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R. I. Cukier and K. E. Shuler

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ON THE MICROSCOPIC CONDITIONS FOR LINEAR MACROSCOPIC LAWS*

R. I. Cukier and K. E. Shuler

Department of Chemistry
University of California, San Diego
La Jolla, California 92037

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ABSTRACT

We have investigated the conditions which must be imposed on the microscopic equations of motion to obtain exact linear laws for macroscopic (phase averaged) variables. The starting point in this study has been the lowest order master equation (Pauli equation) which is a linear microscopic equation in the state probabilities with a time-independent transition matrix. Discrete and continuous variable master equations as well as their multivariate generalizations have been considered. In the case of continuum state variables, we have used various Fokker-Planck equations and their corresponding Langevin equations as our starting microscopic equation of motion. In each case the conditions which must be imposed to obtain linear macroscopic transport equations have been derived and discussed. The problem of the derivation of linear macroscopic laws from non-linear microscopic laws has been discussed in the context of our results on linear microscopic laws. We find that exact linear macroscopic laws can be derived even from linear microscopic laws only when stringent conditions are imposed on the form of microscopic transition rates.

Key Words: Non-equilibrium statistical mechanics, stochastic processes, transport laws, master equation, Fokker-Planck equation.

I. INTRODUCTION

Linear macroscopic laws, by which we mean relations of the form

$$\frac{d\vec{a}}{dt} = -\underset{\sim}{M}\cdot\vec{a} \tag{1.1}$$

where $\vec{a}$ is a set of macroscopic (phase averaged) variables and $\underset{\sim}{M}$ a matrix of time independent transport coefficients, play an important role in non-equilibrium statistical mechanics. They have been the subject of much theoretical work which can be divided into two classes: 1) the derivation of linear macroscopic laws from microscopic equations of motion and 2) the evaluation of the transport coefficient matrix $\underset{\sim}{M}$. It is to the first question that this paper is addressed.

It is important to point out that we are concerned here only with the derivation of exact linear laws of the form (1.1), i.e., with the conditions on the microscopic equations which lead to exact linear laws valid for all times t and valid for all initial (microscopic) conditions. We do discuss in the body of this paper some of the conditions and circumstances leading to approximate linear laws, but we do so only in passing and to illustrate some specific points.

The ultimate objective of such a study would be to determine the necessary and sufficient conditions on the Hamiltonian of the microscopic equations of motion which lead to exact macroscopic linear laws. Such an objective is, however, too ambitious since the relation between the Liouville equation and the macroscopic equation is a quite distant one and the connection is not easy to make. We have therefore chosen as our starting point the lowest order master equation (the Pauli equation)$^{(1)}$

$$\frac{d\vec{P}(t)}{dt} = \underset{\sim}{A}\,\vec{P}(t) \tag{1.2}$$

where $\vec{P}(t)$ is a vector of state probabilities and $\underset{\sim}{A}$ is the transition rate matrix which is taken to be independent of time. In conjunction with Eq. (1.2) we also consider the related Fokker-Planck equations and Langevin equations as suitable starting points for our inquiry.

In using the master equation (1.2) as our microscopic transport equation we have greatly limited the scope of our study. The master equation (1.2) is based on the assumption of weak interactions between a subsystem and a time-invariant heat bath. Also, in using Eq. (1.2), we are restricting ourselves to Markovian processes since we do not consider time dependent transition matrices, i.e., transition kernels non-local in time. The master equation (1.2) is furthermore a linear microscopic equation; we do not consider here the problem of the derivation of linear macroscopic laws from non-linear microscopic equations. It is important to note, and one of the main results of this work, that severe restrictions must still be placed on the form of the transition matrix $\underset{\sim}{A}$ to obtain an exact linear law even though the transition matrix is already independent of time and even though the microscopic transport equation is already linear in the microscopic variables.

In a recent paper van Kampen(2) has pointed out that some known linear macroscopic laws have their antecedents in what are probably non-linear microscopic laws and thus should be derivable from such non-linear microscopic laws. To quote: "The basic remark is that linearity of the macroscopic law is not at all the same as linearity of the microscopic equation of motion. In most substances Ohm's law is valid up to a fairly strong field; but if one visualizes the motion of an individual electron and the effect of an external field E on it, it becomes clear that microscopic linearity is restricted to only extremely small field strength. Macroscopic linearity, therefore, is not due to microscopic linearity, but to a cancellation of non-linear terms when averaging over all particles."

Following up van Kampen's remarks, Bixon and Zwanzig(3) derived the macroscopic transport equation for the average position and velocity for a non-linear oscillator (Duffing's oscillator) under the influence of a random Gaussian force. They succeeded in deriving a linear equation for the averaged motion which was, however, valid only for small deviations of the averaged variables from thermal equilibrium and which contained a time dependent (non-Markovian) term that depended on the non-linear term of the original microscopic equation of motion. Their model thus did not yield an exact linear macroscopic equation valid for all initial conditions and all times. As far as we are aware, the van Kampen and Bixon-Zwanzig papers are the first attempts so far to establish the relation between non-linear microscopic and linear macroscopic laws of motion.

In view of the stringent conditions which must be imposed already on linear microscopic laws to obtain linear macroscopic laws and in view of the serious difficulties encountered by van Kampen and by Bixon and Zwanzig it would appear that van Kampen's analysis of the problem as quoted above should be considered as a tentative working hypothesis. It is very reasonable but has not yet been verified. The clarification of this problem presents an important area of research in non-equilibrium statistical mechanics and transport processes.

The following interesting point should be noted. If a linear law is obtained for the mean of some variable, it will also apply to the mean of this variable conditional on some given initial value. Since the time autocorrelation function can be written as the average over the initial distribution of the conditional mean it is clear that the time dependence of the autocorrelation function is identical to that of the mean value of the variable itself. Thus, a macroscopic linear law for the relaxation of an averaged variable implies the exponential relaxation of the autocorrelation function of the microscopic variable.

In our discussion we consider separately, for the sake of convenience, the case of discrete and continuous variables. In Section II we focus our attention on the discrete, univariate master equation and develop the necessary and sufficient conditions which must be imposed on the transition matrix. In Section III we reformulate the problem in terms of an eigenvalue - eigenfunction analysis of the solution of the master equation. Section IV is devoted to relating the linear law transition matrix to the corresponding Hamiltonian through the perturbation responsible for the relaxation. As an example, we consider a particular Hamiltonian which could be a model of phonon-phonon interaction. In Section V we study the generalization to the multivariate discrete master equation and treat spin relaxation, via the Redfield and Bloch equation as an example of an approximate linear macroscopic law. In Section VI we turn our attention to the continuous master equation. We investigate there the conditions which must be imposed on various Fokker-Planck equations and their counterpart Langevin equations to obtain exact linear macroscopic laws.

