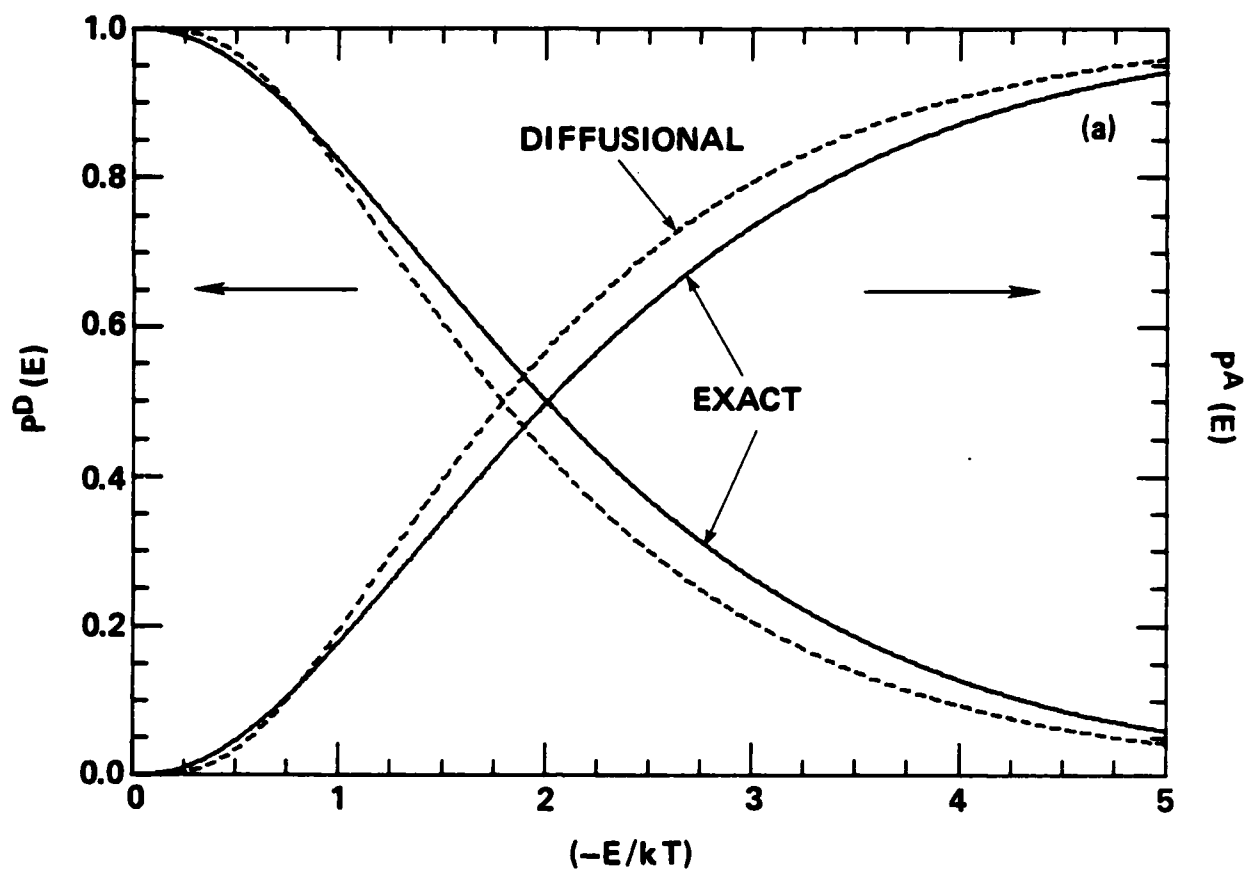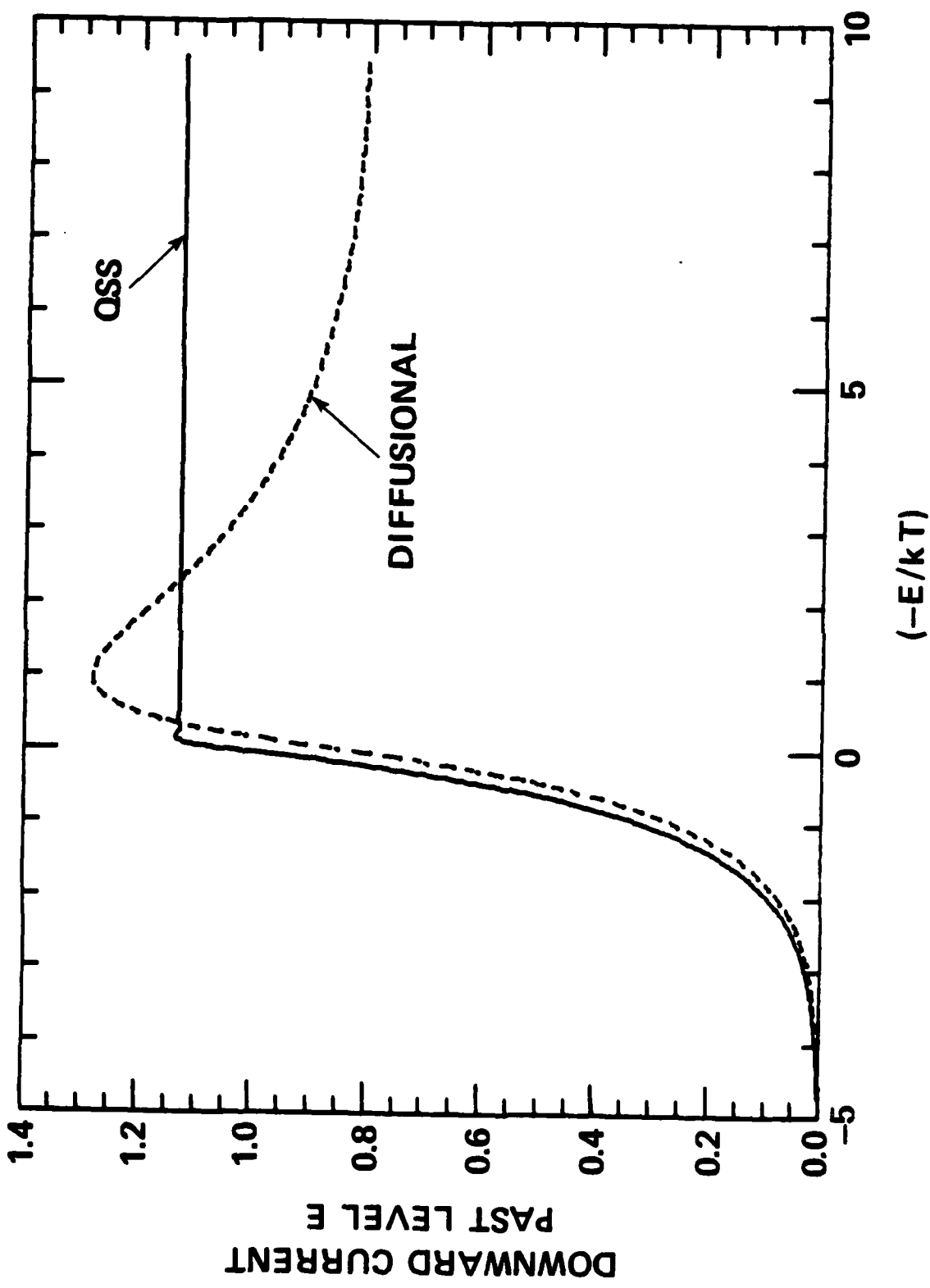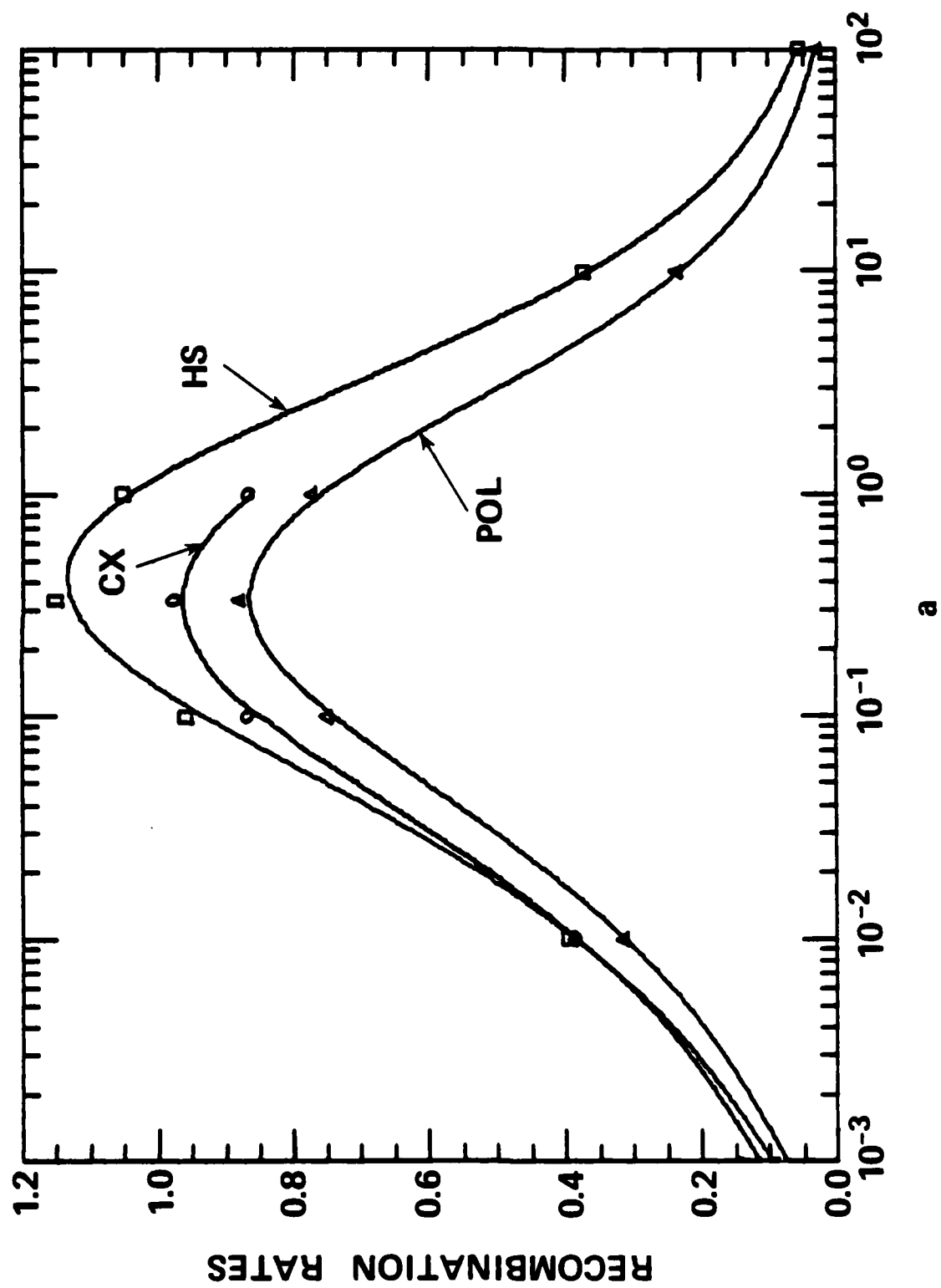
Figure 3

Figure 4

Figure 5

Appendix C

Microscopic Basis and Analytical and Numerical Solutions of

the Debye-Smoluchowski Equation

Microscopic Basis and Analytical and Numerical Solutions
of the Debye-Smoluchowski Equation

M. R. Flannery and E. J. Mansky

School of Physics

Georgia Institute of Technology

Atlanta, Georgia 30332

By explicitly including collisions and by operating at a level more basic than the macroscopic Debye-Smoluchowski Equation (DSE), various assumptions within the DSE-treatment of transport influenced reactions of A and B in a dense medium M become naturally exposed. The appropriate modification of DSE to description of the kinetics within the region of the sink is provided.

Analytical expressions for probability densities and rates are derived which are exact solutions of DSE (a) at all times t and large internal separations R of the pair (A-B), (b) at long times t and all R and (c) at short times t and all R. Not only are the transient rates $\alpha_S(t)$ and $\alpha_L(t)$ exact at short and long times, respectively, but they are naturally bounded for all times with $\alpha_S(t \to \infty)$ and $\alpha_L(t \to 0)$ tending to the correct limit, albeit with an incorrect transience. Comparison with exact numerical solutions of DSE illustrates the effectiveness of a proposed solution over the full range of time.

Contents

1. Introduction

In chemical kinetics of reactions in the condensed phase or in solution and of coagulation of colloids, the Debye-Smoluchowski Equation (DSE)[1-3] has received widespread application. It involves solution of the continuity equation

$$\partial n(\underset{\sim}{R},t)/\partial t + \underset{\sim}{\nabla}\cdot\underset{\sim}{J}^d(\underset{\sim}{R},t) = 0 \quad , \quad R \geqslant R_s \tag{1.1}$$

subject to the radiation boundary condition

$$4\pi R_s^2 \; J^d(R_s,t) = -\alpha_3 \; n(R_s,t) \quad , \tag{1.2}$$

which equates (as in heat-conduction problems) the frequency of transport with the frequency of absorption, assumed to proceed at a local rate $\alpha_3 (cm^3 \; s^{-1})$ at the boundary of a spherical sink of radius R_s. The number density of pairs AB with internal separation $\underset{\sim}{R}$ between $\underset{\sim}{R}$ and $\underset{\sim}{R} + d\underset{\sim}{R}$ is $n(\underset{\sim}{R})d\underset{\sim}{R}$ and $J^d(R)d\underset{\sim}{R}$ is the intramolecular net current within pairs which are in the state of internal expansion across interval $d\underset{\sim}{R}$ about $\underset{\sim}{R}$ within some medium M. In the absence of any sources, the rate of disappearance of pairs with $R \geqslant R_s$ is,

$$(\partial/\partial t) \int_{R_s}^{\infty} n(\underset{\sim}{R},t)d\underset{\sim}{R} = 4\pi R_s^2 \; J^d(R_s,t) = - \alpha(t)N_A N_B \tag{1.3}$$

where α is the overall rate of association of species A and B with averaged number densities $N_{A,B}$ at time t. Hence the rate,

$$\alpha(t) = \alpha_3 \; n(R_s,t)/N_A N_B \tag{1.4}$$

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relies <u>only</u> on the macroscopic density $n(R_s,t)$ at the sink boundary <u>provided</u> the local rate α_3 is regarded as a pre-assigned parameter. The net current $\underset{\sim}{J}^d$ in (1.1) can be related to the total density n via[2-4]

$$\underset{\sim}{J}^d(R,t) = -D \underset{\sim}{\nabla} n(\underset{\sim}{R},t) + (K/e)(\underset{\sim}{\nabla}V) n(\underset{\sim}{R},t) \tag{1.5}$$

where $V(R)$ is the energy of interaction between A and B. In terms of the diffusion and mobility coefficients $D_{A,B}$ and $K_{A,B}$, respectively, for the isolated species A and B in the medium M, the coefficients in (1.5) for relative diffusion and relative mobility are $D = D_A + D_B$ and $K = K_A + K_B$. Hence the rate $\alpha(t)$ can be determined from the solution of (1.1) at the sink via (1.4) and the overall problem is reduced to one of transport alone.

Although the DSE-method has been applied to reactions in solution, its de-facto generalization to lower densities of the medium (as a gas) is not immediately obvious, nor are the assumptions intrinsic to validity of DSE transparent. The effective decoupling of reaction from transport as in (1.2) and in (1.4) is likely to be valid in the limit of high gas densities when reaction proceeds much faster than transport which is then the rate-limiting step. As the density is reduced, reaction and transport are coupled, and address is required at a microscopic level[4] more basic than (1.1)-(1.5). In §2, this microscopic basis[5] of DSE is summarized so that the validity requirements of DSE are naturally exposed. It is shown that the DSE-method when applied to transport-influenced reactions in a gas retains its usefulness for evaluation of time dependent rates $\alpha(t)$ via determination of that particular time-dependent combination of the individual transport and reaction rates α_{TR} and α_{RN}, respectively, which are time-independent and which are regarded as being independent parameters, externally assigned.

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Although DSE can be solved exactly for the field-free case (V = 0), no simple exact analytical solution yet exists for general interaction V(R) between A and B. For the pure Coulomb case, DSE has been solved[6] in terms of Mathieu functions, which can be expressed as infinite series of products of modified Bessel functions but which are as complicated to evaluate as the exact numerical solution. For approximate solution of (1.1) with general V(R) a large body of literature (see ref. 7) exists on various schemes based on Green's function,[8] "prescribed" diffusion[9] and "matched perturbation"[10] techniques.

Here (in §3 and §4), highly accurate analytical solutions for general V(R) are proposed, and are then tested (in §5) explicitly for pure Coulombic attraction. Exact analytical expressions for the densities $n(\underset{\sim}{R},t)$ and the rates $\alpha(t)$ are derived (a) for short times and all R, (b) for long times and all R, and (c) for all times t and large R. The only simple analytical expression available up to now has been that derived[11] from the method of "matched perturbation solutions"[10] for the exact asymptotic transient $(t \to \infty)$. The present long-time solution,(b) above,not only yields this exact asymptotic transient but provides an analytical solution which is exact down to much shorter times. Some preliminary reports of these analytical expressions have already been presented.[12-14] Finally, an approximate and highly accurate combination of short-time and long-time solutions is proposed in §6 for the rates $\alpha(t)$ at all times t.

The aim of the present paper is therefore to examine the foundation and validity requirements of DSE within a modern perspective and, then to present analytical solutions of DSE under a general interaction V(R) between the species A and B reacting in a thermal gas bath M. The microscopic theory used in this paper has been developed earlier[5].

2. Microscopic Basis of the Debye-Smoluchowski Equation

For the closed system,

$$A + B + M \rightleftarrows AB + M \tag{2.1}$$

with no external sources or sinks as discussed previously,[5] the continuity equation

$$\frac{\partial}{\partial t} n^S(\underset{\sim}{R},t) + \underset{\sim}{\nabla} \cdot \underset{\sim}{J}^d(\underset{\sim}{R},t) = 0 \tag{2.2}$$

holds for the integrated macroscopic distribution

$$n^S(\underset{\sim}{R},t) = \int_{-V(R)}^{\infty} n_i^S(\underset{\sim}{R},E_i,t)dE_i \tag{2.3}$$

in number density (cm^{-3}) of AB pairs. The microscopic distribution n_i^S is such that $n_i^S d\underset{\sim}{R}dE_i$ is the number density of pairs with internal separation $\underset{\sim}{R}$ and internal energy E_i within the interval $d\underset{\sim}{R}dE_i$ about $(\underset{\sim}{R},E_i)$ and $n^S d\underset{\sim}{R}$ is then the number density within interval $d\underset{\sim}{R}$ of pairs with all possible internal energies between the lowest bound level $-V(R)$ consistent with a fixed R and the far continuum. The interaction between A and B is $V(R)$. The net $\underset{\sim}{R}$-macroscopic current vector

$$\underset{\sim}{J}^d(\underset{\sim}{R},t) = \int_{-V}^{\infty} \underset{\sim}{J}_i^d(\underset{\sim}{R},E_i,t)dE_i \tag{2.4}$$

is the energy-integration of the $(\underset{\sim}{R},E_i)$-microscopic net current $\underset{\sim}{J}_i^d$ in

$$\underset{\sim}{J}_i^{S,d}(\underset{\sim}{R},E_i,t) = \int_{(+)} n_i(\underset{\sim}{R},E_i,\hat{\underset{\sim}{v}}_i;t)\underset{\sim}{v}_i \, d\hat{\underset{\sim}{v}}_i \pm \int_{(-)} n_i(\underset{\sim}{R},E_i,\hat{\underset{\sim}{v}}_i;t)\underset{\sim}{v}_i \, d\hat{\underset{\sim}{v}}_i \tag{2.5}$$

$$\equiv \underset{\sim}{J}_i^+(\underset{\sim}{R},E_i,t) \pm \underset{\sim}{J}_i^-(\underset{\sim}{R},E_i,t)$$

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where the conditional pair distribution $n_i(\underset{\sim}{R},E_i,\hat{\underset{\sim}{v}}_i;t)$ is such that the number density of pairs AB with internal separation $\underset{\sim}{R}$, internal energy $\underset{\sim}{E}_i$ and with the direction $\hat{\underset{\sim}{v}}_i$ of the internal relative velocity $\underset{\sim}{v}_i$ in interval $d\underset{\sim}{R}\ dE_i\ d\hat{\underset{\sim}{v}}_i$ about $(\underset{\sim}{R},E_i,\hat{\underset{\sim}{v}}_i)$ is $n_i(\underset{\sim}{R},E_i,\hat{\underset{\sim}{v}}_i;t)d\underset{\sim}{R}dE_id\hat{\underset{\sim}{v}}_i$ at time t. Corresponding to (2.5) define the sum (s) and difference (d) of microscopic densities by

$$n_i^{s,d}(\underset{\sim}{R},t) = n_i^{s,d}(\underset{\sim}{R},E_i,t) = \underset{(+)}{\int} n_i(\underset{\sim}{R},E_i,\hat{\underset{\sim}{v}}_i;t)d\hat{\underset{\sim}{v}}_i \underset{(-)}{\pm \int} n_i(\underset{\sim}{R},E_i,\hat{\underset{\sim}{v}}_i;t)d\hat{\underset{\sim}{v}}_i \qquad (2.6)$$

$$\equiv n_i^+ \pm n_i^-$$

The integrations in (2.5) and (2.6) are over the positive (+) region where $\underset{\sim}{R}\cdot\underset{\sim}{v}_i \geq 0$, and the negative (-) region where $\underset{\sim}{R}\cdot\underset{\sim}{v}_i \leq 0$, such that the net current J_i^d and the net density n_i^d of pairs which are in the states of internal expansion (+) or contraction (-) are $(J_i^+ - J_i^-)$ and $(n_i^+ - n_i^-)$ respectively. Also n_i^s and J_i^s are the respective sums $(n_i^+ + n_i^-)$ and $(J_i^+ + J_i^-)$ of densities and currents of internally expanding (+) and contracting (-) pairs.

