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OFFICE OF NAVAL RESEARCH
CONTRACT N00014-81-C-0776
TASK NO. NR-051-0775
TECHNICAL REPORT #41

STRUCTURE OF THE ELECTRIC DOUBLE LAYER

1989

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Prepared for Publication in Advances in Chemical Physics
S.A. Rice, Editor

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report #41	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Structure of the Electric Double Layer		5. TYPE OF REPORT & PERIOD COVERED Technical Report
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) L. Blum		8. CONTRACT OR GRANT NUMBER(s) N 00014-81-C-0776
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Physics University of Puerto Rico, P.O. Box 23343 Río Piedras, PR 00931-3343		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Code 472 Office of Naval Research Arlington, Virginia 22217		12. REPORT DATE
		13. NUMBER OF PAGES 67
14. MONITORING AGENCY NAME & ADDRESS(If different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Prepared for publication in Davances in Chemical Physics (S.A., Rice, Editor)

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Electrodes, surfaces, integral equations sum rules, phase transitions.

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A review of some recent developments in the theory of electrode surfaces is made. The subject index is:

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

Unclassified
SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

STRUCTURE OF THE ELECTRIC DOUBLE LAYER

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CONTENTS

INTRODUCTION:THE EXPERIMENTAL EVIDENCE

The general problem of the interface between two phases which are charged and or conducting is of relevance to a number of systems which occur in nature: colloids, micelles, membranes, solid-solution interefaces in general and metal solution interfaces in particular, form a bewildering array of systems of enormous complexity. The investigation of the structure of these systems poses considerable difficulties, both experimentally as well as theoretically. The experimental problem is that the interface has 10^{-8} particles relative to the bulk, solid or liquid phases. For this reason one needs a surface specific method, which is able to discriminate between the signal from the surface from the rest. Electrons do not penetrate into solids and for that reason have been used extensively for the determination of the surface structure of solids. However they must be used in vacuum and that precludes their use in the study of the liquid solid interface. The study of electrode surfaces removed from the liquid cell under various conditions has provided an enormous wealth of useful data which we will not try to review here[1]. The only way to understand the relation between the ex-situ and is to measure both.

Neutrons are another possible choice: unfortunately there is no mechanism by which the neutrons can be made surface selective, and for that reason only systems with large specific surface, which in general are disordered, can be studied.

X-rays are a viable alternative for the study the solid-liquid interfaces. The X-ray probes are reviewed in the excellent chapter by H.D. Abruna. There are three techniques that have been used to determine structural features in well characterized metal electrolyte interfaces:

1) EXAFS or extended X-ray absorption fine structure[2], which permits the determination of the near neighbor structure of a given target atom, and also yields information about the electronic state of that atom when it is adsorbed at the surface[3].

2) GIXS, or grazing incidence X-ray diffraction[4]. This method permits the determination of the in-plane structure of an adsorbed monolayer of a target atom on the surface. It is a very exacting technique, and requires that the structure of the adsorbed monolayer should be

different of that of the substrate[5].

3) Standing wave methods[6]. In this case an X-Ray standing wave is set up at the interface of the solid and the fluid . There are several modes in which these standing waves can be formed; they allow the determination of the distance from the surface of the solid into the fluid phase[7].

The spectroscopic methods using ultraviolet, visible or Raman spectroscopy are very useful in situ probes[8]. Although they are not directly related to the geometrical structural parameters, these can be extracted from theoretical considerations with a fair degree of reliability. The optical spectroscopic methods do not require special installations such as the synchrotron, and are most useful for complex molecular species. The techniques are the surface enhanced Raman[9], surface infrared spectroscopy[10], second harmonic generation[11], which permits to discriminate between different geometries of the adsorbates on single crystal surfaces.

A technique that provides with direct structural information of the electrode surface is the Scanning Tunnel Microscope (STM). It has been recently shown by various groups that the STM is capable of resolving structural details of metal surfaces in contact with electrolytic solutions[12]. However when the electrochemical potential is scanned, then the tunnel voltage of the STM also changes. This does not affect the study of surface geometry, since the images are relatively independent of the tunnel voltage[13]. The resolution of the STM pictures of the metal electrolyte interface is of the order of 1-2 Angstroms.