II. LINEAR LAWS FROM DISCRETE, UNIVARIATE MASTER EQUATIONS

In order that the master equation for the discrete states n=0,1,...

$$\frac{dP_m(t)}{dt} = \sum_n A_{mn} P_n(t) \tag{2.1}$$

where $P_m(t)$ is the probability of finding the system in state m at time t and where the A_{mn} are the transition rates between states n and m represent a physically realistic situation we impose, for all n and t, the following restrictions:

$$P_n(t) > 0 \quad ; \quad \sum_n P_n(t) = 1; \tag{2.2}$$

$$\sum_n A_{nm} = 0 \tag{2.3}$$

$$A_{nm} P_m^{(e)} = A_{mn} P_n^{(e)} \tag{2.4}$$

The conditions (2.2) state that the probabilities are positive and correspond to a closed system. The conditions (2.2) in turn imply the sum rule (2.3). Condition (2.4), where the $P_n^{(e)}$ are the equilibrium probabilities is a statement of detailed balance. The above conditions are sufficient to prove that the eigenvalues $\{\lambda_i\}$ of the matrix $\underset{\sim}{A}$ are real and negative except for one which is zero and corresponds to the equilibrium solution P_n^e. For the systems studied in this paper Eqs. (2.2) - (2.4) are always satisfied.

We define the average value, $\mu(t)$, of the state variable n as

$$\mu(t) \equiv \sum_n n\, P_n(t) \tag{2.5}$$

As has been shown(4) the necessary and sufficient condition to obtain a linear law of the form (1.1) for the moment $\mu(t)$ is

$$\sum_m m\, A_{mn} = \alpha n + \delta \qquad (2.6)$$

where α and δ are constants. This linear law is, as can be seen from Eqs. (2.1), (2.5) and (2.6),

$$\frac{d\mu(t)}{dt} = \alpha\mu(t) + \delta \qquad (2.7)$$

from which it follows that the constants α and δ are related by

$$\frac{\delta}{\alpha} = -\mu^{(e)} \qquad (2.8)$$

where $\mu^{(e)}$ is the equilibrium value of the moment $\mu(t)$ corresponding to the equilibrium distribution $P_m^{(e)}$. The two sum rules on the matrix $\underset{\sim}{A}$, Eq. (2.3) and (2.6) are not sufficient to determine the form of the A_{mn}. In order to make some progress it is necessary to place further restrictions on the system.

As a specific example, we assume that only nearest neighbor transitions are permitted but place no restrictions on the level spacing. For such a system we have just enough conditions for an explicit determination of the A_{mn}. From Eqs. (2.3) and (2.6) we obtain

$$\sum_m m\, A_{mn} = A_{n+1,n} - A_{n-1,n} = \alpha n+\delta \qquad (2.9).$$

We write the detailed balance equation (2.4) for a canonical ensemble as

$$A_{n+1,n}\, g_n e^{-\beta\epsilon_n} = A_{n,n+1}\, g_{n+1}\, e^{-\beta\epsilon_{n+1}} \quad ; \qquad \beta = 1/kT \qquad (2.10)$$

where ϵ_k is the energy of the k'th state and g_k its degeneracy. Defining

$$S_n \equiv g_{n+1}\, e^{-\beta\epsilon_{n+1}}\, A_{n,n+1} \qquad (2.11)$$

one finds from Eqs. (2.6) through (2.9)

$$S_n - S_{n-1} = g_n e^{-\beta\varepsilon_n} (\alpha n+\delta); \quad S_{-1} = 0 \tag{2.12}$$

$$S_o = g_o e^{-\beta\varepsilon_o} \delta \tag{2.13}$$

from which it follows that $\delta = A_{10}$. The constant α can be expressed in terms of the transition matrix by considering the limit

$$\lim_{n\to\infty} S_n = \lim_{n\to\infty} g_n e^{-\beta\varepsilon_{n+1}} A_{n,n+1} = 0 \tag{2.14}$$

where we have noted that $\varepsilon_n > \varepsilon_{n-1}$. Summing (2.12) over all n and using (2.14) yields, in agreement with Eq. (2.8),

$$\alpha = - \frac{\delta}{\mu^{(e)}} \tag{2.15}$$

where

$$\mu^{(e)} = \frac{\sum_{n=o}^{\infty} n g_n e^{-\beta\varepsilon_n}}{\sum_{n=o}^{\infty} g_n e^{-\beta\varepsilon_n}} \tag{2.16}$$

is the equilibrium average of the variable n. Summation of (2.12) up to a finite n, and the use of Eqs. (2.9), (2.13) and (2.16) then gives our desired result

$$A_{n,n+1} = A_{10} \frac{\sum_{k=o}^{n} g_k e^{-\beta\varepsilon_k}\left(1-k/\mu^{(e)}\right)}{g_{n+1} e^{-\beta\varepsilon_{n+1}}} \tag{2.17}.$$

In the case of nearest neighbor transitions then, we find that the matrix $\underset{\sim}{A}$ is uniquely determined, albeit by a summation formula.

To give an example of the evaluation of Eq. (2.17) we consider the case of harmonic oscillators in weak interaction with a heat bath as discussed by Montroll and Shuler.(5) In this system, only nearest neighbor transitions can take place. The degeneracies are

$$g_n = 1 \qquad n = 0, 1, \ldots \tag{2.18}$$

and the energies ε_n are given by

$$\varepsilon_n = n\varepsilon \tag{2.19}.$$

Evaluating the sum in Eq. (2.17) yields

$$A_{n,n+1} = (n+1)A_{01} \tag{2.20}$$

and from detailed balance

$$A_{n+1,n} = (n+1)e^{-\beta\varepsilon}\, A_{01} \tag{2.21}.$$

These are the transition probabilities used by Montroll and Shuler who indeed found that they led to a linear law for the mean vibrational energy.

The above formulation has been restricted to nearest neighbor transitions. We now wish to remove this restriction. We consider a system with a transition matrix having a finite range, i.e., $|m-n| < \infty$ and an infinite set of states $(-\infty < n < +\infty)$. The infinite set of states is not essential to the argument but simplifies the analysis since it avoids difficulties with boundary conditions.

From Eqs. (2.3) and (2.6) one has

$$\sum_{m=-\infty}^{+\infty} mA_{mn} = \sum_{k=1}^{p} k(A_{n+k,n} - A_{n-k,n}) = \alpha n+\delta \tag{2.22}$$

where $k = m-n$ and $k = 1,2,..p$ with $p < \infty$. Introduction of the variable

$$f(n,k) \equiv \frac{P^{(e)}_{n-k}}{P^{(e)}_{n}} = \frac{g_{n-k}}{g_n}\;\frac{e^{-\beta\varepsilon_{n-k}}}{e^{-\beta\varepsilon_n}} \tag{2.23}$$

and the use of detailed balance leads to the condition

$$\sum_{k=1}^{p} k[A_{n+k,n} - f(n,k)A_{n,n-k}] = \alpha n+\delta \tag{2.24}.$$

The condition (2.24) is the non-nearest neighbor transition analogue of condition (2.9). Equation (2.24) does not suffice to determine the A_{mn} uniquely and additional restriction are required.