The continuity equation corresponding to (2.2) but for the microscopic distribution $n_i^s(\underset{\sim}{R},t)$ has already been derived[5] from a Boltzmann-type equation for the two-particle correlation function $n(\underset{\sim}{R},\underset{\sim}{v},t)$ and is[5]

$$\frac{\partial}{\partial t} n_i^s(\underset{\sim}{R},E_i,t) + \underset{\sim}{\nabla}\cdot\underset{\sim}{J}_i^d(\underset{\sim}{R},E_i,t) = \int_{-V(R)}^{\infty} S_{fi}^s(R,t)dE_f \qquad (2.7)$$

where the net frequency of collisional transitions (i → f) is S_{fi}^s given in

$$S_{if}^{s,d}(R,t) = n_i^{s,d}(\underset{\sim}{R},t)\ \nu_{if}(R) - n_f^{s,d}(\underset{\sim}{R},t)\ \nu_{fi}(R) = -S_{fi}^{s,d}(R,t) \qquad (2.8)$$

in terms of the frequency $\nu_{if}\ dE_f$ of AB-M collisions, which change the internal energy of a pair AB from E_i to between E_f and $E + dE_f$ at a fixed

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nuclear separation $\underset{\sim}{R}$ of A and B. Thus, the net rate at time t of collisional production of (R,E_i)-pairs from all levels f within the accessible energy range $[-V \rightarrow \infty]$ is the RHS of (2.7). On integration of (2.7) over the full energy range of E_i, the macroscopic continuity equation (2.2) for the closed system is recovered since the overall effect of collisions $\int_{-V}^{\infty} dE_i \int_{-V}^{\infty} dE_f \, S_{fi}^S$ is null. Although the macroscopic net current $J^d(\underset{\sim}{R},t)$ can be related[4] to the summed densities $n^S(\underset{\sim}{R},t)$ via the excellent approximation,[4]

$$\underset{\sim}{J}^d(\underset{\sim}{R},t) = -D \underset{\sim}{\nabla} n^S(\underset{\sim}{R},t) + (\frac{K}{e}) \, (\underset{\sim}{\nabla}V) \, n^S(\underset{\sim}{R},t) \qquad (2.9)$$

in term of the macroscopic coefficients D and K for relative diffusion and relative mobility of A and B in medium M, no similar relation has yet been derived for the corresponding microscopic current $J_i^d(\underset{\sim}{R},E_i,t)$. As has previously[5] been shown, (2.7) must then be coupled to the following equation

$$\frac{\partial}{\partial t} n_i^d(\underset{\sim}{R},E_i,t) + \underset{\sim}{\nabla} \cdot \underset{\sim}{J}_i{}^S(\underset{\sim}{R},E_i,t) - \left[\frac{2}{R} - (E_i-V)^{-1} \frac{\partial V}{\partial R} \right] n_i^\pm(\underset{\sim}{R},E_i,\hat{\underset{\sim}{R}} \cdot \hat{\underset{\sim}{\chi}}_i = \frac{\pi}{2};t) v_i \qquad (2.10)$$

$$= \int_{-V}^{\infty} S_{fi}^d (R,t) dE_f$$

in terms of the quantities J_i^S, n_i^d and S_{fi}^d defined in (2.5), (2.6) and (2.8) respectively. When equilibrium is established in the internal angular momentum L of the pair (A-B), n_i is then independent[5] of v_i so that $J_i^{S,d}$ in (2.7) and (2.10) are simply $\frac{1}{2} n_i^{S,d} v_i$. Also $n_i^\pm$ in (2.10) is then given by[5] $n_i^- = \frac{1}{2} (n_i^S - n_i^d)$ for all R and $E_i \geq 0$, and for bound levels $E_i \leq 0$ by $n_i^+ = \frac{1}{2} (n_i^S + n_i^D)$ for $R \leq A$ or by $n_i^- = \frac{1}{2} (n_i^S - n_i^d)$ for $A \leq R \leq B$. Here A is the radius of the bound circular orbit (associated with maximum angular momentum L), and B is the radius of the outermost turning point of the orbit with $L = 0$ where $|E_i| = V(B)$. Under

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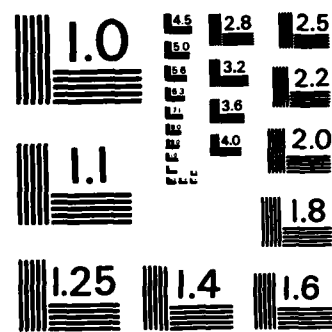
conditions of thermodynamic equilibrium in L, $J_i^{s,d} = \frac{1}{2} n_i^{s,d} v_i$ in (2.7) and

(2.10) which are therefore coupled in n_i^s and n_i^d; in contrast to the direct

use of (2.9) in (2.2) for the macroscopic densities $n^s(\underset{\sim}{R},t)$. Operation at a

level more basic than (2.2) therefore necessitates solution of coupled

time-dependent equations, rather than the single equation (2.2). It is

therefore advantageous to explore the conditions for which a macroscopic

treatment based on (2.2) can be invoked.

2.1 Macroscopic Transport-Collisional Equations

For a given R, subdivide the energy range into three blocks: a block

of strongly bound levels between levels -V(R) and -S within which the pairs

are considered to be fully associated, a block S of excited levels between -S

and the dissociation limit taken at zero energy within which the pairs are in

the process of associating or dissociating, and a continuum block C which

describes fully dissociated pairs. The sum of the distributions n_c and n_e of

pairs in blocks C and E respectively,

$$n(\underset{\sim}{R},t) = \int_{-S}^{\infty} n_i^{s}(\underset{\sim}{R},E_i;t)dE_i \equiv n_c(\underset{\sim}{R},t) + n_e(\underset{\sim}{R},t) \qquad (2.11)$$

and the corresponding net current

$$J(\underset{\sim}{R},t) = \int_{-S}^{\infty} J_i^{d}(\underset{\sim}{R},E_i;t)dE_i \equiv J_c(\underset{\sim}{R},t) + J_e(\underset{\sim}{R},t) \qquad (2.12)$$

then satisfy, with the aid of (2.7), the equation

$$\frac{\partial}{\partial t} n(\underset{\sim}{R},t) + \underset{\sim}{\nabla} \cdot \underset{\sim}{J} = - \int_{-S}^{\infty} dE_i \int_{-V}^{-S} S_{if}(R,t)dE_f \quad ; \quad R \leq R_s \qquad (2.13)$$

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for $R \leq R_s$, the outermost turning point associated with level $-S$. In (2.13) and in what follows S_{if}^S is written simply as S_{if}. For $R \geq R_s$, block S does not exist so that

$$\frac{\partial}{\partial t} n(\underset{\sim}{R},t) + \underset{\sim}{\nabla} \cdot \underset{\sim}{J} = 0 \quad ; \quad R \geq R_s \tag{2.14}$$

Integration of (2.13) yields,

$$\frac{\partial}{\partial t} \int_0^{R_s} n(\underset{\sim}{R},t)d\underset{\sim}{R} + 4\pi R_s^2 \, J(\underset{\sim}{R}_s,t) = -\int_0^{R_s} dR \int_{-S}^{\infty} dE_i \int_{-V}^{-S} S_{if}(R,t)dE_f \tag{2.15}$$

On introducing

$$S_{if}(t) = \int_0^{R_{if}} S_{if}(R,t)d\underset{\sim}{R} = - S_{fi}(t) \tag{2.16}$$

the net frequency per unit $dE_i dE_f$ of collisional transitions between levels E_i and E_f, where R_{if} is the lesser of R_i and R_f, the turning points associated with levels E_i and E_f, integration of (2.7) over all accessible R-space yields

$$\frac{\partial}{\partial t} n_i(E_i,t) = -\int_0^{R_i} d\underset{\sim}{R} \int_{-V}^{\infty} S_{if}(R,t)dE_f = -\int_{-D}^{\infty} S_{if}(t)dE_f \tag{2.17}$$

Eq. (2.15) is then

$$\frac{\partial}{\partial t} \int_0^{R_s} n(\underset{\sim}{R},t)d\underset{\sim}{R} + 4\pi R_s^2 \, J(\underset{\sim}{R}_s,t) = -\int_{-S}^{\infty} dE_i \int_{-D}^{-S} S_{if}(t)dE_f = - \partial n_s(t)/\partial t \tag{2.18}$$

where the density of pairs in block S is

$$n_s(t) = \int_0^{R_s} n_s(\underset{\sim}{R},t)d\underset{\sim}{R} = \int_0^{R_s} d\underset{\sim}{R} \int_{-V}^{-S} n_i^S(\underset{\sim}{R},E_i;t)dE_i = \int_{-D}^{-S} n_i(E_i,t)dE_i \tag{2.19}$$

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Eq. (2.18) states that the flux, $-4\pi R_s^2 J$, entering the (reaction) sphere of radius R_s equals the net collisional rate of production of S-pairs plus the rate of increase of the contribution from the reaction volume to the density (2.11) of C and S pairs. On assuming no net flux at infinite separation R, integration of (2.14) yields

$$\frac{\partial}{\partial t} \int_{R_s}^{\infty} n(\underset{\sim}{R},t)d\underset{\sim}{R} = 4\pi R_s^2 \, J(R_s,t) \tag{2.20}$$

which, when added to (2.18), provides

$$\frac{\partial}{\partial t} \int_{o}^{\infty} n(\underset{\sim}{R},t)d\underset{\sim}{R} + \frac{\partial}{\partial t} n_s(t) = 0 \tag{2.21}$$

the conservation equation as expected for this closed system. On defining the averaged local rate α_3 $(cm^3 \, s^{-1})$ for production of block S via collisional absorption from blocks C and S by

$$\alpha_3 \, n(R_s,t) = \int_{-S}^{\infty} dE_i \int_{-D}^{-S} S_{if}(t)dE_f = \partial n_s(t)/\partial t \tag{2.22}$$

The effective two body rate α $(cm^3 \, s^{-1})$ for association of dissociated species A and B with densities $N_{A,B}(t) \, (cm^{-3})$ and the frequency k (s^{-1}) for dissociation of S-pairs AB with density $n_s(t)$ are related by[5]

$$\partial n_s(t)/\partial t = \alpha N_A(t)N_B(t) - k \, n_s(t) \tag{2.23}$$

when quasi-steady-state (QSS) conditions $(\partial n_i/\partial t)$ are assumed for block E. On further assuming that those pairs within the reaction volume of blocks C and E are also in QSS i.e.,

$$\frac{\partial}{\partial t} \int_0^{R_s} n(\underset{\sim}{R}_s, t) d\underset{\sim}{R} = 0 \qquad (2.24)$$

then (2.18) and (2.22) yield

$$\partial n_s(t)/\partial t = -4\pi R_s^2 J(\underset{\sim}{R}_s, t) = -\alpha_3 n(R_s, t) \qquad (2.25)$$

so that the effective two-body rate of association is

$$\alpha(t) = \alpha_3 [1 - \Gamma(t)]^{-1} n(R_s, t)/N_A(t)N_B(t) \qquad (2.26)$$

where the quantity

$$\Gamma(t) = [\tilde{N}_A \tilde{N}_B / N_A(t)N_B(t)] [n_s(t)/\tilde{n}_s] \qquad (2.27)$$

is a measure of the departure of the densities of the dissociated A,B and associated AB species from their corresponding time-dependent values $\tilde{N}_{A,B}$ and $\tilde{n}_s$ appropriate to full thermodynamic equilibrium ($\Gamma = 1$) with the gas bath M. Since

$$n_s(t) - n_s(0) = \alpha_3 \int_0^t n(R_s, t) dt, \qquad (2.28)$$

$\Gamma(t)$ can therefore be determined given $N_{A,B}(t)$.

Provided the local rate α_3 in (2.22) is specified as some external parameter or else is obtained by other means, α is therefore determined via (2.26) solely by the transport equation (2.14),

$$\frac{\partial}{\partial t} n(\underset{\sim}{R}, t) + \underset{\sim}{\nabla} \cdot \underset{\sim}{J} = 0 \quad , \quad R \geq R_s \qquad (2.29a)$$

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solved subject to the radiation boundary condition

$$4\pi R_s^2 \, J(R_s,t) = \alpha_3 \, n(R_s,t) \qquad (2.29b)$$

at the sink. When (2.9) is used for J, this combination (2.29) represents
the Debye-Smoluchowski Equation (DSE), familiar in kinetics of reactions in
the condensed phase[1-3] and in solution[7-10] and to coagulation of colloids.
It was obtained originally by applying the macroscopic continuity Eqn. (2.2)
outside $(R \gtrsim R_s)$ the sink region, and by equating the transport and absorption
rates at $R = R_s$, as in (1.1) - (1.5). Since the reaction rate α_3 is considered
as a pre-assigned parameter, DSE concentrated solely on solution of the
transport portion $J^D(R \gtrsim R_s,t)$ of the problem, external to the sink.

2.2 Assumptions Intrinsic to DSE

By operating at a level more basic than DSE, the present treatment has
exposed the two underlying criteria for validity of DSE

$$\left.\begin{array}{l} \dfrac{\partial}{\partial t} \, n_i(E_i,t) \approx 0 \qquad 0 \gtrsim E_i \gtrsim -S \\[18pt] \dfrac{\partial}{\partial t} \displaystyle\int_0^{R_s} n(\underset{\sim}{R},t) d\underset{\sim}{R} \approx 0 \end{array}\right\} \qquad (2.30)$$

i.e., quasi-steady-state conditions are assumed for pairs in the intermediate
block E of excited levels and for those pairs with internal separation $R \leq R_s$
and with internal energies in the E and the continuum block C.

The present treatment has also provided the logical transport equation
(2.13) for description of the sink. It is also usual to consider a situation
of high non-equilibrium $(\Gamma \ll 1)$ so that the association rate is simply

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$$\alpha(t) = \alpha_3 \, n(R_s,t)/N_A N_B \tag{2.31}$$

where $N_{A,B}$ is the averaged concentration of dissociated species A and B.

If however α_3 is not predetermined (as is the general case) then the complete microscopic treatment based on the solution of the coupled transport-collision equations (2.7) and (2.10) for the microscopic densities $n_i^{s,d}$ is required.

Since α_3 in (2.22) is also determined by the collisional frequency ν_{if} in S_{if} assignment and use within DSE as an external parameter can, however, provide very valuable insight to chemical kinetics in a dense medium. For example the steady state solution ($\partial n/\partial t = 0$) of (2.29) yields the steady-state rate[3-4] which can be written as,[4,12]

$$\alpha_\infty = \frac{\alpha_{RN} \, \alpha_{TR}}{(\alpha_{RN} + \alpha_{TR})} \tag{2.32}$$

in terms of the reaction rate, defined by

$$\alpha_{RN} = \alpha_3 \, \exp(-KV(R_s)/De) \tag{2.33}$$

and of the transport rate

$$\alpha_{TR} = 4\pi D \, \tilde{R}_s \tag{2.34}$$

where

$$\tilde{R} = [\int_R^\infty \exp(KV/De)R^{-2} \, dR]^{-1} \tag{2.35}$$

The steady state rate α_∞ is therefore controlled by the rate limiting step. However, there are at present no exact analytical solutions of DSE (2.29) - for general V(R), although a large body of literature[7-10] exists for

various types of approximations. For the pure Coulombic case, DSE can be solved formally[6] in terms of Mathieu functions, which in turn can be expressed as an infinite series of products of modified Bessel functions, the full evaluation of which is however as time consuming and as illuminating as the direct numerical solution of (2.29).

In the following section § 3, useful time-dependent analytical solutions for the rates $\alpha(t)$ and densities $n(R,t)$ of (2.24) for general $V(R)$ are proposed. The assumed initial ($t = 0$) condition and asymptotic ($R \to \infty$) boundary condition

$$n(R,t=0) = N_0 \exp(-KV/De) = n(R\to\infty,t) \qquad (2.36)$$

are appropriate to association of (A-B) pairs with an initial Boltzmann distribution in internal separation R, and to a continuous source at infinity which maintains the Boltzmann distribution only at asymptotic R.

2.3 Field-Free Expressions

For reference purposes, the analytical solution[15] for the field-free case ($V=0$) of (2.29) subject to (2.36) can be written as[4]

$$n(R,t) = N_0\{1 + (\alpha_\infty/\alpha_d)(S/R)\ [\exp(\chi_0{}^2)\exp(2\chi_0\Omega_0)\ erfc(\chi_0+\Omega_0) - erfc\ \Omega_0]\}(2.37)$$

in terms of the time-dependent pair (χ_0,Ω_0) of functions,[4]

$$\chi_0(t) = (\alpha_3/\alpha_\infty)(Dt/S^2)^{1/2}\ ; \Omega_0(R,t) = (R-S)/2(Dt)^{1/2}\ , \qquad (2.38)$$

and of the steady-state (field-free) rate

$$\alpha_\infty^{(0)} = (\alpha_3\alpha_d)/(\alpha_3 + \alpha_d) \tag{2.39}$$

where α_3 is the pre-assigned rate of reaction at $R_s = S$, the sink-radius, and where

$$\alpha_d = 4\pi DS \tag{2.40}$$

is the rate of pure diffusion at S. The exact transient rate of association from (2.31) is therefore,

$$\alpha(t) = \alpha_3\{1 + (\alpha_\infty^{(0)}/\alpha_d) \; [\exp x_0^2 \; \text{erfc} \; x_0 - 1 \;]\} \tag{2.41a}$$

$$\equiv \alpha_\infty \; [1 + (\alpha_3/\alpha_d) \; \exp x_0^2 \; \text{erfc} \; x_0] \tag{2.41b}$$

which initially decreases from the finite reaction rate α_3 as

$$\alpha(t\to0) = \alpha_3^{(0)}[1 - (2/\pi^{1/2})(\alpha_3/\alpha_d)(Dt/S^2)^{1/2}] \; , \tag{2.42}$$

and approaches the steady-state rate $\alpha_\infty^{(0)}$ via the asymptotic transient

$$\alpha(t\to\infty) = \alpha_\infty^{(0)}[1 + (\alpha_\infty^{(0)}/\alpha_d)(S^2/\pi Dt)^{1/2}] \tag{2.43}$$

In the diffusion limited region $\alpha_\infty^{(0)} \to \alpha_d \ll \alpha_3$, then (2.41b) reduces exactly to (2.43). It is worth noting that the only exact analytical expression[11] yet available (to the author's knowledge) for the rate $\alpha(t)$ under general $V(R)$ is the asymptotic transient which may be rewritten[12] compactly as,

$$\alpha(t\to\infty) = \alpha_\infty[1 + (\alpha_\infty/\alpha_{TR}) \; (\tilde{S}^2/\pi Dt)^{1/2}] \tag{2.44}$$

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which corresponds to the same level of approximation as (2.43) but with α_3, α_d, $\alpha_\infty^{(0)}$ and S all replaced by α_{RN}, α_{TR}, α_∞ and $\tilde{S}$ of (2.32) - (2.35), respectively. The basic expression had been earlier obtained[11] from a straightforward application of the method[10] of "matched perturbation solutions". An expression which covers a time range considerably broader than the asymptotic transient (2.44) is derived in the following section, together with a corresponding short-time solution which tends to the initial transient

$$\alpha(t\to 0) = \alpha_{RN} \left[1-(2/\pi^{1/2})(\alpha_{RN}/\alpha_{TR})(d\tilde{R}/dR)_S (Dt/\tilde{S}^2)^{1/2}\right] , \qquad (2.45)$$

This transient is the appropriate generalization of (2.42) to arbitrary interaction V(R), but with inclusion of the additional factor

$$(d\tilde{R}/dR) = (\tilde{R}/R)^2 \exp(KV/De) \qquad (2.46)$$

which is absent in the corresponding generalization (2.44) of the asymptotic transient (2.43).