An in situ electrochemical technique that has been established recently is the quarz microbalance: this instrument can measure small changes in the mass of a metallic electrode that is attached to a quarz oscillator[14]. In this way the electrosorption valency[15] can be calculated directly from the amount of charge from the, voltamogram, and the mass obtained from the microbalance. Proper interpretation of the results of this instrument requires electrode surfaces that have large molecularly smooth regions.

A further method that has yielded very interesting information about the structure and interactions in the diffuse part of the double layer is the direct measurement of forces between colloidal particles[16]. Here the forces between two mica plates are measured directly in the presence of different solutions. Quite interestingly the forces give raise to oscillations of a period similar to the dimensions of the molecules enclosed between the mica plates.

Amongst the optical techniques there are also the more traditional methods such as the ellipsometry, electroreflectance and particularly, surface plasmons[17], where experimental and theoretical advances[18] have made it possible to offer a picture of the surface electronic states of the metal in some selected cases, such as the silver (111) phase. We should mention here the measurement of image potential induced surface states by electroreflectance spectroscopy[19]. In this case, besides the normal surface states which arise from the termination of the crystal lattice, there are discrete states due to the existence of an image potential for charges near the conducting interface.

And last, but certainly not least, there is a very extensive literature on the differential capacitance of solutions near either solid (polycrystalline or single crystal) or liquid (mercury) electrodes which we will not try to cover[20]. We should mention the recent work on the influence of the crystallographic orientation of silver on the potential of zero charge of the electrodes, in which a detailed mapping of the influence of the crystal face on the differential capacitance of the inner layer is made[21].

The complexity of the system described by the experimental methods defies any simple theoretical interpretation. Yet these are needed for the understanding of what is actually going on at the charged interface. It is clear that there are two kinds of forces in these systems: the long ranged Coulomb forces and the short ranged forces that are at the origin of the chemical bonds and are also responsible of the repulsion between atomic cores. There are important quantum effects at the interface due essentially to the quantum nature of the electrons in a metal. For this reason we have organized the theoretical discussion of the chapter starting with very simple model systems about which a lot is known, and to systems which are much more realistic but difficult to handle theoretically. The emphasis of the theoretical treatment will be on the structure functions, or distribution functions $\rho_i(1)$, $\rho_{ij}(1,2)$,.... which give the probability of finding an ion(s) or solvent molecule(s) at specified position(s) near the interface. The properties of the interface can be calculated from these distribution functions.

One of the very interesting theoretical developments of recent years has been the exactly solvable model developed by Jancovici, Cornu and co-workers[22]. This is a two dimensional model at a particular value of the reduced temperature, and is particularly useful to elucidate the subtle properties of the long ranged Coulomb forces. For the non primitive model with solvent molecules there is a one dimensional exactly solvable model[23]. Exactly solvable models serve as benchmarks for approximate theories and to test exact and general sum rules.

In this chapter we will not discuss the solvent structure, because this is a subject under development. in our discussion we will restrict ourselves to models in which the solvent is a continuum of dielectric constant ε. The focus of this article is the structure of the inner layer of the interphase, the layer of ions that is directly adsorbed onto the metal surface. We discuss the sticky site model (SSM), in which the adsorption sites are sticky points at the interface. This model requires the distribution functions of the undecorated, smooth surface as an input. The theory of these distribution functions is reviewed in section I. In section II we review exact sum rules for the interface. In section III we discuss the structured interface in the SSM.

I-THEORIES FOR THE SINGLET AND PAIR DISTRIBUTION FUNCTIONS

In recent years there has been significant progress in the statistical mechanics of inhomogeneous charged systems such as the metal electrolyte interface. The real interface is much too complex to be described by a tractable model, so that simple models that focus on some of the more relevant aspects of these systems are used. Most of the effort in the past has been directed to understanding models in which the metal side is an ideally smooth, charged surface, with or without image forces. The solvent is either a continuum of dielectric constant ε, or hard spheres with embedded point dipoles. It is possible to study models with realistic solvents near charged or neutral surfaces in the absence of electrolytes[24], and less realistic models such as the models with quadrupoles[25], or with sticky octupoles[26], in the presence of electrolytes, but for the time being extensive calculations have not been made. The primitive model of charged hard spheres near a charged hard wall, all embedded in a continuum dielectric is by far the most studied, and to date, the best understood of the three dimensional models of the electric double layer.