We shall assume that the transition rates A_{nm} are polynomials of degree N in n

$$A_{n+k,n} = \sum_{j=o}^{N} c_j(k)(n+k)^j \tag{2.25}$$

It will be seen that this is a natural choice for the A_{mn} when we make a connection between the transition rate matrix and the Hamiltonian of the relaxing system in Section IV. Substitution of Eq. (2.25) into (2.24) yields

$$\sum_{k=1}^{p} k \sum_{j=o}^{N} c_j(k) \left[(n+k)^j - f(n,k)n^j\right] = \alpha n+\delta \tag{2.26}$$

It follows from the form of f(n,k), Eq. (2.23), that (2.26) cannot be satisfied unless $f(n,k) = f(k)$; i.e., f(n,k) is independent of n. This implies, as is evident from Eq. (2.23), that the energies, ε_n must be of the form $\varepsilon_n = n\varepsilon$; i.e., the energy levels are equally spaced. If Eq. (2.26) is now rewritten as

$$\sum_{k=1}^{p} k \sum_{j=o}^{N} c_j(k) \left\{[(1-f(k)]n^j + \sum_{\ell=1}^{j} \binom{j}{\ell} n^{j-\ell} k^{\ell}\right\} = \alpha n+\delta \tag{2.27}$$

it can readily be verified that the equality is obeyed only for N=1. We have therefore shown that, subject to the polynomial form of $A_{n+k,n}$, Eq. (2.25), a linear law for the moment can only be obtained if the transition probabilities are linear in the occupation number, n,

$$A_{n+k,n} = c_o(k) + c_1(k)[n+k] = a_o(k) + a_1(k)n \tag{2.28}$$

and if the states of the system are uniformly spaced. Note that the harmonic oscillator transition rates given by Eq. (2.20) are of this form.

In Eqs. (2.17) and (2.28) we have derived for two well specified systems the forms of the transition rates which lead to linear laws. Evidently, by making different assumptions about the level spacing, the types of allowed transitions and the form of the transition rates [analogous to Eq. (2.25)], we could obtain additional expression for transition rates which lead to linear laws. The allowed transition rates can not be determined uniquely from Eqs. (2.3) and (2.6) alone since these are just conditions on the zeroeth and first moments of $\underset{\sim}{A}$. Only if the time dependence of higher moments of $\underset{\sim}{A}$ were specified would it be possible to determine the form of the transition rates A_{nm} which lead to a linear law without placing subsidiary restrictions on the spacing of the states and the transitions between them.

III. EIGENFUNCTION ANALYSES FOR LINEAR LAWS

In the previous section we have presented "sum rule" conditions for obtaining a linear law for macroscopic variables. These rules can be reformulated in terms of an eigenvalue-eigenfunction analyses.

The eigenvalue solution of the master equation (2.1) is$^{(1)}$

$$\vec{P}(t) = \sum_{j=o}^{\infty} [\vec{L}^j \cdot \vec{P}(o)] \vec{R}^j e^{\lambda_j t} \tag{3.1}$$

where $\vec{P}(o)$ is the initial value of the probability vector $\vec{P}$, and where $\vec{L}^j$ and $\vec{R}^j$ are, respectively, the left and right eigenfunctions of the transition matrix $\underset{\sim}{A}$,

$$\begin{aligned} \vec{L}^j \cdot \underset{\sim}{A} &= \lambda_j \vec{L}^j \\ & \qquad\qquad j = 0,1,2,\ldots \\ \underset{\sim}{A} \cdot \vec{R}^j &= \lambda_j \vec{R}^j \end{aligned} \tag{3.2}$$

For the case of non-degenerate eigenvalues λ_j, which is insured by the conditions (2.2) through (2.4), the $\vec{L}^j$ and $\vec{R}^j$ are orthonormal

$$\vec{L}^j \cdot \vec{R}^k = \delta_{jk} \tag{3.3}$$

It has been pointed out by van Kampen$^{(2)}$ that in order to obtain a linear law for the averaged variable it is necessary that the left eigenvector $\vec{L}^j$ (expressed in component form) when operating on the matrix $\underset{\sim}{A}$ yields

$$\sum_n L_n^j A_{nm} = \alpha m + \delta \tag{3.4}$$

where α is one of the eigenvalues λ_j. This implies that the eigenvector $\vec{L}_j$ must be

$$\vec{L}^j = \begin{pmatrix} 1 \\ 2 \\ 3 \\ \vdots \end{pmatrix} + \beta \begin{pmatrix} 1 \\ 1 \\ 1 \\ \vdots \end{pmatrix} \tag{3.5}$$

This can readily be verified by substituting Eq. (3.5) into Eq. (3.4). In component form one then finds

$$\sum_n L_n^j A_{nm} = \lambda_j (m+\beta) \qquad (3.6)$$

which is of the form given in Eq. (3.4). A comparison of Eqs. (3.4) and (3.6) and the use of the general relation (2.8) shows that

$$\alpha = \lambda_j \ ; \quad \delta = \beta\lambda_j \ ; \quad \beta = -\mu^{(e)} \qquad (3.7).$$

It is clear from Eqs. (3.4) and (3.6) that van Kampen's condition is identical with the sum rule (2.6) of Shuler and Weiss.(4)

If we now multiply Eq. (3.1) for $\vec{P}(t)$ by the eigenvector $\vec{L}^j$ given in Eq. (3.5) and sum over all states, we find

$$\mu(t) - \mu^{(e)} = [\mu(o) - \mu^{(e)}]e^{\alpha t} \qquad (3.8)$$

where we have used Eqs. (3.2), (3.3) and (3.7). One should note that the linear law condition (3.4), or equivalently (3.5), implies that the relaxation of the moment $\mu(t)$ proceeds by the single exponential term $e^{\alpha t}$ instead of a sum of exponential terms. We shall return to this point at the end of this section.

As an example of this formulation for linear law conditions we consider the relaxation of harmonic oscillators in weak interaction with a heat bath studied by Montroll and Shuler.(5) The transition rates for this process are

$$A_{nm} = ne^{-\theta} \delta_{n-1,m} - [n+(n+1)e^{-\theta}]\delta_{nm} + (n+1)\delta_{n+1,m}$$
$$n,m = 0,1,\ldots.. \qquad (3.9).$$

We have already remarked in Section II that these transition rates obey the sum rule for a linear law; we want to demonstrate here that they also satisfy the eigenfunction condition given above. The eigenfunctions and eigenvalues of this transition matrix (3.9) have been computed in reference (5); they are

$$L_m^j = e^{-j\theta}\, e^{m\theta}\, (1-e^{-\theta})^{-1}\, \ell_m^j \tag{3.10}$$

$$R_m^j = \ell_m^j\, (1-e^{-\theta})^2 \tag{3.11}$$

where the function ℓ_m^j, the Gottlieb polynomial, is defined by

$$\ell_m^j = \frac{e^{-m\theta}}{1-e^{-\theta}} \sum_{k=o}^{\infty} (1-e^{\theta})^k \binom{m}{k}\binom{j}{k} \tag{3.12}$$

for integer values of m. In particular

$$\ell_m^1 = \frac{e^{-m\theta}}{1-e^{-\theta}} \,[(1-e^{\theta})m+1] \tag{3.13}.$$