3. <u>Exact Analytical Solutions (a) for All Times and Large R, (b) for Long Times and All R, and (c) for Short Times and All R.</u>

Under the nonlinear transformation[4,12,16]

$$\tilde{R} = [\int_R^\infty \exp(KV/De) \; R^{-2} \; dR]^{-1} \qquad (3.1)$$

the Debye-Smoluchowski Equation (1.1) for general interaction $V(R)$ has been shown to reduce to[12]

$$\partial \rho(\tilde{R},t)/\partial t = D(d\tilde{R}/dR)^2 \; \nabla_{\tilde{R}}^2 \; \rho(\tilde{R},t) \qquad (3.2)$$

where the fractional departure from Boltzmann equilibrium is

$$\rho(R,t) = n(R,t)/[N_0 \; \exp(-KV/De)] \qquad (3.3)$$

At temperature T of the gas, the Einstein relation $De = K(kT)$ holds for weak fields so that the argument of the exponent in (3.1) and (3.3) is (V/kT). In this 'tilda' space[12], the total flux

$$4\pi R^2 \; J(R,t) = 4\pi \tilde{R}^2 \; \tilde{J}(\tilde{R},t) \qquad (3.4)$$

remains invariant, with the current vector in this $\tilde{R}$-space being defined as

$$\underset{\sim}{\tilde{J}} = -DN_0 \; \nabla_{\tilde{R}} \rho \qquad (3.5)$$

which is formally equivalent to the current due to field-free diffusion in $\tilde{R}$-space but with $n(R,t)$ replaced by $N_0 \; \rho(R,t)$.

In terms of this solution ρ of (3.2) and of the rates α_{RN} and α_{TR} in (2.33) and (2.34) for reaction and transport under interaction $V(R)$, the association rate $\alpha(t)$ of (1.4) and the "radiation" boundary condition RBC of (1.2) yields

$$\alpha(t) = \alpha_{RN} \, \rho(\tilde{S},t) = \alpha_{TR} \, \tilde{S}[\partial\rho/\partial\tilde{R}]_{\tilde{S}} \tag{3.6}$$

which shows that $\rho(\tilde{S},t) \to 0$ when $\alpha_{TR} \ll \alpha_{RN}$, as in the limit of high gas densities N, and that $(\partial\rho/\partial\tilde{R}) \to 0$ (which implies the Boltzmann distribution, $\rho = 1$) when $\alpha_{TR} \gg \alpha_{RN}$, as in the limit of vanishing N. At each of these respective limits, α_∞, the steady-state rate (2.32) tends to the rate limiting step of transport or of reaction, respectively.

Introduce the dimensionless variables,

$$\tilde{r} = \tilde{R}/\tilde{S} - 1, \quad \tau = Dt/S^2, \quad \phi = (\tilde{R}/\tilde{S})\rho = (\tilde{r}+1)\rho \tag{3.7}$$

so that (3.2) reduces to

$$\partial\phi(\tilde{r},\tau)/\partial\tau = (d\tilde{r}/dr)^2 \, (\partial^2\phi/\partial\tilde{r}^2) \tag{3.8}$$

subject to the initial and asymptotic boundary conditions (2.36), rewritten as

$$\phi(\tilde{r},\tau = 0) = (\tilde{r}+1) = \phi(\tilde{r}{\to}\infty,\tau) \tag{3.9a}$$

and to RBC in (3.6), rewritten as

$$\alpha(\tau) = \alpha_{RN} \, \phi(0,\tau) = \alpha_\infty[\partial\phi(\tilde{r}{\to}0,\tau)/\partial\tilde{r}] \tag{3.9b}$$

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since the sink is located at $\tilde{r} = 0$.

Under Laplace transformation,

$$\tilde{\phi}(\tilde{r},s) = \int_0^\infty \phi(\tilde{r},\tau)\ \exp(-s\tau)d\tau \qquad (3.10)$$

then, with the initial condition (3.9a) incorporated, (3.8) yields

$$(\partial^2\tilde{\phi}/\partial\tilde{r}^2) = (dr/d\tilde{r})^2\ s[\tilde{\phi} - (\tilde{r}+1)/s], \qquad (3.11)$$

with formal solution,

$$\tilde{\phi}(\tilde{r},s) = A(s)\ \exp[-\gamma(\tilde{r},s)s^{1/2}] + (\tilde{r}+1)/s, \qquad (3.12)$$

in terms of unknown functions $A(s)$ and $\gamma(r,s)$. The asymptotic boundary condition (3.9a) specifies that $\gamma(\tilde{r}\to\infty,s) \to \infty$. On setting

$$k = (dr/d\tilde{r}) \equiv (\tilde{S}/S)(dR/d\tilde{R}) \qquad , \qquad (3.13)$$

then (3.12) in (3.11) yields the differential equation

$$s^{-1/2}(dy/d\tilde{r}) = y^2(\tilde{r},s) - k^2(\tilde{r}) \qquad (3.14a)$$

to be solved for y and hence γ in

$$y(\tilde{r},s) = d\gamma(\tilde{r},s)/d\tilde{r} \qquad (3.14b)$$

With knowledge of y and γ, and with RBC in (3.9b) used to

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determine $A(s)$ in (3.12), the Laplace transform $\tilde{\rho}$ of the departure function ρ, (3.3), is therefore

$$\tilde{\rho}(\tilde{r},s) = \tilde{\phi}(\tilde{r},s)/(\tilde{r}+1) = \left\{ \frac{1}{s} - \left(\frac{\alpha_{RN}}{\alpha_{TR}} \right) \frac{\exp-[\gamma(\tilde{r},s)-\gamma(o,s)]s^{1/2}}{(\tilde{r}+1)s[y(o,s)s^{1/2}+\alpha_{RN}/\alpha_{\infty}]} \right\} \qquad (3.15)$$

The corresponding Laplace transform $\tilde{\alpha}$ of the transient association rate $\alpha(t)$, (3.6), is therefore

$$\tilde{\alpha}(s) = \alpha_{RN} \tilde{\rho}(0,s) = \alpha_{RN} \left\{ 1/s - (\alpha_{RN}/\alpha_{TR})[s\{y(o,s)s^{1/2} + \alpha_{RN}/\alpha_{\infty}\}]^{-1} \right\}, \qquad (3.16)$$

Progress in the search for simple analytical formulae is now limited by the availability or determination of closed expressions for the inverse Laplace transforms of the overall s-functional dependence in (3.15) and (3.16), which are mainly governed by the form of $\gamma(\tilde{r},s)$ and its derivative $y = (d\gamma/d\tilde{r})$.

For attractive interactions of the general form $(V/kT) = -(R_e/R)^n$, where R_e is the natural unit of length characterized by $V(R_e) = kT$, integration of (3.1) then yields,

$$\tilde{x} = (\tilde{R}/R_e) = n\, \gamma[(1/n), x^n] \quad ; \quad x = R/R_e \qquad (3.17)$$

where the incomplete Gamma function is

$$\gamma(1/n,x^{-n}) = \frac{n}{x} \left[1 + \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \frac{x^{mn}}{(mn+1)} \right] \qquad (3.18)$$

In the limit of small x, $R \ll R_e$, and $\gamma \rightarrow \Gamma(1/n)$, the complete Gamma function, so that

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$$\tilde{x} \to n \, \Gamma^{-1}(1/n) = x_0, \qquad x = R/R_e \ll 1 \qquad (3.19)$$

a constant; 1 ($n = 1$), 1.1284 ($n = 2$), 1.1200 ($n = 3$), 1.1032 ($n = 4$) and 1.0779 ($n = 6$) for the Coulombic ($n = 1$), Dipole ($n = 2$), Quadrupole ($n = 3$), Polarization ($n = 4$) and Van der Waals ($n = 6$) attractions, respectively.

For large $R \gg R_e$ then

$$\tilde{x} = x\left[1 + \frac{1}{(n+1)}\, x^{-n} + \left\{\frac{1}{(n+1)^2} - \frac{1}{2(2n+1)}\right\}\, x^{-2n} + \left\{\frac{1}{(n+1)^3} - \frac{1}{(n+1)(2n+1)}\right.\right.$$
$$\left.\left. + \frac{1}{6(3n+1)}\right\}\, x^{-3n} + \ldots\right] \qquad (3.20)$$

to give

$$\tilde{x} = x + 1/2 + (1/12x) + O\,(x^{-3}) \qquad\qquad , (n = 1)$$

$$= x + (1/3x) + (1/90x^3) - (11/1890x^5) + \ldots \quad , (n = 2)$$

$$= x + (1/5x^3) - (7/450x^7) + \ldots \qquad\qquad , (n = 4)$$

$$= x + (1/7x^5) - (23/1274x^{11}) + \ldots \qquad\qquad , (n = 6)$$

for the various attractions, respectively. The derivative which appears in the basic expression (3.2) is

$$(d\tilde{R}/dR) = (\tilde{x}/x)^2 \exp(-x^{-n}) \xrightarrow{x \ll 1} (x_0/x)^2 \exp(-x^{-n}) \qquad (3.21)$$

so that

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$$(d\tilde{R}/dR) = \left\{ 1 - \left(\frac{n-1}{n+1}\right) x^{-n} + \left[\frac{1}{2} - \frac{1}{(2n+1)} - \frac{(2n-1)}{(n+1)^2} \right] x^{-2n} + \ldots \right\} \qquad (3.22)$$

As illustrated in Fig. 1a for the various attractions, $(dR/d\hat{R})$ increases rapidly from zero at $\tilde{x} = x_0$ to its unit asymptote at large $x \gtrsim 1$. Note that the coefficient of x^{-1} in $(d\tilde{R}/dR)$ and of x^{-2} in $\tilde{x} = (\tilde{R}/R_e)$ vanishes for Coulombic attraction, so that $(d\tilde{R}/dR)$ tends to its unit asymptote as $[-(1/12)x^{-2} + 0(x^{-4})]$ which is somewhat faster than that $[-(1/3)x^{-2} + 0(x^{-4})]$ for the pure dipole case.

Particular values of the nonlinear function

$$(\tilde{R}/R_e) = \tilde{x} = [1 - \exp(-1/x)]^{-1} \qquad (3.23)$$

for Coulomb attraction and of its derivative

$$(d\tilde{R}/dR) = (d\tilde{x}/dx) = \tilde{x}^2 (1 - \tilde{x}^{-1}) \ln^2(1 - \tilde{x}^{-1}) \qquad (3.24)$$

are displayed in Table 1 which shows that the derivative attains its unit asymptotic value

$$(d\tilde{x}/dx) \rightarrow 1 - \frac{1}{12} [\tilde{x}^{-2} + \tilde{x}^{-3} + (13/15) \tilde{x}^{-4} + \ldots]$$

very rapidly. This variation is also amplified in Fig. (1b) over the important range $0 \leq \tilde{R} \leq 1.5$ of $\tilde{R}$.

(a) On this basis, the solution at large $\tilde{R}$ ($\gtrsim 1.5$ n.u.) is therefore obtained by replacing $(d\tilde{R}/dR)$ in (3.13) by unity so that the solutions of y and γ of (3.14) are,

$$y(\tilde{r},s) = \tilde{S}/S \quad , $$

$$\gamma(\tilde{r},s) = \overset{\approx}{S}\tilde{r}/S = (\tilde{R}-\tilde{S})/S \qquad\qquad (3.25)$$

which are all independent of s.

(b) At long times (when $s \to o$), y in (3.14a) is therefore constant for all $\tilde{r}$, so that

$$y(\tilde{r},s \to o) = \tilde{S}/S \equiv y_\ell \quad , $$

$$\gamma(\tilde{r},s \to o) = \overset{\approx}{S}r/S \equiv \gamma_\ell \qquad\qquad (3.26a)$$

which are all identical with (3.25). The criterion for validity of (3.26) is that

$$s^{1/2}[(\tilde{S}/S)^2 - (dr/d\tilde{r})^2] \to 0 \qquad\qquad (3.26b)$$

which holds, not only for long times and all R as in (b), but also for large R and all times as in (a), so that the solutions <u>at long times for all R</u> and <u>at all times for large R</u> are identical. The closer that $(dr/d\tilde{r})$ is to $(\tilde{S}/S)$. the greater will be the range of t over which (3.26) is valid. The variation of $(d\tilde{r}/dr)$ with r for various values of S is illustrated in Fig. 1(c) which shows quite clearly that the key function $(d\tilde{r}/dr)$ in (3.8) may be considered constant $(S/\tilde{S})$ over a large range of $\tilde{r}$ and S.

(c) At short times when $s \to \infty$, the solutions of (3.14) are,

$$y(\tilde{r},s \gg s_{min}) = k(\tilde{r}) \equiv y_\Delta(\tilde{r}) \quad , $$

$$\gamma(\tilde{r},s) = r \equiv \gamma_\Delta(\tilde{r}) \qquad\qquad (3.27)$$

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In this approximation, (3.14a) yields

$$(y/k) = 1 - s^{-1/2}\left\{\left(\frac{d^2 r}{d\tilde{r}^2}\right)\bigg/\left(\frac{dr}{d\tilde{r}}\right)^2\right\} \tag{3.28a}$$

so that the above approximation (3.27) is valid provided

$$s^{1/2} \gg (d^2 r/d\tilde{r})^2/(dr/d\tilde{r})^2 = s_{min}^{1/2} \tag{3.28b}$$

a condition which is more rigorous and less restrictive than the requirement of infinite s.

For $\tilde{r} \geq 0.25$ in Fig. (1c), $k = (dr/d\tilde{r})$ tends to the constant $(\tilde{S}/S)$ so that the key validity criterion $s \gg s_{min}$ can be satisfied for longer times. Also.(3.27) for y_Δ at "short" times and all $\tilde{r}$ tends at large $\tilde{r}$ to (3.25) for y at all times and large $\tilde{r}$, so that the range of validity of the above short-time solution (3.27) can extend into longer times by increase of $\tilde{r}$.

All of the above three solutions, (3.25) - (3.27), are s-independent so that the inverse Laplace transform of (3.18) can be readily performed to yield the same formal expression

$$\rho(R,t) = n(R,t)/N_0 \exp(-KV/De) = \phi(\tilde{r},t)/(\tilde{r}+1)$$

$$= \{1 + (\alpha_\infty/\alpha_{TR})(\tilde{S}/\tilde{R}) [\exp(2\Omega x) \exp x^2 \text{ erfc } (x+\Omega) - \text{erfc } \Omega]\} \tag{3.29}$$

for each of the above cases (a) - (c) which are distinguished by the pair (x,Ω) of functions,

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$$X_\ell(t) = (\alpha_{RN}/\alpha_\infty y_\ell)\sqrt{\tau} \equiv (\alpha_{RN}/\alpha_\infty)(S/\tilde{S})\sqrt{\tau}$$

$$\left. \Omega_\ell(R,t) = \gamma_\ell(\tilde{r})/2\sqrt{\tau} \equiv (\tilde{R}-\tilde{S})/(2S\sqrt{\tau}) \equiv \tilde{r}(\tilde{S}/S)/2\sqrt{\tau} \right\} \quad (3.30)$$

for cases (a) and (b) i.e., for long times and all R, or for all times and asymptotic $R \gtrsim 1$ n.u., (since (3.25) and (3.26) are identical); and by

$$X_\delta(t) = [\alpha_{RN}/\alpha_\infty \, y_\delta(0)]\sqrt{\tau} = (\alpha_{RN}/\alpha_\infty)(d\tilde{R}/dR)_S(S/\tilde{S})\sqrt{\tau} = (\alpha_{RN}/\alpha_\infty)(d\tilde{r}/dr)_0\sqrt{\tau}$$

$$\left. \Omega_\delta(R,t) = (R-S)/2S\sqrt{\tau} = r/2\sqrt{\tau} \right\} \quad (3.31)$$

for case (c) for short times and all R. For large S note that $X_\delta \rightarrow X_\ell$ and that $\Omega_\delta \rightarrow \Omega_\ell$ for large R and S.

The corresponding transient recombination rates obtained from (3.16) or from (3.6) directly, are written in terms of the steady-state rates (2.26) - (2.28) and of the appropriate (χ,Ω) above as

$$\alpha(t) = \alpha_{RN} \, \rho(S,t) = \alpha_{RN}[1 + (\alpha_\infty/\alpha_{TR}) \{\exp \chi^2 \, \text{erfc} \, \chi - 1\}] \quad (3.32a)$$

$$= \alpha_\infty[1 + (\alpha_{RN}/\alpha_{TR}) \exp \chi^2 \, \text{erfc} \, \chi] \quad (3.32b)$$

Note that (3.29) and (3.32) are all formally identical (in the tilda representation) to the "field-free" expressions (2.31) and (2.35). By comparison, the overall effect of the general field V(R) is therefore to change the transport rate from α_d, (2.40), to α_{TR}, (2.34), the reaction rate from α_3 to α_{RN}, (2.33), and the pair of functions (χ_0, Ω_0) of (2.38) to either of the pairs (3.30) or (3.31) for long or short times, respectively.

Short-time and long-time expansions of (3.29) are facilitated with the aid of the corresponding expansions,

$$\exp \chi^2 \text{ erfc } \chi \to 1 - (2/\pi^{1/2})\chi + \chi^2 - (4/3\pi^{1/2})\chi^3 + \ldots; \chi \to 0 \qquad (3.33)$$

for small χ (at short times) and

$$\exp \chi^2 \text{ erfc } \chi \to (1/\chi\pi^{1/2})(1 - \frac{1}{2}\chi^{-2} + \frac{3}{4}\chi^{-4} - \ldots); \quad \chi \to \infty \qquad (3.34)$$

for large χ (at long times).

Since the higher-order expansion terms above are alternatively positive and negative, the short time limits $\alpha_S^{(n)}$, where n denotes the order of χ included in (3.33), tend to (3.32a) from above or below according as n is even or odd, respectively. At short-times, therefore the rate $\alpha(t)$ initially decreases from α_{RN} as $t^{1/2}$ via

$$\alpha_S^{(1)}(t \to 0) = \alpha_{RN} \{1 - (\alpha_\infty/\alpha_{TR})(2/\pi^{1/2})\chi_\delta\}$$

$$= \alpha_{RN} \{1 - (\alpha_{RN}/\alpha_{TR})(d\tilde{R}/dR)_S (4Dt/\pi\tilde{S}^2)^{1/2}\} \qquad (3.35)$$

which tends to α_S from below. At longer times it decreases as $t^{-1/2}$ via

$$\alpha_L^{(1)}(t \to \infty) = \alpha_\infty [1 + (\alpha_{RN}/\alpha_{TR})/\chi_\ell\pi^{1/2}]$$

$$= \alpha_\infty [1 + (\alpha_\infty/\alpha_{TR})(\tilde{S}^2/\pi Dt)^{1/2}] \qquad (3.36)$$

which tends to α_L from above and then to the asymptotic steady-state limit α_∞.

This asymptotic transient (3.36) is identical to that previously derived[11] by the method[10] of "matched perturbation solutions". Thus (3.30) in (3.32b) provide the appropriate extension of (3.36) down to shorter times; and

(3.31) in (3.32a) extends the new short-time transient (3.35) up to longer times. Both the $t^{-1/2}$ long-time transient and the $t^{1/2}$ short-time transient become suppressed in the "reaction limited region" where $\alpha_{RN} \ll \alpha_{TR}$, and are fully amplified in the "transport limited region" where $\alpha_\infty = \alpha_{TR} \ll \alpha_{RN}$. The resulting formulae for α_S, $\alpha_S^{(1)}$, α_L and $\alpha_L^{(1)}$ appear to be the only simple analytical expressions apart from (3.36) for $\alpha_L^{(1)}$, yet derived for general interactions $V(R)$.