The Gottlieb polynomials satisfy the orthogonality relation

$$\sum_{m=o}^{\infty} e^{m\theta}\, \ell_m^k\, \ell_m^j = \delta_{kj}\, e^{k\theta} \tag{3.14}$$

which implies that the left and right eigenvectors are orthogonal

$$\sum_{m=o}^{\infty} L_m^k\, R_m^j = \delta_{kj} \tag{3.15}.$$

It now remains to verify that the left eigenvector $\vec{L}^1$ given by Eqs. (3.10) and (3.12) satisfies the linear law condition (3.4) with A_{nm} given by Eq. (3.9). If the above indicated substitutions are made one finds, as can be verified by straight forward calculation,

$$\sum_n L_n^1\, A_{nm} = (e^{-\theta}-1)m+e^{-\theta} \tag{3.16}$$

which is clearly of the form (3.4) with $\alpha = -(1-e^{-\theta})$ and $\delta = e^{-\theta}$. Note that

$\alpha = -(1-e^{-\theta}) = \lambda_1$ is indeed an eigenvalue of Eq. (3.2) and that $-\delta/\alpha = (e^{\theta}-1)^{-1}$ is the equilibrium moment $\mu^{(e)}$ (equilibrium vibrational energy) for an ensemble of harmonic oscillators.

It is important to note that the above strict conditions on the eigenvector $\vec{L}^j$ are required only if one wants to obtain an exact linear law of the form (3.8) valid for all times t, $0 \leq t \leq \infty$. If the eigenvalues λ_j of the solution (3.1) of the master equation are well separated, and in particular if the first non-zero eigenvalue, $|\lambda_1|$, is much smaller than all the subsequent eigenvalues, $|\lambda_1| \ll |\lambda_2|, |\lambda_3|, \ldots$, then for $t \gg \frac{1}{|\lambda_1|}$ one can rewrite Eq. (3.1) to a good approximation as

$$\vec{P}(t) = \vec{P}^{(e)} + e^{\lambda_1 t} [\vec{L}^1 \vec{P}(o)]\vec{R}^1 \tag{3.17}$$

It is clear that the approximate solution (3.17) leads to an approximate linear law of the form (3.8). In this case one needs to place no restrictions on the form of the eigenvector $\vec{L}^j$, one only requires that the eigenvalues λ_j of the transition matrix $\underset{\sim}{A}$ are well separated. The spacing of the eigenvalues depends entirely on the form of the matrix $\underset{\sim}{A}$ of the master equation. For infinite matrices $\underset{\sim}{A}$, i.e., for systems with infinite (or semi-infinite) number of states, as are usually found in physical applications, we know of no general relations between the matrix $\underset{\sim}{A}$ and its eigenvalues from which the spacing of the eigenvalues could be predicted a priori. Note that this is entirely different from the exact linear case considered above. If the eigenvector $\vec{L}^j$ is chosen as in Eq. (3.5), the spectra of eigenvalues is completely irrelevant for obtaining a linear law as can be seen from Eq. (3.8) which is exact and does not depend upon the separation of the eigenvalues. The harmonic oscillator example studied above furnishes a good illustration of this point since the eigenvalues $\lambda_j = -j(1-e^{-\theta})$ are equally spaced.

IV. RELATION OF TRANSITION RATES TO HAMILTONIAN FORMULATIONS

We now turn to the interpretation of the results of Section II in terms of a Hamiltonian formulation. Consider a system whose Hamiltonian can be written as a heat bath Hamiltonian, H_b, a relaxing subsystem Hamiltonian, H_s, and an interaction V between the heat bath and subsystem

$$H = H_b + H_s + V \tag{4.1}$$

According to the Golden Rule of time dependent perturbation theory the transition rates are given by

$$A_{mn} = 2\pi N(E)|V_{mn}|^2 , \qquad \hbar = 1 \tag{4.2}$$

where the

$$V_{mn} = \langle m|V|n\rangle \tag{4.3}$$

are the matrix elements of the interaction V expressed in the basis $|n\rangle$ which diagonalizes H_s, and N(E) is the density of bath states at energy E.

As demonstrated in the previous section, Eq. (2.28), in order to obtain a linear law the transition matrix $\underset{\sim}{A}$ must linear in the occupation numbers for the case of equally spaced subsystem levels. This implies that the interaction V must linear in the creation-annihilation operators of the subsystem, b and b^+, i.e.,

$$V \sim (b+b^+) \tag{4.4}$$.

We thus conclude that for a subsystem with equally spaced levels the only polynomial perturbation which can give rise to a linear law are those given by Eq. (4.4).

For the purpose of illustration we will derive, from a given Hamiltonian, the form of the transition matrix $\underset{\sim}{A}$ which leads to a linear law. For our Hamiltonian we chose(6)

$$H = H_b + H_s + V \tag{4.5}$$

where

$$H_b = \frac{1}{2} \sum_k \omega_k a_k^+ a_k \tag{4.6}$$

$$H_s = \frac{1}{2} \Omega_o b^+ b \tag{4.7}$$

$$V = \Omega_o^{-1/2} (b^+ + b) \sum_n \epsilon_n \omega_n^{-1/2} (a_n^+ + a_n) \tag{4.8}$$

$$[a_k^+, a_j] = \delta_{kj} \quad ; \quad [b^+, b] = 1 \tag{4.9}$$

Such a Hamiltonian is applicable, for instance, to a one dimensional solid in the harmonic approximation with a mass impurity. The $\{a_k\}$ are the modes of the equal mass particles (the heat bath) with frequencies ω_k, the operators b and b^+ refer to the impurity (the subsystem) with frequency Ω_o and the heat bath interacts with the subsystem with coupling constants $\{\epsilon_n\}$.

Since the Hamiltonian is a quadratic form it can be diagonalized but in line with our present objective we shall use perturbation theory to calculate $\underset{\sim}{A}$ according to Eqs. (4.1) and (4.2). We take as a basis the direct product of the bath oscillator states $\{M_1\}$, $\{M_2\}, \ldots \{M_N\}$ and subsystem states $\{m\}$. The squares of the nonvanishing matrix elements of the perturbation are given by the usual harmonic oscillator expressions

$$\begin{aligned} &|\langle M_1, \ldots, M_{k-1}, \ldots, M_N, m+1 | V | M_1, \ldots, M_k, \ldots, M_N, m \rangle|^2 \\ &= \sum_k \frac{\epsilon_k^2}{4\omega_k \Omega_o} M_k (m+1) \delta(\Omega_o - \omega_k) \end{aligned} \tag{4.10}$$

where the delta function restricts one to a single energy shell and all equal quantum numbers are suppressed. We now sum over all possible bath transitions in the canonical ensemble and replace this sum by an integration over a continuum of states to obtain from Eq. (4.2)

$$A_{m+1,m} = \frac{\sum\limits_{k}\sum\limits_{M_k} \delta(\Omega_o-\omega_k)\, M_k(m+1)\varepsilon_k^2\, e^{-M_k\varepsilon_k\beta}}{\sum\limits_{M_k} e^{-M_k\varepsilon_k\beta}} \tag{4.11}$$

$$= (m+1)\int_0^{\omega_{max.}} d\omega N(\omega)\varepsilon^2(\omega)\delta(\Omega_o-\omega)\,\frac{\sum\limits_{M_k} M_k e^{-M_k\varepsilon_k\beta}}{\sum\limits_{M_k} e^{-M_k\varepsilon_k\beta}} = (m+1)e^{-\beta\Omega_o} A_{01}$$

where

$$A_{01} = \frac{\pi}{4}\,\frac{N(\Omega_o)\varepsilon^2(\Omega_o)}{\Omega_o^2(1-e^{-\beta\Omega_o})} \tag{4.12}$$

and $N(\omega)$ is the density of bath states. An analogous calculation for the inverse transitions yields

$$A_{m,m+1} = (m+1)A_{01} \tag{4.13}$$

Since these transition probabilities are linear in the occupation numbers of the subsystem a linear law is obtained for the mean value of the microscopic variable m.

There are two important points to note in regard to Eq. (4.4). First, we made a stipulation only about the subsystem interaction, i.e., the perturbation must be linear in the creation – anihilation operators of the subsystem. This would seem to leave the bath interaction of arbitrary strength and form. However, the master equation (Pauli equation) used in this study, Eq. (2.1), is valid only in the limit of weak subsystem-bath coupling. One therefore implicitly assumes that the interaction V is of low order in the bath operators. Secondly, the condition imposed on the interaction V in Eq. (4.4) is necessary if one wants to obtain an *exact* linear law. If one considers *approximate* linear laws, as we do in the next section, the class of acceptable perturbations V is more extensive.

V. MULTIVARIATE DISCRETE LINEAR LAWS (Redfield and Bloch Equations)

In this section we consider the generalization of the univariate linear law condition to the multivariate case. We shall also investigate if there are additional restrictions which permit the reduction of these multivariate linear laws to lower dimensions. Finally, as an important example of a multivariate linear law, we discuss the Bloch equations which play a central role in the theory of spin relaxation.(7)

Let $P_N(\alpha^N,t)$ denote the joint probability for the variables $\alpha_1,\alpha_2 \ldots \alpha_N$ which satisfies the master equation

$$\frac{\partial P_N(\alpha^N,t)}{\partial t} = \sum_{\gamma^N} A(\alpha^N,\gamma^N) P_N(\gamma^N,t) \tag{5.1}$$

where the sum runs over all the states of the N variables $\gamma_1,\ldots,\gamma_N$. The unconditional moment of P_N with respect to the variable α_i is defined as

$$\mu_i(t) = \sum_{\alpha^{N\neq i}} \sum_{\alpha_i} \alpha_i P_N(\alpha^N,t) \tag{5.2}$$

Multiplying Eq. (5.1) by α_i and summing over all α^N, one obtains the multivariate sum rule

$$\sum_{\alpha^{N\neq i}} \sum_{\alpha_i} \alpha_i \, A(\alpha^N,\gamma^N) = \sum_{k=1}^{N} b_{ik}\gamma_k + d_i \tag{5.3}$$

which is the necessary and sufficient condition for the linear relaxation of the moment $\mu_i(t)$ as given by

$$\frac{d\mu_i(t)}{dt} = \sum_{k=1}^{N} b_{ik}\, \mu_k(t) + d_i \tag{5.4}$$.

This can be rewritten in matrix form as

$$\frac{d\vec{\mu}}{dt} = \mathbb{B}\cdot\vec{\mu}+\vec{D} \tag{5.5}$$

which is identical with Eq. (1.1) of the Introduction.

Before illustrating this multivariate sum rule with the example of spin relaxation we consider the problem of reducing an N-variate linear law to an n-variate linear law where $n < N$ ($n=1,2,\ldots N-1$). To carry out this reduction it is necessary to ascertain first whether the N-variable master equation reduces to an n-variable master equation. The condition under which this reduction occurs has recently been derived by Bedeaux, Shuler and Oppenheim$^{(8)}$ and is

$$\sum_{\alpha^{N-n}} A(\alpha^N,\gamma^N) = A(\alpha^n,\gamma^n) \qquad (5.6).$$

This implies that the transition matrix of the n-variate system must be independent of the initial states, γ^{N-n}, of the γ variables. A formulation of the above condition in terms of the eigenvalues and eigenfunctions of the matrices $A(\alpha^N,\gamma^N)$ and $A(\alpha^n,\gamma^n)$ may be found in ref. 8. Let us then assume that condition (5.6) is fulfilled and that the n-variate master equation

$$\frac{\partial P_n(\alpha^n,t)}{\partial t} = \sum_{\gamma^n} A(\alpha^n,\gamma^n)P_n(\gamma^n) \qquad (5.7)$$

as well as the N-variate master equation exist. Then multiplying Eq. (5.1) by α_1 for $i \subset n$ and summing over all α^N one finds, using the linear law condition, Eq. (5.3),

$$\begin{aligned} \sum_{\alpha^N} \alpha_i A_N(\alpha^N,\gamma^N) &= \sum_{\alpha^n} \alpha_i \sum_{\alpha^{N-n}} A_N(\alpha^N,\gamma^N) \\ &= \sum_{\alpha^n} \alpha_i A_n(\alpha^n,\gamma^n) = \sum_{k=1}^{N} b_{ik}\gamma_k + d_i \end{aligned} \qquad (5.8).$$

For $k \subset N-n$ and $i \subset n$ one has

$$b_{ik} = 0 \tag{5.9}$$

so that

$$\sum_{\alpha^N} \alpha_i \, A_N(\alpha^N,\gamma^N) = \sum_{k=1}^{n} b_{ik}\gamma_k + d_i \tag{5.10}$$

which yields the linear law

$$\frac{d\mu_i(t)}{dt} = \sum_{k=1}^{n} b_{ik}\mu_k + d_i \qquad (i,k\subset n) \tag{5.11}$$.

We conclude that the condition (5.6) is sufficiently strong to reduce the n-variate master equation to an n-variate linear law.