Procedures for numerical solution (see § 5) of the basic eq. (3.2) for all times require initialization of ρ and $\partial\rho/\partial\tilde{r}$ either at short times when integrating forward in t, or at long times when integrating backwards in t. Direct differentiation of the basic solution,

$$\rho(\tilde{r},\tau) = 1 + (\alpha_\infty/\alpha_{TR}) \left[\exp \chi^2 \exp(2\chi\Omega) \operatorname{erfc}(\chi+\Omega) - \operatorname{erfc} \Omega\right]/(\tilde{r}+1) \qquad (3.37)$$

where the sets $(\chi_\delta,\Omega_\delta)$ and (χ_ℓ,Ω_ℓ) distinguish short and long times, respectively, yields

$$(\partial\rho/\partial\tilde{r}) = (\alpha_{RN}/\alpha_{TR}) C(\tilde{r})\operatorname{erfc}\Omega/(\tilde{r}+1) + (\alpha_{RN}/\alpha_\infty)[C(\tilde{r})-(\alpha_\infty/\alpha_{RN})/(\tilde{r}+1)](\rho-1) \qquad (3.38)$$

where

$$C_\delta(\tilde{r}) = (d\tilde{r}/dr)_0/(d\tilde{r}/dr)$$

$$\qquad (3.39)$$

$$C_\ell(\tilde{r}) = 1$$

for short (δ) and long (ℓ) times, respectively. The radiation boundary condition,

$$\alpha_{TR}(\partial\rho/\partial\tilde{r})_0 = \alpha_{RN}\,\rho(0,\tau) = \alpha_{RN}\,\{1 + (\alpha_\infty/\alpha_{TR})\,[\exp X^2\,\text{erfc}\,X - 1\,]\,\} \quad (3.40)$$

is of course satisfied by (3.38) at the sink ($\tilde{r} = 0$) at all times. As $\tau \to 0$, $\rho \to 1 - O(\tau^{1/2})$, and $(\partial\rho/\partial\tilde{r})$ varies continuously with $\tilde{r}$ as,

$$(\partial\rho/\partial\tilde{r}) = \frac{(\alpha_{RN}/\alpha_{TR})}{(\tilde{r}+1)}\,C_\delta(\tilde{r})\,\text{erfc}\,\Omega_s \to \begin{cases} (\alpha_{RN}/\alpha_{TR}) & ;\ \tilde{r} \to 0 \\[2ex] \dfrac{(\alpha_{RN}/\alpha_{TR})}{(\tilde{r}+1)}\,\dfrac{2C_\delta(\tilde{r})}{r}\,\left(\dfrac{\tau}{\pi}\right)^{1/2}\exp(-r^2/4\tau) \\ \qquad\qquad\qquad\qquad ;\ r \gg 2\sqrt{\tau} \end{cases} \quad (3.41)$$

which indicates the dramatic decrease, with increase of r,

of $(\partial\rho/\partial\tilde{r})$ at short times from a constant value $(\alpha_{RN}/\alpha_{TR})$ at the

sink. Accurate numerical integration around initial times $\tau \sim 10^{-3}$ therefore

demands intervals Δr in r as small as 10^{-3} so as to ensure dense coverage of

the complementary error function

$$\text{erfc}\,\Omega = \frac{2}{\sqrt{\pi}}\int_\Omega^\infty \exp(-\Omega^2)\,d\Omega \quad (3.42)$$

between unity (at $r = 0$) and zero (at $r \gg 2\sqrt{\tau}$).

4. Extension for Intermediate Times and all R

In an effort to seek extensions of (3.29), with (3.30) for long times, down to intermediate times for all R, insert the expansion

$$y(\tilde{r},s) = y_{\ell}[1 + F_1(\tilde{r})s^{1/2} + F_2(\tilde{r})s + \ldots] \qquad (4.1)$$

in powers of $s^{1/2}$ in (3.14a), and equate equal powers of s. Since the exact solution at large $\tilde{r}$ is y_{ℓ}, (3.26), then F_i $(\tilde{r} \to \infty) \to 0$. The expansion coefficients are therefore determined by

$$F_1(\tilde{r}) = S^{-1} \int_{\tilde{R}}^{\infty} \left[\left(\frac{dR}{d\tilde{R}}\right)^2 - 1\right] d\tilde{R} \quad ,$$

which for Coulomb attraction tends at large $\tilde{R}$ to

$$F_1(\tilde{r}) = (R_e/S) \left[\frac{1}{6} (R_e/R) + \frac{1}{12} (R_e/R)^2 + \ldots\right] \qquad (4.2)$$

and by

$$F_2(r) = - 2S^{-1} \int_{\tilde{R}}^{\infty} F_1(\tilde{r}) d\tilde{R}. \qquad (4.3)$$

On retaining only the F_1-term in (4.1), the rate, obtained directly from the inverse Laplace Transform of (3.16), is

$$\alpha_{LS}(t) = \alpha_{\infty}[1 + (\alpha_{RN}/\alpha_{TR}) \{a_+ \exp x_-^2 \ \mathrm{erfc} \ x_- - a_- \exp x_+^2 \ \mathrm{erfc} \ x_+\} / (a_+ - a_-)]$$

$$(4.4)$$

for long → short times and is restricted to cases for which

$$\chi_{\pm}/\sqrt{\tau} = a_{\pm} = \{1 \pm [1 - 4(\alpha_{RN}/\alpha_{\infty})\tilde{S} F_1(0)/S]^{1/2}\} /2F_1(0) \tag{4.5}$$

remain real i.e., when $F_1(0) \leq \frac{1}{4} (\alpha_{\infty}/\alpha_{RN})(S/\tilde{S})$. The range of application of (4.4) is therefore rather limited.

The corresponding extension from shorter $(s \to \infty)$ to longer times may be accomplished by expanding y in terms of $s^{-1/2}$ so that, on equating equal powers of $s^{-1/2}$,

$$y(\tilde{r},\tilde{s}) = k(\tilde{r}) + [k'(\tilde{r})/2k(\tilde{r})]s^{-1/2} ; k = (dr/d\tilde{r}) , \tag{4.6}$$

where k' is $(dk/d\tilde{r})$. The condition for validity of the short-time solution $y = k(\tilde{r})$ is therefore $s^{1/2} \gg (d^2r/d\tilde{r}^2)/(dr/d\tilde{r})^2$, as before. The required rate, for short→ long times and for all assigned parameters is

$$\alpha_{SL}(t) = \alpha_{RN} [1 + (\alpha_{\infty}/\alpha_{TR}) \{1 + (k'_0/2k_0)(\alpha_{\infty}/\alpha_{RN})\}^{-1} \{\exp \chi_{SL}^2 \text{ erfc } \chi_{SL} - 1\}] \tag{4.7a}$$

$$= \alpha_{\infty}\{1 + (k'_0/2k_0)(\alpha_{\infty}/\alpha_{RN})\}^{-1} [1 + (k'_0/2k_0)+(\alpha_{RN}/\alpha_{TR}) \exp\chi_{SL}^2 \text{ erfc}\chi_{SL}] \tag{4.7b}$$

where k'_0 is $k'(\tilde{r}=0)$ and where

$$\chi_{SL} = [(\alpha_{RN}/\alpha_{\infty}) + (k'_0/2k_0)]\sqrt{\tau}/k_0 \tag{4.8}$$

.

Although (4.7a) has been designed as an extension of the short time result α_S to longer times, it does not, however, tend to the correct

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asymptotic ($t \to \infty$) limit, α_∞, as does α_S, (3.31) in (3.32b). Because it is automatically constrained to vary monotonically between α_{RN} (as $t \to 0$) and (as $t \to \infty$), α_S may indeed yield a better approximation than α_{SL} except perhaps in some intermediate-time range. Although α_S tends to the correct asymptotic limit α_∞, its asymptotic transience (i.e., the rate at which α_S approaches α_∞) will <u>not</u> be correct since it is characterized by χ_Δ rather than by the correct χ_ℓ to give

$$\alpha_S(t \to \infty) = \alpha_\infty[1 + (\alpha_\infty/\alpha_{TR})(dR/d\tilde{R})_S \, (\tilde{S}^2/\pi Dt)^{1/2}] \qquad (4.9)$$

which agrees with the exact transient (3.36) only for large sink radii S when $(dR/d\tilde{R})_S \to 1$ (cf. Fig. 1b).

Analogous considerations also apply to the comparison of α_{LS} of (4.4) with α_L of (3.29) and (3.27). The rate α_L decreases monotonically from α_{RN} to α_∞ as τ increases, in contrast to α_{LS} which does not tend to α_{RN} as $\tau \to 0$. The long-time solution α_L yields, however, the incorrect short-time transience

$$\alpha_L(t \to 0) = \alpha_{RN}[1 - (\alpha_{RN}/\alpha_{TR})(4Dt/\pi\tilde{S}^2)^{1/2}] \qquad (4.10)$$

which agrees with the exact short-time transience (3.35) only for large S when $(d\tilde{R}/dR)_S \to 1$.

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5. Numerical Solutions

The basic equation (3.2) in tilda-space for the fractional departure (3.3) from Boltzmann equilibrium, is

$$\frac{\partial \rho}{\partial \tau} = \left(\frac{d\tilde{r}}{dr}\right)^2 \left[\frac{\partial^2 \rho}{\partial \tilde{r}^2} + \frac{2}{(\tilde{r}+1)}\frac{\partial \rho}{\partial \tilde{r}}\right] \tag{5.1}$$

in dimensionless units (3.7). In numerical algorithms, the assigned initial condition

$$\rho(\tilde{r},0) = 1 \tag{5.2}$$

must be supplemented by an additional initial condition for $(\partial \rho/\partial \tilde{r})$. Eqs. (3.37) and (3.38) with (3.31) for $(X_\delta, \Omega_\delta)$ are used to facilitate forward integration in τ from 10^{-3} when small intervals Δr in r are required. The boundary conditions at the sink ($\tilde{r} = 0$) and at asymptotic $\tilde{r}$ are

$$\left.\left(\partial \rho(\tilde{r},\tau)/\partial \tilde{r}\right)_0 = (\alpha_{RN}/\alpha_{TR})\,\rho(0,\tau),\right\}$$
$$\left.\rho(r\to\infty,\tau) = 1 \right\} \tag{5.3}$$

at all times τ. Eq. (5.1) is a linear partial differential equation with nonlinear coefficients and is of the general form

$$\partial f(x,t)/\partial t = F(x,t,f(x,t), \partial f/\partial x, \partial^2 f/\partial x^2) \tag{5.4}$$

which can be solved by standard numerical procedures[17] subject to the initial conditions,

$$f(x,t=0) = f_0(x) \quad ; \quad \partial f(x,0)/\partial x = \partial f_0/\partial x \qquad (5.5)$$

and the boundary $(x \to 0, \infty)$ conditions

$$\alpha f(x,t) + \beta \, \partial f(x,t)/\partial x = \gamma(t) \quad ; \quad (x \to 0, \infty) \qquad (5.6)$$

where α and β are constants independent of (x,t). In the numerical method adopted,[17] the boundary conditions are imposed indirectly via the differential equation

$$\alpha \, \partial f(x,t)/\partial t + \beta \, \partial^2 f(x,t)/\partial t \partial x = \partial \gamma/\partial t \qquad (5.7)$$

such that $\gamma(t)$ in (5.6) must be either constant or a continuous function of t. The selected algorithm[18] DPDES designed primarily for parabolic problems (as is the case here) solves a system of equations of type (5.4) by a method of lines, wherein the solution is expanded in a series of cubic Hermite basis functions of x. The t-dependent undetermined coefficients are evaluated from a collocation procedure[17] at each t i.e., from the differential equations obtained by imposing the boundary conditions (5.7) at the endpoints (x_0, x_N) and by requiring that the differential equation (5.4) is satisfied at two Gaussian quadrature points between adjacent points x_p, x_{p+1} in the x-discretization: $x_0 \leq x_p \leq x_N$; $x_p = x_0 + ph$ (p = 0, 1, 2, ..., N).

Eq. (5.1) was therefore solved numerically in equal intervals $\Delta r = 10^{-3}$, 10^{-2} and $5 \cdot 10^{-2}$ over the respective ranges $(0 - 10^{-2})$, $(10^{-2} - 5 \cdot 10^{-2})$ and $(5 \cdot 10^{-2} - 30)$ in r; at equal intervals $\Delta \tau = 10^{-3}$, 10^{-2} and $5 \cdot 10^{-2}$ over the respective τ-ranges, $(10^{-3} - 10^{-2})$, $(10^{-2} - 1)$ and $(1 - 100)$. At short times

$\tau \sim 10^{-3} - 10^{-2}$, small intervals $\Delta r \sim 10^{-3}$ in r are required (see § 3) for accurate initialization via (3.37) and (3.38). All calculations were performed on a CDC 7600 computer with a typical execution time of 14 minutes (with a relative error of 10^{-6} in the t-discretization) for a given sink radius S and ratio $(\alpha_\infty/\alpha_{TR})$.

As a test, the numerical results reproduced the exact analytical solutions (2.37) and rates (2.41) for the field-free (V = 0) case.

Figure 2 illustrates for a representative case (S = $\frac{1}{2}$ n.u., $\alpha_\infty/\alpha_{TR}$ = 1/2) of Coulombic attraction, the collapse with scaled time $\tau (\equiv Dt/S^2)$ of the exact fractional departure $\rho(\tilde{r},\tau) = n(R,t)/\exp(-KV/De)$ of the probability density n from its initial Boltzmann distribution, $\rho(\tilde{r},0) = 1$, onto the steady-state $(\partial\rho/\partial\tau \to 0$ as $\tau \to \infty)$ distribution

$$\rho_\infty(\tilde{r},\tau \to \infty) = 1 - (\alpha_\infty/\alpha_{TR})(\tilde{S}/\tilde{R}) \qquad (5.8)$$

as a function of $\tilde{r} = (\tilde{R}/\tilde{S}) - 1$. With increase of the parameter $(\alpha_\infty/\alpha_{TR})$ to its limiting value of unity (characteristic of full transport controlled processes), the steady-state ρ_∞ is approached much more rapidly than those for smaller $(\alpha_\infty/\alpha_{TR})$, and deeper holes in the distribution appear in the neighborhood of the sink at $\tilde{r}$ = 0 where a highly non-equilibrium distribution has developed. As the sink radius S decreases, the curves in Fig. 2 for given $(\alpha_\infty/\alpha_{TR})$ collapse onto ρ_∞ over all r much more slowly i.e., it takes longer to attain steady-state, as expected.

The above asymptote ρ_∞ in Fig. 2 is rendered universal for all $(\alpha_\infty/\alpha_{TR})$ by simply relabelling the ρ-axis from the vertex at $(1 - \alpha_\infty/\alpha_{TR})$ in general, rather than at 0.5, in equal intervals to unity.

The variation with τ of the intercept $\rho(0,\tau)$ provides directly the τ-

variation of the recombination rate,

$$\alpha(\tau) = \alpha_{RN} \, \rho(0,\tau) = \alpha_{TR} \, [\partial\rho(\tilde{r}\to 0,\tau)/\partial\tilde{r}]_0 \qquad (5.9)$$

Since the accuracy of the various schemes (§ 3,4) of analytical approximation improves at all τ for larger r, detailed comparison between the exact numerical intercept $\rho_E(0,\tau)$ and the derived analytical intercepts

$$\rho(0,\tau) = 1 + (\alpha_\infty/\alpha_{TR}) \, [\exp \chi^2 \, erfc \, \chi - 1] = \alpha(\tau)/\alpha_{RN}, \qquad (5.10)$$

or between the corresponding association rates $\alpha(\tau)$, provide the most stringent test of the accuracy of the various approximations for $\rho(\tilde{r},\tilde{\tau})$ and its derivative $(\partial\rho/\partial\tilde{r})$.

5.1 Comparison with Analytical Expressions

As indicated by (3.35) and (3.36), the transience, $\alpha(\tau)$ versus $\tau[\equiv (Dt/S^2)$, in units of (S^2/D) a characteristic time scale for diffusion across a distance S], becomes amplified for larger χ i.e., for transport controlled regions, when $\alpha_{RN} \gg \alpha_\infty$ (i.e., when $\alpha_\infty/\alpha_{TR} \to 1$), and/or for large sink radii S which result in larger $(d\tilde{r}/dr)_0$ for χ_δ (cf. Fig. 1c) and in smaller $(\tilde{S}/S)$ for χ_ℓ (cf. Table 1).

Figs. 3(a-h) - 5(a-h) illustrate comparison with the exact numerical solution α_E of the various short-time solutions α_S and α_{SL}, as in (a-d), and of the various long-time solutions α_L and α_{LS}, as in (e-h), over externally assigned values of both the sink radius (S = 1, 0.75, 0.5, 0.25 n.u.) and of the ratio $\alpha_\infty/\alpha_{TR}$ (= 0.1, 0.5, 0.9). Since the transition from steady-state reaction

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controlled processes to transport controlled processes is characterized by increase from small $\alpha_\infty/\alpha_{TR}$ (where $\alpha_{RN} \ll \alpha_{TR}$) to unit $\alpha_\infty/\alpha_{TR}$ (where $\alpha_{RN} \gg \alpha_{TR}$) as in (2.32), the selected range (0.1 - 0.9) of $\alpha_\infty/\alpha_{TR}$ therefore corresponds to increase in gas density. Since $\alpha(t)$ tends to α_{RN} as $t \to 0$ and to α_∞ as $t \to \infty$, all of the short-time curves (a) - (d) for $\alpha(\tau)/\alpha_{RN}$, and all of the long-time curves (e) - (h) for $\alpha(\tau)/\alpha_\infty$ are normalized so as to tend to unity at their respective short-time and long-time limits. As $t \to \infty$, $\alpha(\tau)/\alpha_{RN}$ in (a) - (d) tends to $[1 - (\alpha_\infty/\alpha_{TR})]$, which gives 0.9, 0.5 and 0.1 for each respective value of $(\alpha_\infty/\alpha_{TR})$; and $\alpha(\tau)/\alpha_\infty$ in (e)-(h) tends as $t \to 0$ to $[1 - (\alpha_\infty/\alpha_{TR})]^{-1}$ i.e., to 1.11, 2, and 10 for each respective case.

Figs. 3(a) - 3(d) for the small ratio $(\alpha_\infty/\alpha_{TR}) = 0.1$ i.e., for $(\alpha_\infty/\alpha_{RN}) = 0.9$ which imply a reduction in $\alpha(\tau)$ of 10% from α_{RN} over the full time range, show that α_S, (3.22a) with (3.31), and α_{SL}, (4.7a) with (4.5), both reproduce the exact numerical results α_E at short times over the given range (1 - 0.25 n.u.) of S. As S increases both α_S and α_{SL} agree with α_E over longer periods of time, as expected from validity criteria (3.28b). They also represent substantial improvements over the short-time transients, $\alpha_S^{(1)}$ and $\alpha_S^{(3)}$ which are the expansions of α_S, (3.32) up to and including terms in $t^{1/2}$ and $t^{3/2}$, respectively. As $t \to 0$ both $\alpha_S^{(1)}$ and $\alpha_S^{(3)}$ eventually converge (from below) to α_S, as expected, and then to α_E. For the larger S, the suggested more rapid variation in all of the rates from α_{RN} is apparent.

As expected, α_{SL} shows some improvement over α_S for longer times up to $\tau \approx 1$, particularly at larger $(\alpha_\infty/\alpha_{TR})$ and smaller S, as is apparent in Figs. 3-5. For longer times $\tau \gg 1$, α_{SL} eventually diverges since it is not automatically constrained, as is α_S, to tend to the limiting asymptote α_∞. This is the essential reason that the short-time expression for α_S exhibits in general a better overall agreement with the exact α_E over the full range of τ. Even for the most extreme case, S = 0.25 n.u. in Figs. (3-5)d, for which

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$(d\tilde{R}/dR)$ is small (cf. Fig. 1b) so that the basic analytical approximation for all times tends to lose validity, α_S departs from α_E at intermediate $\tau \sim 1$ but then eventually approaches α_∞ albeit with an <u>incorrect</u> transience, as $t \to \infty$, in direct contrast to α_{SL}. Note that an overall effect of increase in $(\alpha_\infty/\alpha_{TR})$ in Figs. 3-5 is to effectively shift the amplification from short times (Fig. 3), to intermediate times (Fig. 4) and longer times (Fig. 5).