For our example of a multivariate linear law we consider the problem of spin relaxation. It is well known that a non-equilibrium system of nuclear spins immersed in a fluid will undergo a relaxation to its equilibrium state. One convenient measure of this relaxation is the time rate of change of the average magnetization. In this example the fluid serves as a heat bath and the spins are assumed to be weakly coupled to this system. The master equation (Redfield equation) for the $\alpha\alpha'$ matrix element of the spin density matrix, σ, has the form(9)

$$\frac{\partial\sigma_{\alpha\alpha'}}{\partial t} = -i\omega_{\alpha\alpha'}\,\sigma_{\alpha\alpha'} + \sum_{\beta\beta'} R_{\alpha\alpha'\beta\beta'}\,\sigma_{\beta\beta'}, \tag{5.12}$$

where $\omega_{\alpha\alpha'} = (E_\alpha - E_{\alpha'})/\hbar$ is the energy difference between spin states α and α' and $R_{\alpha\alpha'\beta\beta'}$ is the "relaxation matrix" for the transition between spin states $\beta\beta'$ and $\alpha\alpha'$. Under certain conditions the average magnetization can be shown to obey the Bloch equations(7) which are the linear laws corresponding to the (microscopic) Redfield equation. These Bloch equations are approximate; one does not rigorously obtain a linear law from Eq. (5.12). We now investigate the reduction of the Redfield equation to the Bloch equations in the context of the conditions which have been derived for multivariate linear laws. The Redfield equation involves a relaxation matrix $\underset{\sim}{R}$ which is obtained from the Hamiltonian of the complete system. It involves of course the interaction V between the fluid and spins; this is taken to be of the form

$$V = \sum_q F^{(q)} A^{(q)} \tag{5.13}$$

where the sum is over the q interaction terms and where the $F^{(q)}$ are bath operators and the $A^{(q)}$ are spin operators. If we assume that the fluid is classical, one may derive the following expression for the elements of the relaxation matrix R(9)

$$\begin{aligned} R_{\alpha\alpha'\beta\beta'} = \sum_q \Big\{ & A_q^{\alpha\beta} A_q^{\beta'\alpha'} \left[J^q(\omega_{\alpha\beta}) + J^q(\omega_{\alpha'\beta'}) \right] \\ & - \delta_{\beta'\alpha'} \sum_\gamma A_q^{\alpha\gamma} A_q^{\gamma\beta} J^q(\omega_{\beta\gamma}) - \delta_{\beta\alpha} \sum_\gamma A_q^{\beta'\gamma} A_q^{\gamma\alpha'} J^q(\omega_{\beta'\gamma}) \Big\} \end{aligned} \tag{5.14}$$

where $J(\omega)$ is the spectral density of the autocorrelation function of the various bath functions,

$$J^{(q)}(\omega) = \frac{1}{2} \int_{-\infty}^{+\infty} e^{-i\omega t} \langle F_q F_q(t) \rangle \, dt \tag{5.15}.$$

We shall also assume that only spin transitions that conserve energy contribute significantly to the relaxation; i.e., we require

$$\alpha - \alpha' = \beta - \beta' \tag{5.16}$$

For convenience only the z component of the magnetization of a spin of arbitrary value is considered here. Since we are working in a representation where the z component of spin is diagonal, the formalism developed above is applicable. For the interaction V we choose the dipolar Hamiltonian since it describes the most common mechanism of relaxation. In this case one has the standard expressions(7)

$$
\begin{aligned}
A^{(0)} &= \xi \left\{ -\frac{2}{3} I_z S_z + \frac{1}{6} (I_+ S_- + I_- S_+) \right\} \\
A^{(1)} &= \xi \left\{ I_z S_+ + I_+ S_z \right\} \qquad (5.17) \\
A^{(2)} &= \frac{1}{2} \xi \, I_+ S_+ \quad ; \\
\xi &= -\frac{3}{2} \gamma_I \gamma_S
\end{aligned}
$$

where we have introduced the z, + and - operators for spins I and S of gyromagnetic ratio γ_1 and γ_S. The specific form of the bath operators $F^{(0)}$, $F^{(1)}$ and $F^{(2)}$ are of no concern to us in this context. The first term of Eq. (5.12) always yields a linear law so we just concentrate on the relaxation term. It is evident that for the calculation of the average magnetization, $\langle I_z \rangle$, only the diagonal elements of the density matrix are required. This feature, along with Eq. (5.16), the secular term restriction, implies that the master equation of interest is, in the notation of Eq. (2.1)

$$
\frac{d\sigma(\alpha_1,\alpha_2;t)}{dt} = \sum_{\beta_1,\beta_2} R(\alpha_1,\alpha_2;\beta_1,\beta_2)\sigma(\beta_1,\beta_2;t) \qquad (5.18)
$$

where $\underset{\sim}{R}$ is to be identified with our transition matrix $\underset{\sim}{A}$. We now compute the spin sum rule, Eq. (5.3), by inserting Eq. (5.17) into Eq. (5.14), multiplying by I_z and summing over all states. This yields in operator notation, after a tedious calculation,

$$
\begin{aligned}
I_z \cdot R = \sum_{\alpha_1\alpha_2} \alpha_1 R(\alpha_1,\alpha_2;\beta_1\beta_2) &= \xi^2 \left[\frac{(S_x^2 + S_y^2)}{18} J^{(0)}(\omega_I - \omega_S) + 2S_z^2 J^{(1)}(\omega_I) \right. \\
&\quad \left. + \frac{(S_x^2 + S_y^2)}{2} J^{(2)}(\omega_I + \omega_S) \right] I_z \\
&\quad + \xi^2 \left[-\frac{(I_x^2 + I_y^2)}{18} J^{(0)}(\omega_1 - \omega_S) + 2I_z^2 J^{(1)}(\omega_I) \right. \qquad (5.19) \\
&\quad \left. + \frac{(I_x^2 + I_y^2)}{2} J^{(2)}(\omega_1 + \omega_S) \right] S_z
\end{aligned}
$$

and a similar equation for $S_z \cdot R$.

The terms in brackets correspond to the b_{ik} of Eq. (5.3) with N=2. Owing to the appearence of the operators S_x, S_y, I_x, and I_y in the b_{ik}, these coefficients are not constants as they are in Eq. (5.3). Thus Eq. (5.18) does not lead to an exact linear law. However, in carrying out the final summation

$$\sum_{\beta_1\beta_2} \left[b_{11}(S_x,S_y,S_2)\beta_1 + b_{12}(I_x,I_y,I_2)\beta_2\right]\sigma(\beta_1,\beta_2;t)$$

one makes a high temperature approximation in NMR. In this approximation the coefficients $b_{11}(S)$ and $b_{12}(I)$ become

$$\begin{aligned} b_{11} &= \xi^2\left[\frac{J^{(0)}(\omega_I-\omega_S)}{27} + \frac{2}{3}J^{(1)}(\omega_I) + \frac{1}{3}J^{(2)}(\omega_I+\omega_S)\right] \\ b_{12} &= \xi^2\left[-\frac{J^{(0)}(\omega_I-\omega_S)}{27} + \frac{2}{3}J^{(1)}(\omega_I) + \frac{1}{3}J^{(2)}(\omega_I+\omega_S)\right] \end{aligned} \qquad (5.20)$$

and are now independent of the spin operators I and S. An analogous result is obtained for b_{21} and b_{22}. The "sum rule" formalism we have developed here is thus consistent with the well known result that the master equation for nuclear magnetic relaxation leads to an <u>approximate</u> linear law for the magnetization.