The exact long time rates α_L, (3.30) in (3.32b), the long-short approximation α_{LS} of (4.4), and $\alpha_L^{(1)}$ the asymptotic transient (3.36) to α_L, are all compared in Figures 3(e-h) - 5(e-h) with the exact numerical results α_E. Both α_L and α_{LS} yield considerable improvement over $\alpha_L^{(1)}$ which up to now has been the "best" simple analytical long-time expression yet proposed[11] (via the method of matched perturbation solutions[10]). This result $\alpha_L^{(1)}$ eventually tends to the present analytical result α_L which then tends to α_E (see in particular Fig. 4(h) and Fig. 5(g), 5(h)).

Although α_{LS}, (which, in order to ensure real $a_\pm$ in (4.5), is restricted only to cases (e) of Figs. 3 and 4 and to case (f) of Fig. 3), is designed to extend α_L into the shorter-time regime, it only partially succeeds, but it does not, in general, represent an overall improvement to α_L. The rate α_L is, of course, automatically constrained to vary from the exact asymptotic $(t \to \infty)$ limit with the correct long-time transience to the exact $(t \to 0)$ limit α_{RN}, with, however, the incorrect short-time transience. In contrast α_{LS} does increase with the correct long-time transience from α_∞, but reaches a maximum and then tends as $t \to 0$ to the incorrect limit α_∞.

Corresponding sets of curves are displayed in Fig. 4 for the ratio $\alpha_\infty/\alpha_{TR}$ = 0.5 which is appropriate to atmospheric gas pressures and which represents equal rates of transport and reaction. A 50% decrease in $\alpha(t)$ from α_{RN} to will therefore occur as t develops. Both α_S and α_{SL} again represent a

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considerable improvement over their short-time limits $\alpha_S^{(1)}$ and $\alpha_S^{(3)}$; and α_L is significantly more accurate than the previous standard result $\alpha_L^{(1)}$. Note, for this larger ratio of $\alpha_\infty/\alpha_{TR}$, that the extensive range $[10^{-2} - 10^2]$ in time does not include the short-time limits when $\alpha/\alpha_{RN} \to 1$, as in Fig. 3, but emphasizes rather the intermediate-time and long-time regimes. Fig. 3 illustrates very clearly, even for the worst case (h) with S = 0.25 n.u., the dividend that accrues from the built-in variation of α_L between α_{RN} at short times and α_∞ at long times. At intermediate times, $\alpha_S > \alpha_E$, $\alpha_L < \alpha_E$ and $\alpha_L^{(1)} > \alpha_E$. Since $\alpha_L^{(1)}$ tends to α_L more rapidly than α_L tends to α_E, $\alpha_L^{(1)}$ must therefore cross α_E so that somewhat closer but accidental agreement is exhibited, as in Figs. (4h) and (5h).

The general picture which is therefore emerging is that both α_S and α_L are highly accurate analytical solutions which are, in general, better than their corresponding extensions α_{SL} and α_{LS}, respectively, into the intermediate-time regime, mainly because the basic expression (3.32) automatically varies between the correct limits α_{RN} and α_∞; α_S is the exact short-time transience and α_L is the exact long-time transience. No short-time approximation as α_S, $\alpha_S^{(1)}$, $\alpha_S^{(3)}$, α_{SL} has been previously proposed and the present long-time result α_L is quite superior to $\alpha_L^{(1)}$ which has been the only analytical expression previously reported.[11]

This underlying order has become further clarified in Figure 5 which is appropriate to transport-controlled processes at high gas pressures ($\sim$ tens of atmospheres). This case with $(\alpha_\infty/\alpha_{TR}) = 0.9$, involves a 90% reduction in $\alpha(\tau)$ from α_{RN} to α_∞ as τ develops. The τ-range $[10^{-2} - 10^2]$ emphasizes intermediate $\to$ long times. Figs. 5c,d exhibit quite clearly, for the first time, the marked departure of α_S from α_E at intermediate times $\tau = 1 - 10$ followed by the eventual return of α_S to α_E in the limit of long-times. Also

the convergence of $\alpha_L^{(1)}$ to α_L is quite apparent in Fig. 5h. Even for this most extreme case $S = 0.25$ n.u. where the validity criteria (3.26b) and (3.28b) is being stretched for all times, the present expressions for α_S and α_L are quite superior to $\alpha_S^{(1)}$, $\alpha_S^{(3)}$ and to $\alpha_L^{(1)}$, respectively.

Since the various terms in the expansion (3.33) for α_S of (3.32a), are alternatively negative and positive, $\alpha_S^{(n)}$ tends to α_S from above or below depending on whether the number n of time-dependent terms included in (3.33) is even or odd, respectively. Since α_L is less than α_E and since α_S is greater than α_E at intermediate times, some time-dependent combination of α_S and α_L is suggested (see § 6).

The long-time curves (e) - (h) in Figs. 3-5 show directly that $\alpha_{E,L,S}$ achieve their steady-state value α_∞ more rapidly for transport-controlled recombination, i.e., for $(\alpha_\infty/\alpha_{TR}) \lesssim 1$, than for reaction-controlled recombination, $(\alpha_\infty/\alpha_{TR}) \ll 1$, which is characterized by a much slower rate of decrease to a higher relative value α_∞.

Even with its incorrect short-time transience, α_L is somewhat better than α_S over all time τ for the reaction dominated recombination, (Fig. 3), and α_S, in spite of its incorrect long-time transience, is somewhat better than α_L over all τ for transport dominated recombination (Fig. 5).

6. Validity Criteria and Improved Transient Result

Although the long-time and short-time expressions obtained by inserting (3.30) and (3.31) respectively in (3.29) for $n(R,t)$ and in (3.32) for $\alpha(t)$, have now been shown to be highly accurate, they have been derived from the Laplace-transform technique such that neither do the actual equations satisfied by the derived analytical formulae or do rigorous validity criteria apart from (3.26b) and (3.28b) naturally materialize. The basic equation

$$\left(\frac{\partial\phi}{\partial\tau}\right)_{\tilde{r}} = \left(\frac{d\tilde{r}}{dr}\right)^2 \left(\frac{\partial^2\phi}{\partial\tilde{r}^2}\right)_{\tau} \tag{6.1}$$

for $\phi(\tilde{r},t) = (\tilde{r}+1)\,\rho(\tilde{r},t)$, as in (3.7) and (3.8), where ρ is the fractional departure $n(R,t)/N_0 \exp(-KV/De)$ of the probability density $n(R,t)$ from Boltzmann equilibrium, may be expressed in alternative forms as

$$\left(\frac{\partial\phi}{\partial\tau}\right)_{\tilde{r}} = \frac{\partial^2\phi}{\partial r^2} + \left\{\left(\frac{d\tilde{r}}{dr}\right)^2 \left(\frac{d^2r}{d\tilde{r}^2}\right)\right\}\left(\frac{\partial\phi}{\partial r}\right) \tag{6.2a}$$

$$= \frac{\partial^2\phi}{\partial r^2} - \left(\frac{d^2\tilde{r}}{dr^2}\right)\left(\frac{\partial\phi}{\partial\tilde{r}}\right) \tag{6.2b}$$

used to discuss the short-time solution, or as

$$\left(\frac{\partial\phi}{\partial\tau}\right)_{\tilde{r}} = \left(\frac{S}{\tilde{S}}\right)^2 \left(\frac{\partial^2\phi}{\partial\tilde{r}^2}\right)_{\tau} + \left[\left(\frac{d\tilde{r}}{dr}\right)^2 - \left(\frac{S}{\tilde{S}}\right)^2\right]\left(\frac{d\tilde{r}}{dr}\right)^{-2}\left(\frac{\partial\phi}{\partial\tau}\right)_{\tilde{r}} \tag{6.2c}$$

used to discuss the solutions at large r.

The recombination rate is simply

$$\alpha(\tau) = \alpha_{RN}\,\rho(0,\tau) = \alpha_{TR}\,[\partial\rho(\tilde{r}\to0,\tau)/\partial\tilde{r}] \tag{6.3a}$$

or, equivalently,

$$\alpha(\tau) = \alpha_{RN} \, \phi(0,\tau) = \alpha_\infty \, [\partial\phi(\tilde{r}\to 0,\tau)/\partial\tilde{r}] \qquad (6.3b)$$

in which RBC, the radiation boundary condition (3.6) or (3.9b) between the function and its derivative, is explicitly used.

Provided

$$\left| \partial\phi/\partial\tau \right| \gg (d^2\tilde{r}/dr^2)\left[(\partial\phi/\partial\tilde{r}) - 1 \right] \qquad (6.4)$$

as for all r and small τ (but not for large r and all τ), (6.2b) reduces to

$$\frac{\partial\phi_\delta}{\partial\tau} = \frac{\partial^2\phi_\delta}{\partial r^2} - \frac{d^2\tilde{r}}{dr^2} \qquad (6.5)$$

which, apart from the term $d^2\tilde{r}/dr^2$, is formally identical to field-free diffusion in (r,τ)-space. Provided,

$$\left[\left(\frac{d\tilde{r}}{dr}\right)^2 - \left(\frac{S}{\tilde{S}}\right)^2 \right] \left(\frac{d\tilde{r}}{dr}\right)^{-2} = \left[1 - \left(\frac{dR}{d\tilde{R}}\right)^2 \right] \ll 1 \qquad (6.6)$$

as at large r and all τ, then (6.2c) reduces to

$$\frac{\partial\phi_\ell}{\partial\tilde{\tau}} = \frac{\partial^2\phi_\ell}{\partial\tilde{r}^2} \qquad ; \qquad \tilde{\tau} = (S/\tilde{S})^2 \, \tau \qquad (6.7)$$

which is formally identical with field-free diffusion in $(\tilde{r},\tilde{\tau})$-space.

The exact solutions of (6.5) and (6.7) appropriate to the above initial and boundary conditions (3.9) in $(\tilde{r},\tilde{\tau})$ space are then

$$\phi(\tilde{r},\tau) = (\tilde{r}+1) + (\alpha_\infty/\alpha_{TR}) \left[exp(2\Omega\chi) \, exp \, \chi^2 \, erfc(\chi+\Omega) - erfc \, \Omega \right], \qquad (6.8)$$

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where the pair (χ, Ω) of functions are defined as

$$\chi_{\delta,\ell}(\tau) = a_{\delta,\ell}\sqrt{\tau} \quad ; \quad a_\delta = (\alpha_{RN}/\alpha_\infty)(d\tilde{r}/dr)_0; \quad a_\ell = (\alpha_{RN}/\alpha_\infty)(S/\tilde{S}) \Bigg\}$$

$$\Omega_\delta(r,\tau) = r/2\sqrt{\tau}; \quad \Omega_\ell(\tilde{r},\tau) = \tilde{r}/2\sqrt{\tau} \qquad \qquad \qquad (6.9)$$

with subscript δ appropriate to the exact solution ϕ_S at short times and all r, and with subscript ℓ appropriate to the exact solution ϕ_ℓ for all times and large r.

These approximate solutions $\phi_{\delta,\ell}$ of the basic eq. (6.1) are exactly those (3.29) - (3.31) previously derived via the Laplace Transform technique which procedure is however required to show that the solution ϕ_ℓ for large r and all τ is identical with that for all r and long τ. Direct differentiation of (6.8) yields

$$(\partial\phi_\delta/\partial\tilde{r}) = 1 + (\alpha_{RN}/\alpha_\infty)\frac{(d\tilde{r}/dr)_0}{(d\tilde{r}/dr)}\left[\phi_\delta - (\tilde{r}+1) + (\alpha_\infty/\alpha_{TR})\,\text{erfc}\,\Omega_S\right] \qquad (6.10a)$$

and

$$(\partial\phi_\ell/\partial\tilde{r}) = 1 + (\alpha_{RN}/\alpha_\infty)\left[\phi_\ell - (\tilde{r}+1) + (\alpha_\infty/\alpha_{TR})\,\text{erfc}\,\Omega_\ell\right] \qquad (6.10b)$$

which assume their largest values $[\alpha_{\delta,\ell}(\tau)/\alpha_\infty]$ at the sink (cf. Fig. 2) where RBC, Eq. (6.3b) is of course satisfied. Also, differentiation of (6.8) yields

$$(\partial\phi_{\delta,\ell}(r,\tau)/\partial\tau) = a^2_{\delta,\ell}\left[\phi_{\delta,\ell} - (\tilde{r}+1)+(\alpha_\infty/\alpha_{TR})\{\text{erfc}\Omega_{\delta,\ell}-\exp(-\Omega^2_{\delta,\ell})/(\sqrt{\pi}\chi_{\delta,\ell})\}\right]$$

$$(6.11)$$

which can be used to provide $\partial^2\phi_\delta/\partial r^2$ or $\partial^2\phi_\ell/\partial\tilde{r}^2$ via (6.5) or (6.7), respectively.

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Fig. 1c, which illustrates the variation for Coulomb attraction of $(d\tilde{r}/dr)$ with $\tilde{r}$ for various sink radii shows that the terms of (6.2b) and (6.2c) which are omitted in (6.5) and (6.7), respectively, are largest at the sink. At the sink,

$$\phi_{\delta,\ell}(0,\tau) = 1 + (\alpha_\infty/\alpha_{TR}) [\exp\chi^2 \text{ erfc } \chi - 1] \tag{6.12a}$$

$$= (\alpha_\infty/\alpha_{RN})[\partial\phi_{\delta,\ell}(0,\tau)/\partial\tilde{r}] = \alpha_{S,L}(\tau)/\alpha_{RN}$$

and

$$\partial\phi_{\delta,\ell}(0,\tau)/\partial\tau = (a^2_{\delta,\ell}/\alpha_{RN}) [\alpha_{S,L}(\tau) - \alpha_{S,L}(\tau\to\infty)] \tag{6.12b}$$

where $\alpha_{S,L}(\tau\to\infty)$ are the long-time asymptotic transients,

$$\alpha_{S,L}(\tau\to\infty) = \alpha_\infty [1 + (\alpha_{RN}/\alpha_{TR})/\chi_{\delta,\ell}\sqrt{\pi}] \tag{6.13}$$

of the basic rates,

$$\alpha_{S,L}(\tau) = \alpha_{RN}\{1 + (\alpha_\infty/\alpha_{TR}) [\exp \chi^2_{\delta,\ell} \text{ erfc } \chi_{\delta,\ell} - 1]\} \tag{6.14a}$$

$$= \alpha_\infty [1 + (\alpha_{RN}/\alpha_{TR}) \exp \chi^2_{\delta,\ell} \text{ erfc } \chi_{\delta,\ell}] \tag{6.14b}$$

At long times,

$$\phi_{\delta,\ell}(\tilde{r},\tau\to\infty) = (\tilde{r}+1) - (\alpha_\infty/\alpha_{TR}); (\partial\phi_{\delta,\ell}/\partial\tau) \to 0 \tag{6.15}$$

and at short times,

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$$\phi(\tilde{r}, \tau \to 0) = (\tilde{r}+1); \quad (\partial \phi_{\delta,\ell}/\partial \tau) \to -(\alpha_{RN}/\alpha_{TR})(d\tilde{r}/dr)_0 \exp(-r^2/4\tau)/\sqrt{\pi \tau} \quad (6.16)$$

With the aid of (6.10a) and (6.11), the key criteria (6.4) for validity of the short-time solution ϕ_{δ} for all r is,

$$(\alpha_{RN}/\alpha_{\infty})|\phi_{\delta} - (\tilde{r}+1) + (\alpha_{\infty}/\alpha_{TR})[\text{erfc } \Omega_{\delta} - \exp(-\Omega_{\delta}^2)/x_{\delta}\sqrt{\pi}]|$$

$$\gg \frac{(d^2\tilde{r}/dr^2)}{(d\tilde{r}/dr)_0(d\tilde{r}/dr)}|\phi_{\delta} - (\tilde{r}+1) + (\alpha_{\infty}/\alpha_{TR}) \text{ erfc } \Omega_{\delta}| \quad (6.17a)$$

which specifically excludes long times ($\tau \to \infty$) since then $\Omega_{\delta} \to 0$ and both sides vanish, with the aid of (6.15). This condition becomes more transparent at the sink where (6.4) reduces, with the aid of (6.12a,b) to,

$$(\alpha_{RN}/\alpha_{\infty})(d\tilde{r}/dr)_0^2 [\alpha_S(\tau) - \alpha_S(\tau \to \infty)] \gg (d^2\tilde{r}^2/dr^2)_0 [\alpha_S(\tau) - \alpha_{\infty}] \quad (6.17b)$$

which also specifically excludes long times since α_S tends to $\alpha_S(\tau \to \infty)$, the long-time transient, faster than α_S tends to α_{∞}, the steady-state asymptote. Moreover the validity of this "short time" solution extends into longer times both for the transport controlled regime when $(\alpha_{RN}/\alpha_{\infty}) \gg 1$, and for larger sinks when $(d\tilde{r}/dr)_0$ becomes larger so that $(d^2\tilde{r}^2/dr^2)_0$ becomes smaller (cf. Fig. 1c). This systematic trend is indeed confirmed by Figs. 3-5.

The key criteria (6.6) for validity of the solution ϕ_{ℓ} of (6.7) is satisfied for large R (cf. Fig. 1 and Table 1) at all times. As shown by the Laplace Transform method ϕ_{ℓ} is also the exact solution for all R at long times.

6.1 Effective Transient

Although $\alpha_{S,L}(\tau)$ yield the exact transients at the respective short (S) and long (L) times, $\alpha_S(\tau \to \infty)$ does not tend to the correct long-time transient $\alpha_L^{(1)}(\tau)$ of (3.36), and $\alpha_L(\tau \to 0)$ does not tend to the correct short-time transient $\alpha_S^{(1)}$ of (3.35) since, a_δ and a_ℓ in (6.9) are not equal, except at large sink radii (cf. Figs. 3(a) - 5(a)) when $(d\tilde{r}/dr) \to (S/\tilde{S})$. The appropriate asymptotic limits α_{RN} at zero t and α_∞ at infinite t are however reproduced by both α_S and α_L via the functional dependence (6.14), an asset worth exploitation.

Expand the solution,

$$\phi_A(\tilde{r},\tau) = \phi_\delta(\tilde{r},\tau) \exp - \sigma(\tau) + \phi_\ell(\tilde{r},\tau) [1 - \exp -\sigma(\tau)] , \qquad (6.18)$$

of the basic Eq. (6.1) in terms of the known functions $\phi_{\delta,\ell}$. The exact short-time and long-time transients are ensured by insisting that the unknown function $\sigma(\tau)$ is such that $\sigma(\tau \to 0) \to 0$ and $\sigma(\tau \to \infty) \to \infty$. Also $\phi_A(\tilde{r} \to \infty, \tau) \to (\tilde{r}+1)$, irrespective of $\sigma(\tau)$. The radiation boundary condition in (6.3b) is satisfied provided σ is a function only of τ. This restriction precludes (6.18) from tending to the exact solution $\phi_\ell(\tilde{r},\tau)$ at large r. The combination (6.18) is therefore expected to provide an improved transient in the vicinity of the sink where the transient rates $\alpha(\tau) = \alpha_{RN} \phi(0,\tau)$ are determined.

According to Figs. 3-5, α_S departs most from the exact rate at intermediate times $\tau \gtrsim 10$, and α_L departs most at short times $\tau \lesssim 1$. Plausible combinations consistent with (6.18) are therefore

$$\alpha^{(-)}(\tau) = \alpha_L(\tau) \exp(-\tau^{-1/2}) + \alpha_S(\tau) [1 - \exp(-\tau^{-1/2})] \qquad (6.19)$$

and

$$\alpha^{(+)}(\tau) = \alpha_L(\tau) [1 - \exp(-\tau^{1/2}] + \alpha_S(\tau) \exp(-\tau^{1/2}) \qquad (6.20)$$

In Table 2 are displayed the __maximum__ percentage errors

$$\Delta = 100 \ (\alpha - \alpha_E)/\alpha_E \qquad (6.21)$$

between the exact numerical rates α_E and the analytical rates $\alpha = \alpha_S$, α_L and $\alpha^{(\pm)}$ over all τ. The above combinations for $\alpha^{(\pm)}$ provide considerable improvement over the individual $\alpha_{S,L}$ particularly in the transport limited regime $\alpha_\infty \rightarrow \alpha_{TR}$ for the extreme case of smaller $S \sim 0.25$. The combination (6.20) provides rates within 7% lower than the exact rates over the full τ-range. Other trial combinations involving $\tau^{\pm 1}$ instead of $\tau^{\pm 1/2}$ in (6.20) and (6.19) were adopted with similar but somewhat less accurate results. As Cols. 2 and 3 of Table 2 show, the greatest error occurs for those cases with the largest differences between a_ℓ and a_δ in (6.9). Also α_L involves less error in general than α_S over the full τ-range.

Another possibility is retention of the basic functional forms,(6.8) for ϕ and (6.14) for α, but to allow $X\tau^{-1/2}$ to vary continuously from a_δ, the exact short-time value (6.9) to a_ℓ, the exact long-time value (6.9). The forms (6.8) and (6.14) ensure automatic satisfaction of both boundary conditions (radiation and asymptotic) for well behaved (X,Ω) and provide the correct limits α_{RN} and α_∞ at zero and infinite times, respectively. Since maximum error in the previous analytical expression for α's occurred for those cases with the largest constants $(X_\ell - X_\delta) \ \tau^{-1/2}$, direct approximation to X, under the constraints that $X \rightarrow X_\delta$ as $\tau \rightarrow 0$ and $X \rightarrow X_\ell$ as $\tau \rightarrow \infty$, is therefore indicated.

Figs. 6(a) - 6(c) illustrate the variation of $X_{1,2}^{(-)} \ \tau^{-1/2}$, where

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$$x_n^{(-)}(\tau) = \exp(-\tau^{-n/2})x_\ell + [1 - \exp(-\tau^{-n/2})]\, x_\delta \quad ; \; n = 1,\, 2 \qquad (6.22)$$

between the exact short-time and long-time constant limits, as compared with the numerical solution x_E of (3.32) with α taken as the exact numerical rates α_E. Since $x_\delta \leq x_E \leq x_\ell$, then $\alpha_\delta \leq \alpha_E \leq \alpha_\ell$, as illustrated already by Figs. 3-5. The more gradual variation of $x_1^{(-)}$ is much closer to x_E than is the more abrupt variation of $x_2^{(-)}$, even for those transport limited cases which involved the largest difference $(x_\ell - x_\delta)$.

Figs. 7(a) - 7(c) demonstrate the close agreement of the resulting rates $\alpha[x_1^{(-)}]$ with the exact numerical rate over the full range of τ for the worst cases (transport-limited and small sinks). Although the percentage errors (Table 2) associated with α_L and α_S are here as large as -33% and 68%, respectively, use of $x_1^{(-)}$ in (6.14) involves errors less than 4%, as indicated in Column 9 of Table 2. Inspection of Figs. 6 and 7 shows that α is not too sensitive to variation in x e.g., a 10% variation in x in Fig. 6 results in little variation of α. Also the fact that x_1^- intersects x_E twice $(x_1^- < x_E$ at short times, $x_1^- > x_E$ at intermediate times, $x_1^- < \bar{x}_E$ at long times) results in a corresponding but less of a variation in α.

7. Summary and Conclusions

By operating at a level more basic than the macroscopic Debye-Smoluchowski Equation (DSE), the present treatment (§ 2), has exposed the following assumptions intrinsic to DSE: (1) the densities n and associated net current J in eq. (1) refer to pairs in the combined blocks C (of fully dissociated states) and E (at highly excited states) as in eq. (2.11); (2) steady-state conditions for all pairs in each energy level of block E and (3) steady-state for all pairs with $R \leq R_s$ and all energies in blocks C and E as in eq. (2.30). Also (4) DSE is mainly limited to cases of high non-equilibrium.

In addition, the microscopic treatment has also provided the appropriate modification (2.14) of DSE, which was applicable only to regions $R \geq R_s$ external to the sink, to description of the kinetics within ($R \leq R_s$) the sink.

The microscopic treatment has also indicated that the actual rate (2.20) is determined by the self-consistent solution[5] of the two simultaneous equations (2.7) and (2.10) each of which couple transport and collisions.

The local rate α_3 of reaction in (2.23) thus remains an integral and internal part of the treatment by being determined from the self consistent solutions.

This local rate α_3 (or α_{RN}) is externally assigned in DSE which therefore describes via (2.9) in (2.24a), the transport portion of the problem consistent with this external choice for α_3. Under the provisor that the transport and reaction rates α_{TR} and α_{RN} are fully uncoupled, the DSE-prescription is valuable for investigation of that particular time-dependent combination of α_{RN} and α_{TR} involved in the process as time evolves.

In § 3, a nonlinear transformation[12] into tilda-space $\tilde{R}(R)$, has

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facilitated the search for simple analytical time-dependent solutions of DSE for general interactions $V(R)$. Expressions have been obtained for the time dependent probability density $n(R,t)$, that the pair AB has separation R, and for reaction rates $\alpha(t)$ which are exact (a) at all times and large R, (b) at long times and all R and (c) at short times and all R. In particular, the solutions for cases (a) and (b) are identical. The transformation technique is, in itself, quite general and can be applied to a variety of problems. For example, Cukier[19] by following previous reports[12] of this strategy, recently used this tilda space representation to successfully study concentration dependent fluorescent quenching.

By comparison in § 5.1 with exact numerical transient rates α_E of § 5, the rates $\alpha_S(t)$ and $\alpha_L(t)$, (3.32) with (3.31) and (3.30), are the exact DSE transients at short and long times, and are, respectively, higher and lower than α_E at intermediate times. Over the full time-range, $\alpha_L(t)$ is, in general, closer to α_E than is α_S. Retention of only the first $t^{-1/2}$-term in the $t^{-1/2}$-expansion of $\alpha_L(t)$ provides $\alpha_L^{(1)}(t)$ in (3.36), which is identical with the asymptotic transient derived[11] previously from a perturbation-type method.[10] The present expression (3.32) with (3.30), for $\alpha_L(t)$ provides considerable improvement over $\alpha_L^{(1)}$ which, up to now, has been (to the author's knowledge) the only simple analytical rate available. Similar expansions (3.35) for short times are also provided.

Not only is α_S the exact transient at short times but α_S tends to the correct steady state asymptote α_∞ at long times, albeit with an incorrect transience; and α_L, not only is the exact long time transient but tends (with an incorrect transience) at short times to the correct rate α_{RN} at $t = 0$. The varations of both $\alpha_{L,S}(t)$ with t are therefore bounded, unlike the previous rate $\alpha_L^{(1)}$. This asset is the essential reason that extensions of $\alpha_{L,S}$

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proposed in § 4 to cover intermediate times are not as effective over the full time-range.

By exploitation of this asset, which is based on the unique functional dependence of $\alpha(t)$ in (3.32) on $\chi(t)$, a time-dependent combination of $\chi_\delta(t)$ and $\chi_\ell(t)$ for $\chi(t)$ provides, in § 6.1, rates highly accurate (to within 4% for the worst case) over several decades of time!

Acknowledgement

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Table 1. Values of R and $\tilde{R}$, in natural units ($R_e = e^2/kT$), and of ($d\tilde{R}/dR$) for Coulombic Attraction.

R	$\tilde{R}$	($d\tilde{R}/dR$)
0	1	0
0.25	1.0187	0.3041
0.5	1.1565	0.7241
0.75	1.3580	0.8642
1.0	1.5820	0.9207
1.5	2.0552	0.9638
2.0	2.5415	0.9794
3.0	3.5277	0.9908
6.0	6.5139	0.9977
10	10.5083	0.9992
⋮	⋮	⋮
R	R+0.5	1.0

Table 2: Largest Percentage Errors $\Delta = 100(\alpha - \alpha_E)/\alpha_E$ associated with various levels of approximation.

$(\alpha_\infty/\alpha_{TR})$	S	$a_\delta^\dagger$	$a_\ell^\dagger$	$\overbrace{\alpha_S}^{}$	$-\alpha_L$	$\Delta \atop \alpha^{(-)}$	$-\alpha^{(+)}$	$\alpha[x_1^{(-)}]$	$-\alpha[x_2^{(-)}]$
0.1	1	0.647	0.702	0.15	0.13	0.03	0.04	0.03	0.06
0.1	0.75	0.530	0.614	0.29	0.22	0.05	0.08	0.05	0.09
0.1	0.50	0.348	0.480	0.69	0.45	0.07	0.21	0.07	0.16
0.1	0.25	0.083	0.273	2.98	1.24	-0.24	0.93	-0.43	0.85
0.5	1	1.164	1.264	0.93	0.96	0.26	0.21	0.26	0.45
0.5	0.75	0.955	1.105	1.75	1.62	0.42	0.41	0.39	0.72
0.5	0.50	0.626	0.865	4.33	3.24	0.68	1.09	0.61	1.25
0.	0.25	0.149	0.491	20.63	8.92	1.33	5.67	-2.64	-5.43
0.9	1	5.820	6.322	2.25	3.63	1.23	0.17	1.20	1.77
0.9	0.75	4.773	5.523	4.32	6.14	2.17	0.33	2.05	3.16
0.9	0.50	3.130	4.323	11.24	12.32	4.62	0.87	3.88	6.69
0.9	0.25	0.746	2.454	68.29	32.70	15.06	6.43	3.65	11.24

$\alpha_{S,L}(\tau)$: Eq. (3.32) with (3.31) or (3.30); $\alpha[x_{1,2}^{(-)}]$: Eq. (3.32) with (6.22) for $x_{1,2}^-$.

$\alpha^{(-)}(\tau) = \exp(-\tau^{-1/2})\alpha_L + [1 - \exp(-\tau^{-1/2})]\alpha_S$;

$\alpha^{(+)}(\tau) = \exp(-\tau^{1/2})\alpha_S + [1 - \exp(-\tau^{1/2})]\alpha_L$;

$^\dagger a_{\delta,\ell} = x_{\delta,\ell}\,\tau^{-1/2}$

Fig. 1. Variation of $(d\tilde{R}/dR)$ with $\tilde{R}$(n.u.) for (a) the attractive interactions $V(R) = -(R_e/R)^n$, $n = 1, 2, 4$ and 6. $\tilde{R}$ is in units of R_e, the natural unit (n.u.). The variation for pure Coulomb attraction ($n = 1$, $R_e = e^2/kT$) is amplified in (b) where (X) denote the values selected as sink radii S.(c) Variation of scaled derivative $(d\tilde{r}/dr)$ with scaled distance $\tilde{r}$ for the selected sink radii ($S = 1, 0.75, 0.5$ and 0.25 n.u.).

Fig. 2. Exact numerical solutions for the fractional departure $\rho = n/N_0 \exp(-V/kT)$ of the probability density n from Boltzmann equilibrium as a function of reduced distance $\tilde{r} = (\tilde{R}/\tilde{S})-1$ at scaled sequential times $\tau = (Dt/S^2) = 0.05, 0.5, 1, 2, 5, 10, 20, 30, 100, 200, 500$ up to infinity (∞). Assigned parameters: $\alpha_\infty/\alpha_{TR} = 0.5$, $S = 0.5$ (n.u.).

Fig. 3. Comparison with exact numerical rates of various short-time (a)-(d) and of various long-time (e)-(h) analytical rates over several decades of scaled time $\tau = Dt/S^2$, for various sink radii S(n.u.). Assigned parameter: $\alpha_\infty/\alpha_{TR} = 0.1$.

Fig. 4. As in Fig. 3, but with $\alpha_\infty/\alpha_{TR} = 0.5$.

Fig. 5. As in Fig. 3, but with $\alpha_\infty/\alpha_{TR} = 0.9$.

Fig. 6. Variation of $\chi(\tau)\,\tau^{-1/2}$ with scaled time $\tau = (Dt/S^2)$ for extreme case of small sink radius $S = 0.25$ n.u. and for $\alpha_\infty/\alpha_{TR}$ taken as (a) 0.1, (b) 0.5 and (c) 0.9. Curve E is obtained from exact solution of eq. (3.22) for exact numerical rate, and curves 1 and 2 are obtained from eq. (6.22) of text with $n = 1$ and 2, respectively. Long-time and short-time exact limits $\chi_{\ell,\Delta}(\tau)\,\tau^{-1/2}$ are illustrated.

Fig. 7. Comparison over scaled time $\tau = (Dt/S^2)$ between exact numerical rate α_E and various analytical rates: $\alpha[x_1^{(-)}]$ obtained from eq. (6.22) for x_1^- in eq. (3.22) for α. The exact long-time and short-time transients are α_L and α_S, respectively. Assigned Parameters: $(\alpha_\infty/\alpha_{TR})$ = (a) 0.1, (b) 0.5, (c) 0.9; and S = 0.25 n.u. an extreme case for validity of basic assumptions.
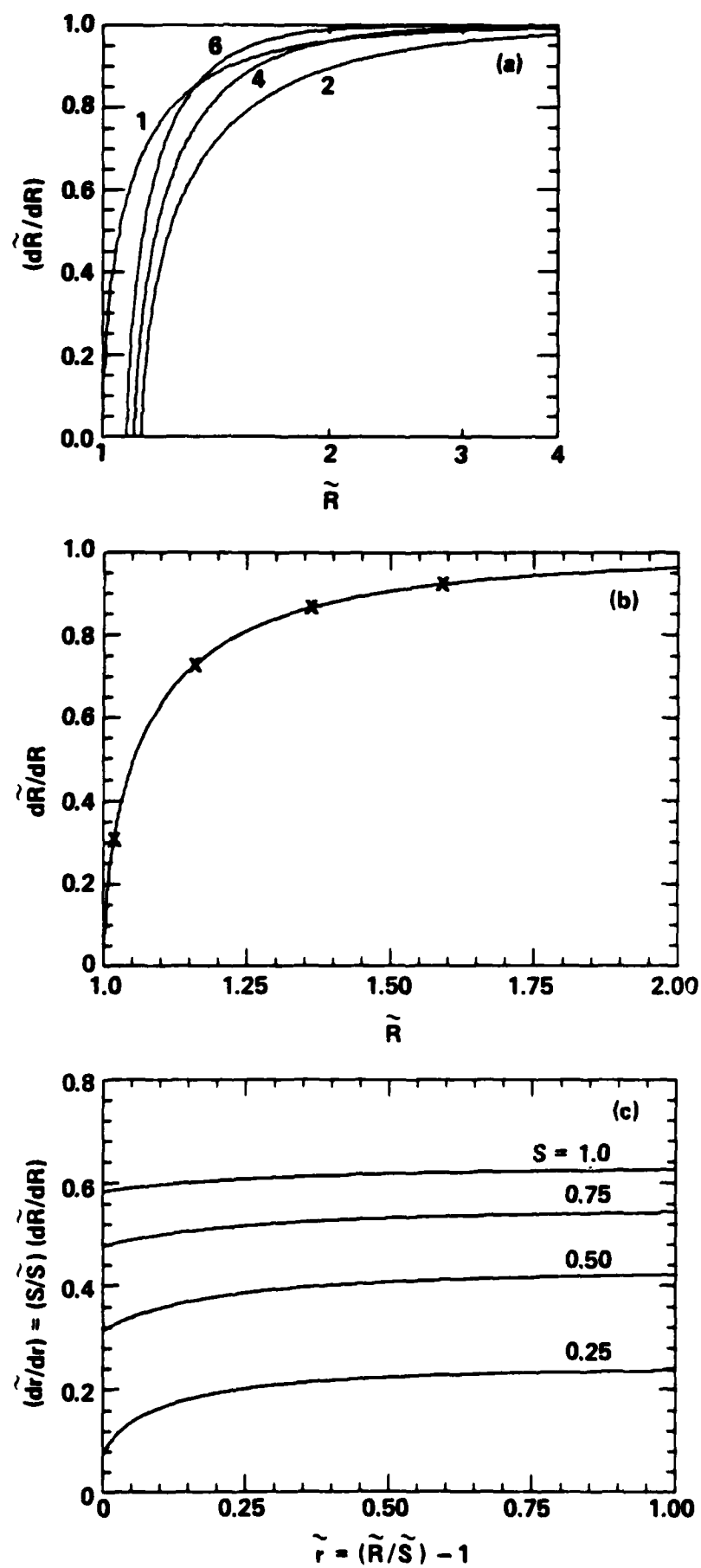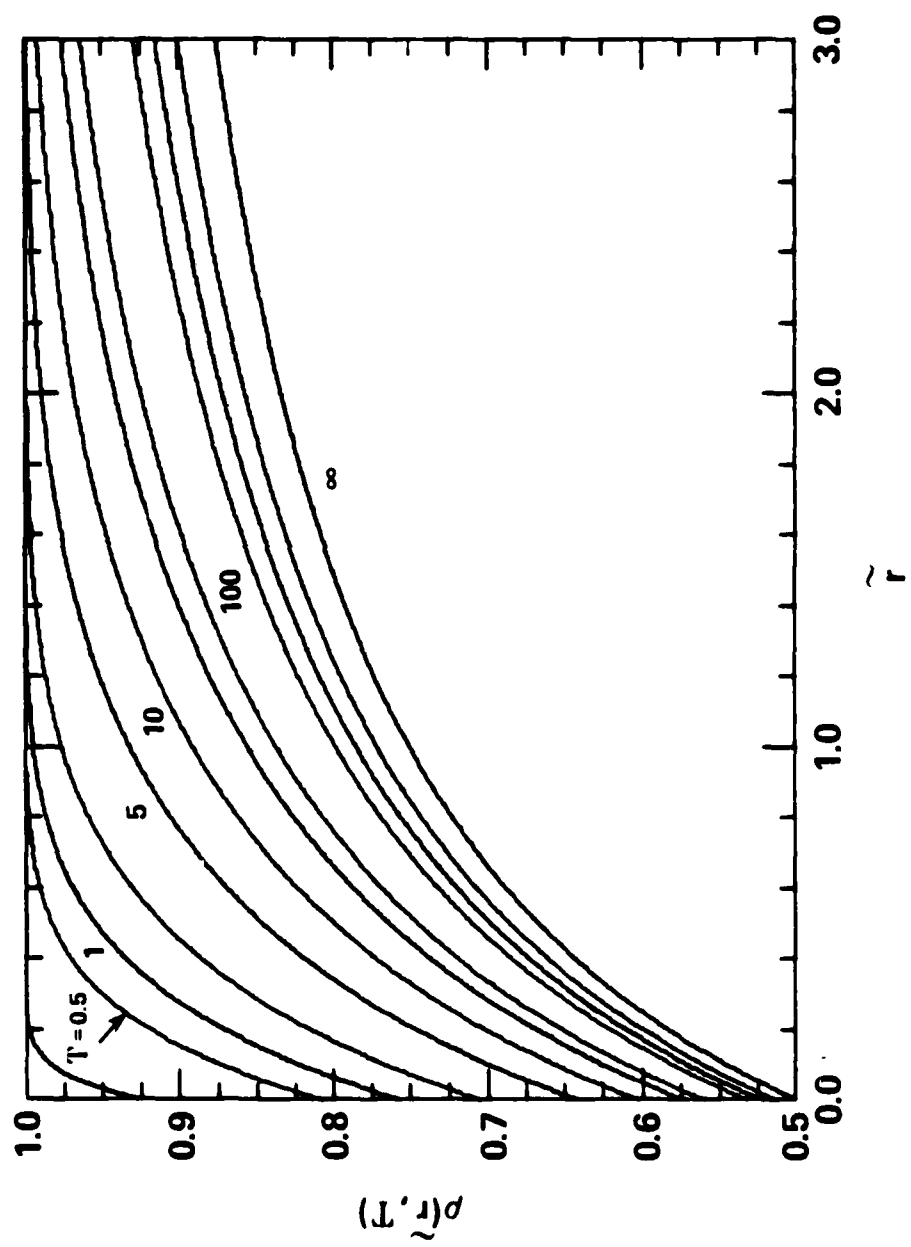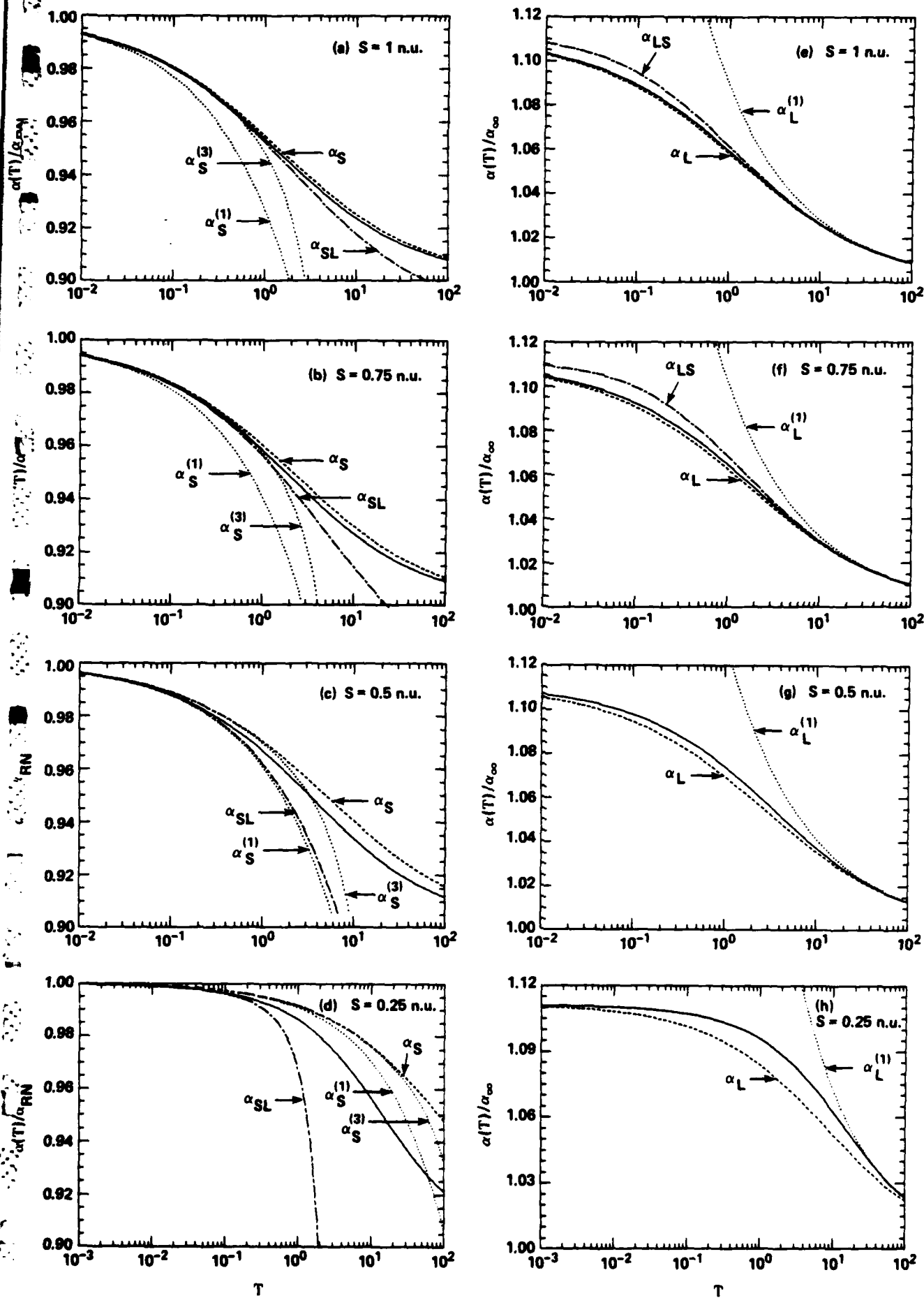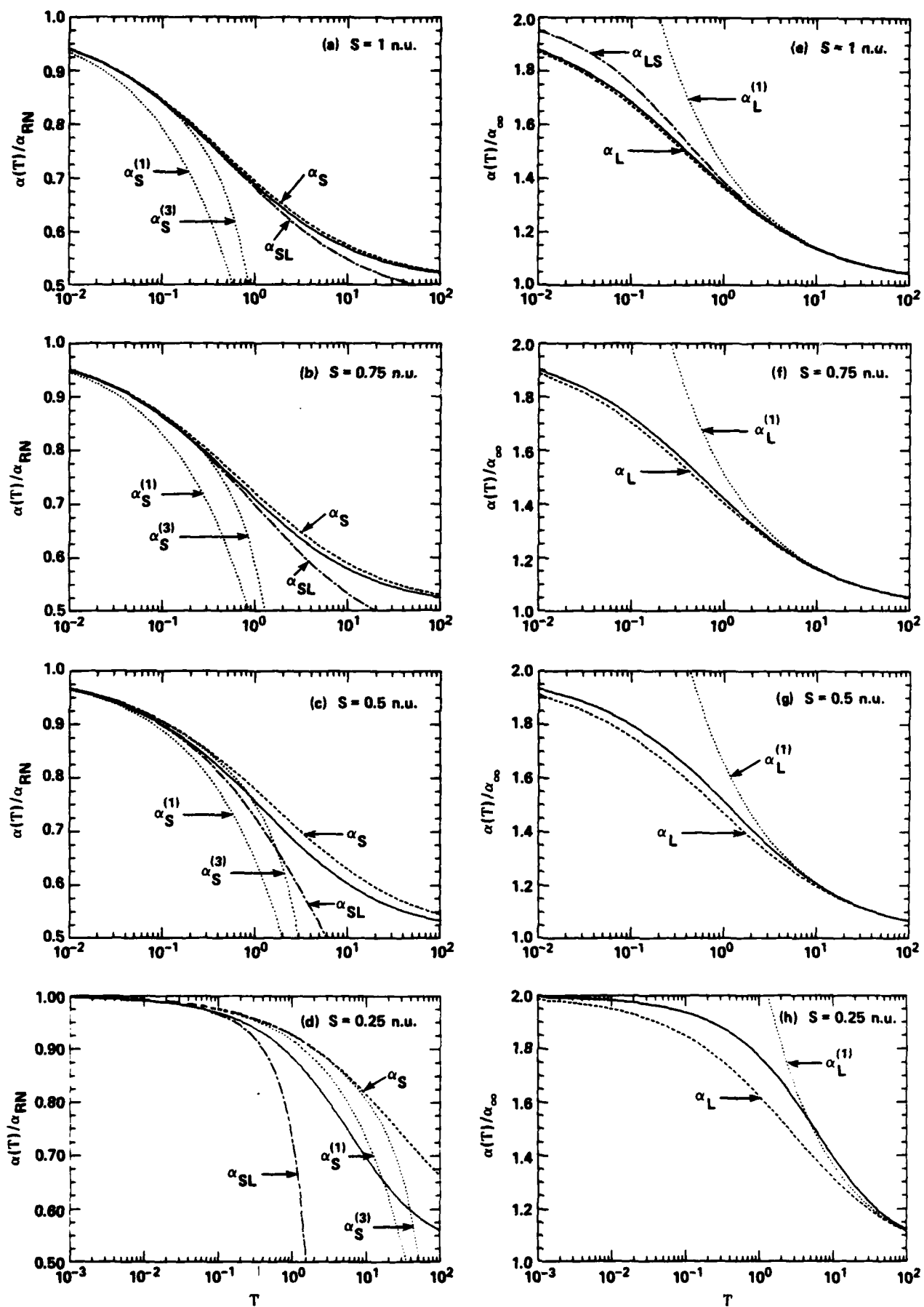
Figure 1