VI. LINEAR LAWS FOR CONTINUOUS VARIABLES (Fokker-Planck and Langevin Equations)

We shall now consider the linear law conditions for master equations in continuous state space. The master equation is now written in the form

$$\frac{\partial P}{\partial t}(x,t) = \int A(x,y)P(y,t)dy \qquad (6.1).$$

Multiplying Eq. (6.1) by x and integrating over the range of the variable x we obtain,(4)

$$\int xA(x,y)dx = \alpha y + \delta \qquad (6.2)$$

as the necessary and sufficient condition to obtain linear law

$$\frac{d\mu(t)}{dt} = \alpha\mu(t) + \delta \qquad (6.3)$$

with $\mu(t)$ given by

$$\mu(t) = \int x\, P(x,t)dx \qquad (6.4).$$

Equation (6.2) is the continuum analogue of Eq. (2.6), and much of the discussion of Section II is applicable to relaxing systems described by Eq. (6.1).

In physical applications one frequently approximates the global kernel A(x,y) by a local operator. It is this case which we want to study here in some detail. We accordingly write A(x,y) as a local operator of the form

$$A(x,y) = b_1(y)\delta'(x-y) + \frac{1}{2} b_2(y)\delta''(x-y) \qquad (6.5)$$

where the prime indicates differentiation with respect to the argument of the delta function. Substituting Eq. (6.5) into Eq. (6.1) converts the differential-integral equation to the local differential equation (Fokker-Planck equation)

$$\frac{\partial P(x,t)}{\partial t} = -\frac{\partial}{\partial x}\left[b_1(x)P(x,t)\right] + \frac{1}{2}\frac{\partial^2}{\partial x^2}\left[b_2(x)P(x,t)\right] \qquad (6.6).$$

The coefficients $b_1(x)$ and $b_2(x)$ are respectively the first and second transition moments of the matrix A:

$$b_1(x) = \int dx(x-y)A(x,y) \tag{6.7}$$

$$b_2(x) = \int dx(x-y)^2 \, A(x,y) \tag{6.8}.$$

In terms of these moments the necessary and sufficient condition for a linear law, as derived by Shuler and Weiss,$^{(4)}$

$$b_1(x) = ax + d \tag{6.9}$$

where a, d are constants. Note that $b_2(x)$ is arbitrary; the condition for a linear law involves only the first transition moment $b_1(x)$.$^{(10)}$

As an example of the condition (6.9) leading to a linear law we cite the relaxation of the Rayleigh gas$^{(11)}$ (heavy mass in heat bath of light particles) where the mean kinetic energy follows the linear law (6.3) for all times t. For the Lorentz gas (light mass in heat bath of heavy particles), Eq. (6.9) is not obeyed, and as has been shown in ref. (11), the mean kinetic energy of the light particles does not relax via a simple linear law. The energy relaxation of neutrons in a heavy moderator obeys the same Fokker-Planck equation as the relaxation of the Lorentz gas.$^{(12)}$ Thus, as is well known, the energy relaxation of neutrons in a reactor does not follow a simple one-term exponential law. It is useful to realize that these predictions can be made directly from the structure of the Fokker-Planck equations without the need of obtaining a solution for the distribution functions $P(x,t)$.

The multivariate generalization of Eq. (6.6) for the vector $\vec{\alpha}$ is

$$\frac{\partial P(\vec{\alpha};t)}{\partial t} = - \frac{\partial}{\partial \vec{\alpha}} \left[\vec{B}_1(\vec{\alpha}) P \right] + \frac{1}{2} \frac{\partial^2}{\partial \vec{\alpha} \partial \vec{\alpha}} \left[\mathcal{B}_2(\vec{\alpha}) P \right] \tag{6.10}$$

where

$$\vec{B}_1(\vec{\alpha}) = \int\cdots\int (\vec{\alpha}-\vec{\alpha}')A(\vec{\alpha}',\vec{\alpha})d\vec{\alpha}' \tag{6.11}$$

$$\underset{\sim}{B}_2(\vec{\alpha}) = \int\cdots\int (\vec{\alpha}-\vec{\alpha}')^2\, A(\vec{\alpha}',\vec{\alpha})d\vec{\alpha}' \tag{6.12}.$$

In component form one has

$$\frac{\partial P(\vec{\alpha},t)}{\partial t} = -\sum_i \frac{\partial}{\partial \alpha_i}\left(B_1^i(\vec{\alpha})P\right) + \frac{1}{2}\sum_i\sum_j \frac{\partial^2}{\partial\alpha_i\partial\alpha_j}\; B_2^{ij}(\vec{\alpha})P \tag{6.13}.$$

The linear law condition for this multivariate case is obtained by multiplying Eq. (6.13) by α_k and then integrating over all components α_i. This yields in component form

$$\frac{\partial}{\partial t}\int\cdots\int d\vec{\alpha}\alpha_k P = -\sum_i \int\cdots\int d\vec{\alpha}\alpha_k \frac{\partial}{\partial\alpha_i}\left(B_1^i(\vec{\alpha})P\right) + \frac{1}{2}\sum_i\sum_j\int\cdots\int d\vec{\alpha}\alpha_k \frac{\partial^2}{\partial\alpha_i\partial\alpha_j}\left(B_2^{ij}(\vec{\alpha})P\right)$$

$$= \int d\vec{\alpha}B_1^k(\vec{\alpha})P\ , \tag{6.14}$$

where, in order to obtain the last expression on the r.h.s. of Eq. (6.14), we have integrated by parts repeatedly and assumed that the probabilities go to zero at the limits of integration, i.e., on the boundary of the sphere in $\vec{\alpha}$ space. Therefore, in order to obtain a linear law of the form

$$\frac{\partial}{\partial t}\mu_k(t) = \sum_j M_{kj}\mu_j(t) \tag{6.15}$$

we require that

$$B_1^k(\vec{\alpha}) = \sum_j M_{kj}\alpha_j = \underset{\sim}{M}\cdot\vec{\alpha} \tag{6.16}.$$

Equation (6.16) is the multivariate generalization of Eq. (6.9).