Figure 2
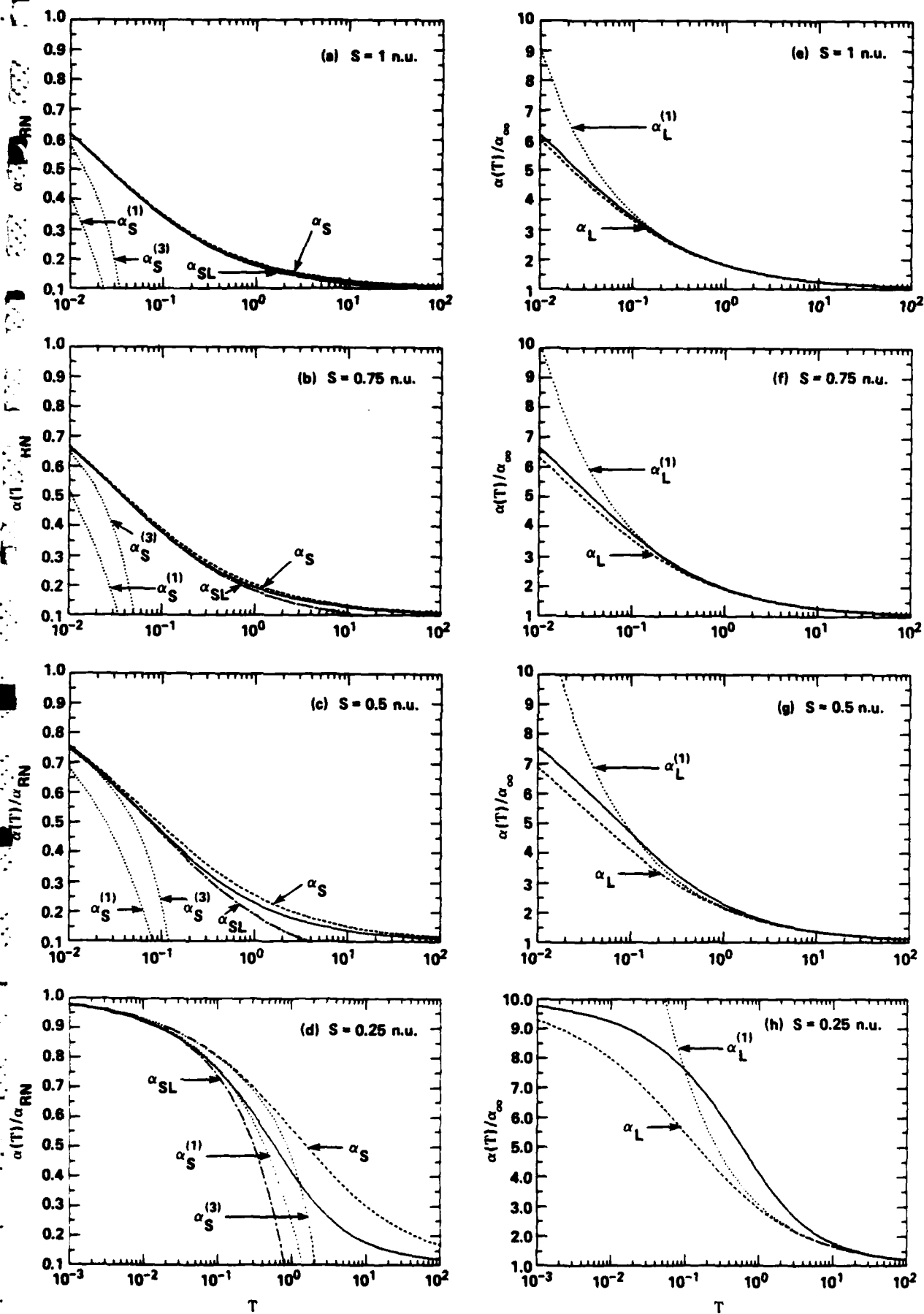
Figure 3

Figure 4

Figure 5

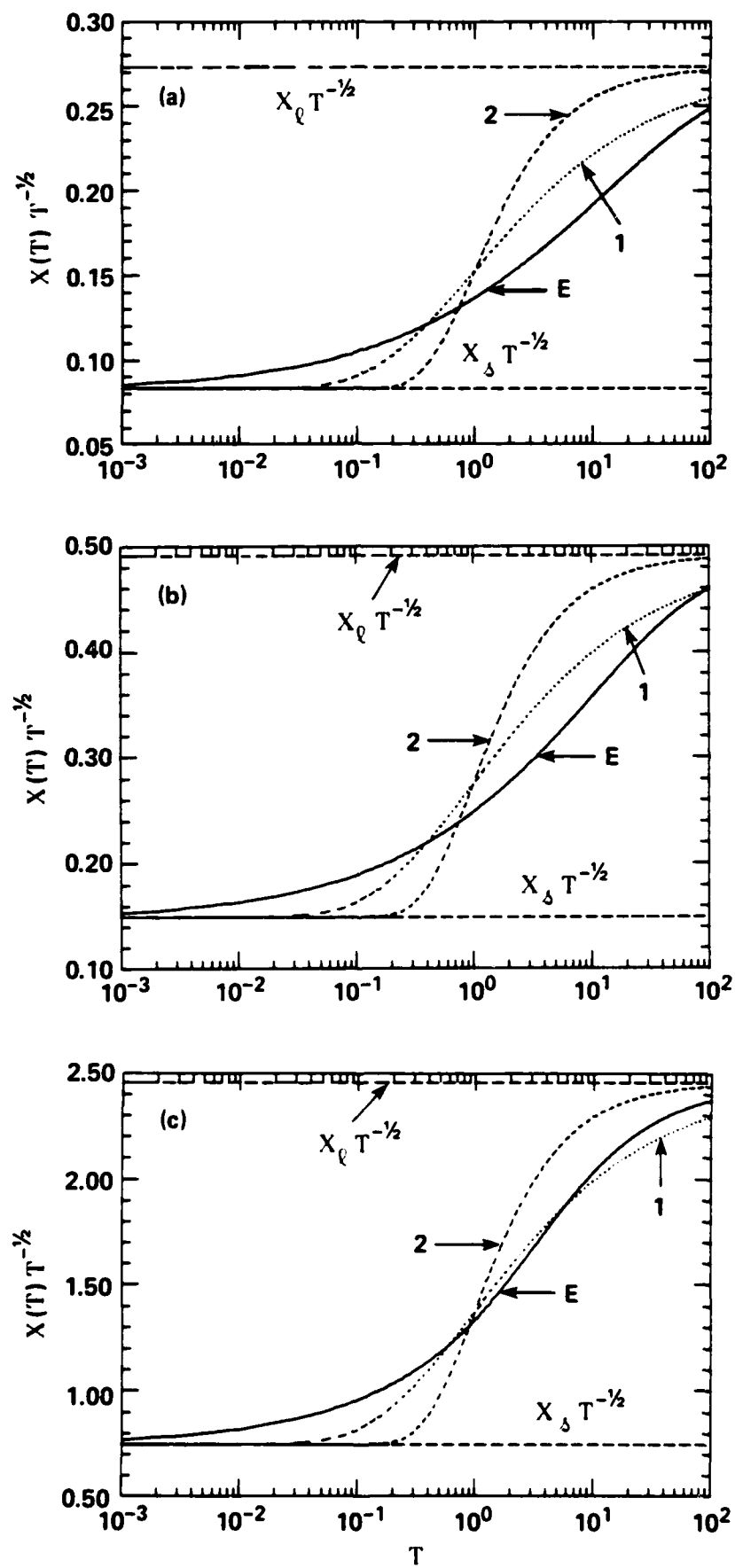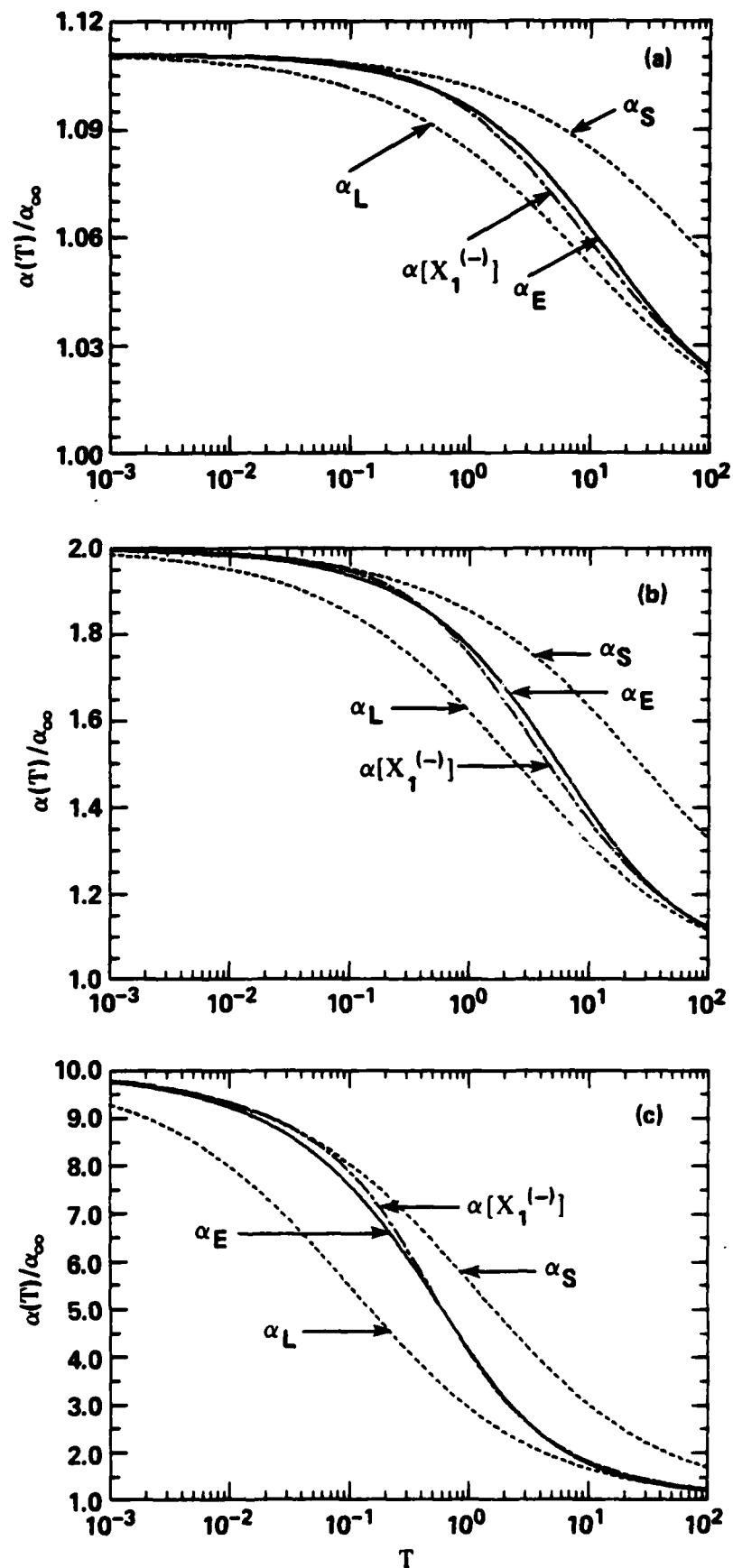Figure 6

Figure 7

Appendix D

Ion-Ion Recombination at High Ion Density

Ion-Ion Recombination at High Ion Density

M. R. Flannery

School of Physics

Georgia Institute of Technology

Atlanta, Georgia   30332, U.S.A.

Abstract. By appeal to a Thomson-type treatment of recombination, it is shown that the rate for recombination of ions generated with uniform frequency within a reaction volume is a factor of (9/4) times greater than the rate for recombination of ions which approach each other from infinite separation. A valuable relationship connecting the two problems is uncovered. The analysis is pertinent to recombination involving dilute and high degrees of ionization.

For (X^+-Y^-) ion-ion recombination in an ambient gas Z (neutral or ion), the following important distinctions between the cases of low and high ion densities $N^\pm$ are evident:

(A) For dilute ionization with ion densities $N^\pm \leq 10^8$ cm^{-3}, recombination can be based on consideration of the flow of positive ions X^+ (say) towards a central stationary negative ion Y^-. Steady-state conditions are then maintained by a source of ionization at infinity. For high ionization with $N^\pm \geq 2 \times 10^{14}$ $(T/300)^{3/2}$ cm^{-3}, when the Debye-Huckel shielding distance $R_s \leq R_e$, the natural unit (e^2/kT) of length characteristic of ion-ion recombination in a low density gas at temperature T, the positive ions X^+ already exist in a pre-assigned configuration with respect to Y^-, and the steady-state source is then distributed uniformly throughout the volume (Bates 1981).

(B) Recombination results not only from ion-neutral gas collisions but also from ion-ion (X^+-X^+), (Y^--Y^-), (X^+-Y^-) collisions which tend to increase the rate (Bates 1982).

(C) The interaction between the ions may no longer be considered as pure Coulomb at low gas densities N but will involve some appropriate measure of screening as determined by the self-consistent Poisson-Boltzmann treatment (Flannery 1981, 1982a,b).

(D) There are no longer isolated sinks, as for low $N^\pm$, but cooperative and competitive effects can arise between the closely spaced sinks distributed throughout the region.

Bates (1981) has reasoned that screening (C) does <u>not</u> affect the recombination at high gas densities N, on the basis that ions which are initial nearest neighbours remain nearest neighbours, and drift towards one

another until recombination occurs, with the result that the usual Langevin-Harper rate at high N is _not_ affected by increase of ion-densities $N^{\pm}$. Flannery (1981, 1982a) has shown that the recombination rate α is, in general, determined as a function of N and $N^{\pm}$ by the _self-consistent_ solution of the Boltzmann equation for the two particle distribution function and of Poisson's equation for the interaction between the ions. Calculation (Flannery 1981) indicates that increase in ion density up to 10^{14} cm^{-3} causes some reduction to α only at low and intermediate N. A molecular dynamics simulation (Morgan et al 1982) which incorporates this self-consistent idea (Flannery 1981) illustrates that the reduction can become quite significant when higher densities $N^{\pm} \gtrsim 10^{15}$ at gas pressures $\lesssim 1$ atm are reached. Bates (1982) demonstrated that the effect of ion-ion collisions in (B) then tends to oppose the decrease resulting from (C) particularly at lower temperatures T and $N^{\pm} \gtrsim 10^{15}$ cm^{-3}. The isolated effects of (A) and (D) have not yet been addressed.

The present goal is to investigate the effect of distinction (A) above, in isolation from (C) and (D). Since a detailed treatment based on microscopic principles (Flannery 1982a) would couple (A)-(D), and would therefore tend to obscure the key issue, it is worthwhile to illustrate the general trend by appeal to a Thomson-style treatment (constant speed, full absorption upon suitable collision). In so doing, a valuable connection between two distinct problems becomes apparent.

In the following analysis, diffusional drift which influences the approach of the ions at intermediate gas densities N is ignored so that the present treatment is appropriate to low $N \lesssim 10^{17} - 10^{18}$ cm^{-3}. At higher $N \gtrsim 10^{20} - 10^{21}$ cm^{-3}, the distinction A loses its significance since the radius R_T of the reaction sphere, within which recombination occurs, becomes

very small in comparison with both the Debye-Hückel radius R_s and the natural unit R_e, so that ions are generated well outside the reaction volume.

Let the positive ions X^+ be born isotropically with frequency F_r at a point $\underline{r}$ from the central negative ion Y^-. The flux (number of ions per sec) which escapes in all directions $\underline{\Omega}_E$ through a convex surface of area S enclosing a volume V (Figure 1a) is

$$F_E(\underline{r}) = (F_r/4\pi) \int_S R^{-2} \exp(-R/\lambda)(\underline{\Omega}_E \cdot \underline{n})dS = (F_r/4\pi) \int_{\Omega_E} \exp(-R/\lambda)d\Omega_E \qquad (1)$$

where R is the length from the internal point source $\underline{r}$ to the exit point on S in the direction $\underline{\Omega}_E$, where λ is the mean free path of the ion X^+ in the gas, and where $d\Omega_E$ is the solid angle $(\underline{\Omega}_E \cdot \underline{n})dS/R^2$ subtended at $\underline{r}$ by elemental area dS with outward normal $\underline{n}$. The probability for escape through S of ions born at $\underline{r}$ is therefore

$$P_E(\underline{r}) = F_E(\underline{r})/F_r = (1/4\pi) \int_{\Omega_E} \exp(-R/\lambda)d\Omega_E \qquad (2)$$

and provided the production frequency F_r is the same constant at all points $\underline{r}$ within V, the averaged probability for escape is

$$<P_E> = \frac{1}{V} \int_V P_E(\underline{r})d\underline{r} = (1/4\pi V) \int_V dV \int_{\Omega_E} \exp(-R/\lambda)d\Omega_E \qquad (3)$$

Subdivide V into tubes with axes directed along $\underline{\Omega}_E$, as in Figure 1(b), such that the elemental volume at $\underline{r}$ is,

$$dV = (\underline{n}_i \cdot \underline{\Omega}_E)dSdR \qquad (4)$$

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where R is the distance along Ω_E of r from elemental area dS with normal n_i pointing inward. On integration over R between zero and the maximum chord length $R_m(\Omega_E, n_i)$ consistent with the specified directions Ω_E and n_i, the averaged escape-probability is

$$\langle P_E \rangle = \frac{1}{4\pi} (\lambda/V) \int_S dS \int_{\Omega_E} d\Omega_E (\Omega_E \cdot n_i)[1-\exp(-R_m/\lambda)] \qquad (5)$$

where the region of integration is such that $\Omega_E \cdot n_i > 0$.

The averaged probability for absorption within V is therefore

$$\langle P_A \rangle = 1 = \langle P_E \rangle \qquad (6)$$

so that, the rate α_V ($cm^3 s^{-1}$) of volume recombination (absorption) within V is,

$$\alpha_V = \langle P_A \rangle S v \qquad (7)$$

where v is speed of the ions across surface S. This rate holds for ions generated with constant frequency F_r at all points within any volume V enclosed by any convex surface of area S. Under steady-state conditions, the source frequency is

$$F_r = \alpha_V \langle \rho \rangle \qquad (8)$$

where $\langle \rho \rangle$ is the averaged density $(1/V)\int_V \rho(r)dr$ within volume V in terms of the density distribution $\rho(r)$ of ions within V.

For a sphere of radius R_T, in particular, R_m is $2(\Omega_E \cdot n_i)R_T$, so that the absorption probability obtained via (6) is

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$$\langle P_A \rangle = 1 - (3\lambda/4R_T)W(R_T/\lambda) \tag{9}$$

where

$$W(X) = 1 - (1/2X^2)[1 - (1 + 2X)\exp(-2X)] \tag{10}$$

$$\to (\frac{4}{3}X)[1 - \frac{3}{4}X + \frac{2}{5}X^2 - \frac{1}{6}X^3 + \dots], \qquad X \to 0$$

$$\to 1 - (1/2X^2) \qquad , \qquad X \to \infty$$

is the well-known Thomson probability (Thomson 1924, Loeb 1955), the relevance of which to the present problem will become apparent below. The recombination rate (8) for ions distributed with uniform frequency within the reaction sphere is therefore,

$$\alpha_V = 4\pi R_T^2 v[1 - (3\lambda/4R_T)W(R_T/\lambda)] \tag{11}$$

which tends at low gas densities (where $\lambda \gg R_T$) to

$$\alpha_V = (\frac{9}{4})(\frac{4}{3}\pi R_T^3)(v/\lambda) \tag{12}$$

which is a factor of (9/4) higher than the corresponding Thomson rate for recombination of ions approaching from infinite separation (Thomson 1924, Loeb,1955), rather than from the pre-assigned configuration.

For dilute ionization, the number of ions per sec which travel (still in the absence of diffusional drift) from infinity and enter the volume V through S from all directions Ω_0 is

$$\frac{dN_{EN}}{dt} = - (\rho_\infty v/4\pi) \int_S dS \int_{\Omega_0} (\Omega_0 \cdot n)d\Omega_0 = \frac{1}{4}\rho_\infty vS \tag{13}$$

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where $\underset{\sim}{n}$ is the outward-pointing normal to surface area dS. The density within V is

$$\rho(\underset{\sim}{r}) = \int \rho(\underset{\sim}{r},\underset{\sim}{\Omega})d\Omega \tag{14}$$

where the angular density at the internal point $\underset{\sim}{r}$ in direction $\underset{\sim}{\Omega}$ is

$$\rho(\underset{\sim}{r},\underset{\sim}{\Omega}) = -(\rho_\infty v/4\pi)\int dS \int K(\underset{\sim}{r},\underset{\sim}{\Omega};\underset{\sim}{r}_0,\underset{\sim}{\Omega}_0)(\underset{\sim}{\Omega}_0 \cdot \underset{\sim}{n})d\Omega_0 \tag{15}$$

in terms of $K(\underset{\sim}{r},\underset{\sim}{\Omega};\underset{\sim}{r}_0,\underset{\sim}{\Omega}_0)$ which is the angular density of ions at $\underset{\sim}{r}$ travelling in direction $\underset{\sim}{\Omega}$ which originate from a source radiating with a unit (flux) rate at $\underset{\sim}{r}_0$ in direction $\underset{\sim}{\Omega}_0$ at surface S. This propagator satisfies the principle of microreversibility,

$$K(\underset{\sim}{r},\underset{\sim}{\Omega};\underset{\sim}{r}_0,\underset{\sim}{\Omega}_0) = K(\underset{\sim}{r}_0,-\underset{\sim}{\Omega}_0;\underset{\sim}{r},-\underset{\sim}{\Omega}) \tag{16}$$

which is such that the angular density at $\underset{\sim}{r}$ in direction $\underset{\sim}{\Omega}$ which originates from a unit source radiating at $\underset{\sim}{r}_0$ in direction Ω_0, is equivalent to the angular density generated at $\underset{\sim}{r}_0$ in direction $-\Omega_0$ by a unit source radiating at $\underset{\sim}{r}$ in direction $-\underset{\sim}{\Omega}$. In terms of this propagator, the probability of escape of ions born at $\underset{\sim}{r}$ is, by definition,

$$P_E(\underset{\sim}{r}) = (v/4\pi)\int dS \int K(\underset{\sim}{r}_0,\underset{\sim}{\Omega}_0;\underset{\sim}{r},\underset{\sim}{\Omega})(\underset{\sim}{\Omega}_0 \cdot \underset{\sim}{n})d\Omega_0 \tag{17}$$

the ratio (2) of the frequency at which ions emerge (with $\underset{\sim}{\Omega}_0 \cdot \underset{\sim}{n} > 0$) through surface S in directions $\underset{\sim}{\Omega}_0$ to the frequency of their internal production at $\underset{\sim}{r}$. Upon use of (16) in (15), and upon reversal of signs of Ω_0 and $\underset{\sim}{\Omega}$ in

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the resulting expression for (14), the internal density (14) is simply

$$\rho(\underset{\sim}{r}) = P_E(\underset{\sim}{r})\rho_\infty \qquad . \qquad (18)$$

The average escape probability is then

$$\langle P_E \rangle = \frac{1}{V} \left[\int_V \rho(\underset{\sim}{r}) d\underset{\sim}{r} \right]/\rho_\infty = \langle \rho \rangle/\rho_\infty \qquad (19)$$

for any surface geometry.

This expression (19) therefore provides the unique link common to the two distinct problems addressed here i.e., between the escape probability for ions generated isotropically at constant frequency within a confined volume V and the averaged density of ions injected into V from an external bath extending to infinity.

Since the rate of ion entry into V from the bath is given by (13), and since the number of ions which exit per second from V back into the bath is

$$\frac{dN_{EX}}{dt} = (\rho_\infty v/4\pi)\int dS \int \exp(-R_m/\lambda)(\underset{\sim}{\Omega}_0 \cdot \underset{\sim}{n}) d\Omega_0 \qquad (20)$$

the number of ions which are absorbed per second within V is

$$\frac{dN_A}{dt} = \frac{d}{dt}(N_{EN} - N_{EX}) = (\rho_\infty v/4\pi)\int dS \int (\underset{\sim}{\Omega}_0 \cdot \underset{\sim}{n})[1-\exp(-R_m/\lambda)] d\Omega_0 = \alpha_\infty \rho_\infty \qquad (21)$$

where $\alpha_\infty \rho_\infty$ is the frequency of generation of ions at infinity.

The treatment assumes that absorption (recombination) occurs following collision at constant speed v so that the absorption frequency is also

$$\frac{dN_A}{dt} = (N\sigma v) \int_V \rho(\underline{r})dV = (\frac{v}{\lambda})<\rho>V \tag{22}$$

where σ is the cross section for collisions with the third bodies Z of density N. With the equivalence of (21) and (22) in (19), the escape probability (19) is then

$$<P_E> = <\rho>/\rho_\infty = \frac{1}{4\pi} (\lambda/V) \int_S dS \int_{\Omega_0} d\Omega_0 (\underline{\Omega}_0 \cdot \underline{n})[1-\exp(-R_m/\lambda)] \tag{23}$$

which is precisely the relation (6) previously derived <u>ab-initio</u> without the connection (19). The fraction of ions that are absorbed within V is

$$f = (dN_A/dN_{EN}) = (4V/S\lambda)<P_E> \tag{24}$$

which, for a sphere of radius R_T, reduces to

$$f = (4R_T/3\lambda)<P_E> \equiv W(R_T/\lambda) \tag{25}$$

which is, as expected, simply the Thomson probability (10) for collision, within the trapping sphere, of ions which enter the sphere from an external bath.

The connection of $<P_E>$ to the rates of both problems is demonstrated by comparison of the rate

$$\alpha_\infty = \frac{<\rho>}{\rho_\infty} V(\frac{v}{\lambda}) = <P_E>V(\frac{v}{\lambda}) = \frac{1}{4} fSv \tag{26}$$

obtained from (21) and (22) for recombination of ions entering S from infinity with the rate (7),

$$\alpha_V = [1 - <P_E>]Sv = [1 - (\frac{4V}{S\lambda})f]Sv \qquad (27)$$

for recombination of ions generated isotropically within V at a uniform frequency. The appearance of f ($\equiv$ the Thomson probability W for a sphere) in both problems is now evident.

Moreover, the averaged density $<\rho>$ within the reaction volume follows from (19) directly or from (26) where the frequency $\alpha_\infty \rho_\infty$ of ion production at infinity is set equal to the frequency $(v/\lambda)<\rho>V$ of absorption within V to give

$$<\rho> = \alpha_\infty \rho_\infty (\lambda/vV) \qquad (28)$$

irrespective of the mode of transport from inifinity to S. When α_∞ is controlled by reaction alone (i.e. α_∞ is $\frac{1}{4}$ fSv), then, for a spherical volume

$$<\rho> = [(3/4x)W(x)]\rho_\infty \qquad (29)$$

which tends at low gas densities N (where $X = R_T/\lambda \ll 1$) to $\rho_\infty[1 - 3R_T/\lambda + ...]$. The linear dependance on $N(\sim 1/\lambda)$ of α_∞ in (28) therefore arises from the constant term ρ_∞ in this expansion of $<\rho>$ so that the recombination rate at low N follows directly by taking either $<\rho> = \rho_\infty$ in (28) or $<P_E> = 1$ in (26) to give

$$\alpha_\infty \xrightarrow{\lambda \gg R_T} V(v/\lambda) = (4/3)\pi R_T^3 (v/\lambda) \qquad (30)$$

thereby providing a one-line derivation (from (28)) of the Thomson N-linear

rate at low N. Nonlinear variation of α_∞ with N arises from the departure of $\langle P_E \rangle$ from unity.

In the presence of diffusional drift, the above Thomson rates (26) and (27) can be regarded as reaction rates (Flannery 1982a,b). As the gas density N increases then, for a sphere, the ratio (α_V/α_∞) increases from 2.25 to 4 when $\lambda \ll R_T$. The factor 4 is simply the relative measure of flux for both problems. This enhancement will favor an earlier onset with N of diffusional-drift which will eventually become the rate limiting step.

In summary, the partial recombination rate arising from (X^+-Z) collisions for the (dilute-ionization) case of (X^+-Y^-) approach from infinite separation at speed v_{12} is the Thomson rate,

$$\alpha_T = \pi R_T^2 v_{12} W(R_T/\lambda) \xrightarrow{\lambda \gg R_T} (\tfrac{4}{3} \pi R_e^3)\beta^{-3}(v_{12}/\lambda) \; ; \qquad \beta = 3/2 \; , \qquad (31)$$

(which incidentally identifies R_e as the natural unit (e^2/kT) for volume recombination). This is to be compared with the corresponding rate

$$\alpha_V = 4\pi R_T^2 v_{12}[1 - (3\lambda/4R_T)W(R_T/\lambda)] \qquad (32)$$

$$\xrightarrow{\lambda \gg R_T} \frac{9}{4}(\tfrac{4}{3}\pi R_e^3)\beta^{-3}(v_{12}/\lambda) = \frac{9}{4}\alpha_T$$

for the present (dense ionization) case where a steady-state distribution of ions X^+ is maintained by constant-frequency isotopic sources (8) distributed uniformly within the reactive sphere centered at Y^-. The full rate is the sum of the partial rates based on X^+-Z and Y^--Z collisions. So as to account for the inefficiency of energy transfer between dissimilar masses, the Thomson-rate (31) can be multiplied by a mass-dependent efficiency factor designed to

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reproduce the highly accurate rates (cf Flannery 1982b) obtained from solution of the conventional collisional input-output Master Equation at low gas densities. This overall normalization should not affect the basic connection between (31) and (32), or the basic prediction that the effect of the distinction (A) between the cases of dilute and high degrees of ionization is to increase the recombination rate (by a factor $\sim 9/4$).

The effect of ion-ion collisions (B) can now be incorporated directly within (32) by regarding (Bates 1982) third bodies Z as ions X^+(or Y^-). Thomson- recombination between ions of separation $R < R_T = (2/3)e^2/kT$ occurs upon any collision which is assumed to transfer energy $\Delta E > (3/2)kT$. For ion-ion Coulomb scattering between equal masses at relative energy $(3/2)kT$, this energy is transferred provided the (CM) scattering angle is greater than $(\pi/2)$. The cross section for such collisions, after a straightforward exercise, is

$$\sigma = (1/9)\pi R_e^2 \tag{33}$$

In a gas of electrons of mass m and density N^-, (33) in (31) yields

$$\alpha_T^{(e)} = (4\pi^2/27\beta^3)(8kT/\pi m)^{1/2} R_e^5 N^- \tag{34}$$

$$\equiv 3.5 \ 10^{-9} T^{-4.5} N^- \ (cm^3 s^{-1})$$

for the rate of electron-ion collisional recombination which, remarkably, is 92% of the identical collisional rates (Mansbach and Keck 1967, Stevefelt et al. 1975) based on the detailed Master Equation. Generalization of (34) to cover ion-ion recombination in an ion gas may be deduced as in Bates (1982). Incorporation of ion-ion collisions within (32) will also increase the

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recombination rate, particularly for ion-densities $N^{\pm} \gtrsim 10^{15}$ cm^{-3} and lower temperatures (Bates 1982).

In conclusion, the rate for recombination of ions distributed uniformly within a reaction volume V has been shown to be a factor of (9/4) greater than the rate for ions which approach the reaction sphere from infinity. These two situations are respectively appropriate to the present examination of the effect of distinctions A and B (in isolation from C and D) on the cases of high and dilute ionization, respectively. In so doing, a valuable relationship (19) which connects the two distinct problems of approach from infinity and of escape from a confined volume of generation has been uncovered.

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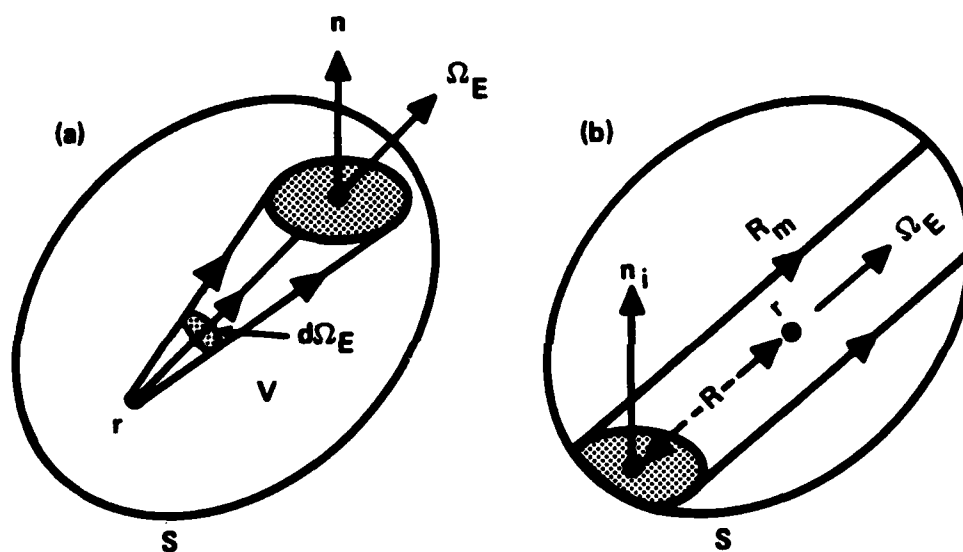
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Figure 1: (a) Ions borns at point $\underset{\sim}{r}$ within volume V enclosed by surface S escape within solid angle $d\underset{\sim}{\Omega}_E$ through elemental area with outward normal $\underset{\sim}{n}$. (b) Elemental volume $dV \simeq (\underset{\sim}{\Omega}_E \cdot \underset{\sim}{n}_i)dSdR$ of tubes with axis along $\underset{\sim}{\Omega}_E$ at angle to inward normal $\underset{\sim}{n}_i$ of surface element dS. R_m is maximum chord length for specified directions $\underset{\sim}{n}_i$ and $\underset{\sim}{\Omega}_E$.

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