To obtain some insight into the import of these sum rules we consider a number of special cases which are used frequently in the discussion of physical relaxation processes. The simplest case is the Gaussian-Markov process. This process, by definition, fixes both conditional moments. They are given by

$$B_1^i(\vec{\alpha}) = \sum_j M_{ij}\alpha_j \tag{6.17}$$

$$B_2^{ij}(\vec{\alpha}) = D^{ij} \tag{6.18}$$

where $\underset{\sim}{M}$ is independent of $\vec{\alpha}$. Comparing Eqs. (6.16) and (6.17) we see that the linear law condition is satisfied. As is well known, a linear law is obtained for a Gaussian-Markov process.(13) It is to be noted from Eqs. (6.14) and (6.16) that $\underset{\sim}{B}_2$ need not be specified to obtain a linear law. Thus while a Gaussian-Markov process necessarily leads to a linear law, there are other processes which can also give rise to linear laws. Before studying such other types of stochastic processes, we briefly consider the Langevin equation corresponding to the Gaussian-Markov process. This is(13)

$$\frac{d\vec{\alpha}}{dt} = -\underset{\sim}{R}\cdot\vec{\alpha} + \vec{F}(t) \tag{6.19}$$

where $\underset{\sim}{R}$ is the "friction constant" matrix and $\vec{F}(t)$ a fluctuating force which is assumed to be Gaussian, i.e.,

$$\begin{aligned}
&\langle\vec{F}(t)\rangle = 0\\
&\langle\vec{F}(t)\vec{F}(t')\rangle = \underset{\sim}{D}\delta(t-t')\\
&\langle\vec{F}(t_1)\ldots\vec{F}(t_{2n+1})\rangle = 0\\
&\langle\vec{F}(t_1)\ldots\vec{F}(t_{2n})\rangle = \sum_{\substack{\text{all products}\\ \text{of pairs.}}} \langle\vec{F}(t_1)\vec{F}(t_2)\rangle\ldots\langle\vec{F}(t_{2n-1})\vec{F}(t_{2n})\rangle
\end{aligned} \tag{6.20}$$

It is evident from the form of the Langevin equation (6.19) and the first relation in (6.20) that a linear law is obtained for the averaged variables $\langle \vec{\alpha} \rangle$.

The next case that we consider is a stationary Markov process where both the "friction constant" and the fluctuating force are space dependent. For simplicity we consider only the univariate case; the generalization to many variables does not introduce any new features. This process can be described by the Langevin equation

$$\frac{dx}{dt} + \beta(x)x = F(t) \tag{6.21}$$

where

$$\begin{aligned} &\langle F(t) \rangle = 0 \\ &\langle F(t_1)F(t_2) \rangle = D(x)\delta(t_1 - t_2) \end{aligned} \tag{6.22}$$

and where the higher correlations are of the form given in Eq. (6.20). The Fokker-Planck equation which corresponds to the Langevin equation (6.21) is

$$\frac{\partial P(x,t)}{\partial t} = -\frac{\partial}{\partial x}[x\beta(x)P(x,t)] + \frac{\partial^2}{\partial x^2}[D(x)P(x,t)] \tag{6.23}$$.

Since this equation does not have a transition moment $b_1(x)$ of the proper form as given by Eq. (6.9), it clearly does not lead to linear law for $\mu(t) \equiv \langle x(t) \rangle$.

The third Fokker-Planck equation that we discuss corresponds to a Gaussian, non-Markovian process which may be shown to satisfy the Fokker-Planck equation$^{(14)}$

$$\frac{\partial P(x,t)}{\partial t} = -\beta(t)\frac{\partial}{\partial x}(xP) + \frac{D(t)}{2}\frac{\partial^2 P}{\partial x^2} \tag{6.24}$$

where

$$\begin{aligned} &\frac{\beta(t)}{D(t)} = \phi = \text{constant} \\ &\beta(t) = \frac{d\ln\rho(t)}{dt} \end{aligned} \tag{6.25}$$

and

$$\rho(t) = \langle x x(t) \rangle \tag{6.26}$$

Equation (6.24) can be derived by differentiating the conditional probability which defines a Gaussian process. If one multiplies Eq. (6.24) by x and then integrates over all x one obtains

$$\frac{d\mu(t)}{dt} = -\beta(t)\mu(t) \tag{6.27}$$

Since the coefficient β is now a function of time, no linear law of the form (1.1) exists for this case. The Langevin equation corresponding to the Fokker-Planck equation (6.24) is

$$\frac{dx}{dt} + \beta(t)x = F(t) \tag{6.28}$$

with

$$\begin{aligned} &\langle F(t) \rangle = 0 \\ &\langle F(t)F(t_2) \rangle = D(t_1)\delta(t_1 - t_2) \end{aligned} \tag{6.29}$$

and where it is assumed that the variation in time of $\beta(t)$ and $D(t)$ are sufficiently slow so as to be essentially constant over the time required to produce a small displacement of x.

It should be noted that of the varieties of general Langevin (and corresponding Fokker-Planck equations) considered here, only the simple Gaussian-Markov process (6.19) leads to a linear law.

As an example of a multidimensional Markov process which can yield a linear law under the appropriate circumstances we consider the Kramers$^{(15)}$ equation. Kramers' equation is a Fokker-Planck equation which describes the joint probability of being at a position x with a velocity v for a particle in an external field of force. For simplicity we consider just the one dimensional problem. Kramers' equation is

$$\frac{\partial P(x,v,t)}{\partial t} + v\,\frac{\partial P}{\partial x} + \frac{1}{m}\,\mathfrak{F}_e(x)\,\frac{\partial P}{\partial v}$$

$$= \beta\left[\frac{\partial}{\partial v}(vP) + \frac{kT}{m}\,\frac{\partial}{\partial v^2}\,P\right] \qquad (6.30)$$

where $\mathfrak{F}_e(x)$ is the external force and m is the mass of the particle. In our vector notation we have

$$\frac{\partial P(\vec{\alpha},t)}{\partial t} = \underset{\sim}{R}^{\dagger}:\ \frac{\partial}{\partial\vec{\alpha}}(\vec{\alpha}P) + \underset{\sim}{Q}:\ \frac{\partial^2}{\partial\vec{\alpha}\partial\vec{\alpha}}\,P \qquad (6.31)$$

$$x = \alpha_1 \quad , \quad v = \alpha_2$$

where

$$\underset{\sim}{R} = \begin{pmatrix} 0 & -1 \\ \dfrac{\mathfrak{F}_e(\alpha_1)}{\alpha_1 m} & \beta \end{pmatrix} \quad , \quad \underset{\sim}{Q} = \begin{pmatrix} \dfrac{kT}{m}\beta & 0 \\ 0 & 0 \end{pmatrix} \qquad (6.32).$$

Note that $\underset{\sim}{R}$ is a function of α_1 except when $\mathfrak{F}_e(\alpha_1) = -\kappa\alpha_1$. It is only in this case, i.e., when the external force is a harmonic one, that one obtains the linear law

$$\frac{d\vec{\mu}}{dt} = -\underset{\sim}{M}\cdot\vec{\mu} \qquad (6.33)$$

where $\vec{\mu}$ is the vector $\begin{pmatrix}\langle\alpha_1\rangle \\ \langle\alpha_2\rangle\end{pmatrix}$ and where $\underset{\sim}{M} = \begin{pmatrix} 0 & -1 \\ k & -\beta \end{pmatrix}$.

For the harmonic force $\mathfrak{F}_e(x)$ considered here, the Kramers equation for the average position, $\langle x\rangle$, and velocity, $\langle v\rangle$, can be written as

$$\frac{d\langle x\rangle}{dt} = \langle v\rangle$$

$$\frac{d\langle v\rangle}{dt} = -\kappa\langle x\rangle + \beta\langle v\rangle \qquad (6.34).$$

These moment equations which are equivalent to vector equation (6.33) are clearly linear.

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