There has been considerable progress in the theory of the primitive model of the electric double layer. The theories are constructed as direct improvements on the original Gouy-Chapman theory, such as the Modified Poisson Boltzmann (MPB)[27], theories, the theories based on functional density expansions[28] and then there are the theories derived from integral equations. The MPB theories have been adequately reviewed in another review in this series[29]. The integral equation theories can be classified into three groups: those derived from the Ornstein Zernike (OZ)[30] equation and those derived from the Born-Green-Yvon (BGY)[31], Wertheim-Lovett-Mou-Buff (WLMB)[32] and Kirkwood's[33] equations.

As it happens in other areas of condensed matter physics, the forces between molecules is not known, but rather the properties that are measured are interpreted in terms of these forces. Since the equations are only approximate, it is impossible to estimate from the comparison of the theory to experiment the accuracy of the theories. For that reason computer experiments play an important role, since here one knows the input intermolecular potential, and the properties and structure can be computed for systems consisting of a few hundred to a few thousend particles. There are two techniques used to perform these simulations: molecular dynamics (MD), in which the equations of motion of the molecules are solved simultaneously, and the Monte Carlo method (MC), in which an equilibrium ensemble is generated from a random walk algorithm (a Markov Chain). For systems of hard charged spheres the MD technique cannot be used because the forces are both singular and very long ranged, and this produces insurmountable technical problems. The MC techniques are more amenable to simulate the primitive model of the electric double layer[34], although because of the long range of the Coulomb forces the relatively small size of the system poses problems[35].

Models in which the solvent is represented by dipolar hard spheres or even higher multipolar solvents have not been simulated in the neighborhood of charged walls. The full solution of the HNC1 equation has not been achieved for the planar wall, only in the the Mean Spherical Approximation (MSA) and in the Generalized Mean

Spherical Approximation (GMSA) have been solved.

BASIC DEFINITIONS: THE GOUY CHAPMAN THEORY

We have a mixture of ions of density ρ_i, charge $e_i = ez_i$, where e is the elementary charge, z_i is the electrovalence, the ion diameter is σ_i, the number density profile of i at a distance z is $\rho_i(z)=\rho_i(1)$ from the electrode, which is always assumed to be flat and perfectly smooth. (see figure 1).

The singlet distribution function is

$$g_i(z)=h_i(z)+1$$
$$=\rho_i(z)/\rho_i \tag{1}$$

where ρ_i is the bulk density of species i. The charge density q(z) is given by

$$q(z)=\sum_i^m e_i\rho_i(z) \tag{2}$$

where m is the number of ionic species. The electrostatic potential $\phi(z)$ is obtained by integration of Poisson's equation

$$\nabla^2\phi(z) = \frac{d^2\phi(z)}{dz^2} = -4\pi\; q(z)/\varepsilon \tag{3}$$

we have

$$\phi(z)=4\pi\int_z^\infty dt(t-z)q(t)/\varepsilon \tag{4}$$

The total potential drop $\Delta\phi$ is obtained from (4) by either letting z=0 or $z\to-\infty$, depending on the reference potential of the model. In general the latter choice is adopted. An important quantity is the differential capacitance C_d which defined by

$$C_d=dq_s/d\Delta\phi \tag{5}$$

where q_s is the surface charge on the electrode. This quantity is seldom measured directly, it is inferred from either surface tension measurements, or frequency dependent AC measurements of the capacitance.

The surface charge satisfies the electroneutrality condition

$$q_s = -\int_0^\infty dz\, q(z) \tag{6}$$

$$= E_z(0)\varepsilon/4\pi$$

where $E_z(0)$ is the external or applied field.

For low applied field, the Gouy -Chapman -Stern[36 37] theory (or modified Gouy-Chapman Theory, MGC) is accurate for the primitive model in comparison to computer experiments.

Consider the Poisson equation (3). If we approximate the density of the ions by Boltzmann' distribution formula

$$\rho_i(1) = \rho_i \exp[-\beta e_i \phi(1)] \tag{7}$$

replacing into (3) we obtain the Poisson Boltzmann equation

$$\nabla^2 \phi(1) = -4\pi/\varepsilon \sum_i e_i\ \rho_i \exp[-\beta e_i \phi(1)] \tag{8}$$

This equation has been solved analytically for several cases of interest. A first integral can be obtained multiplying by $\nabla\phi(1)$, both sides of this equation. For planar electrode this yields

$$E_z^2 = [\nabla\phi(1)]^2 = -4\pi kT/\varepsilon \sum_i \rho_i \{\exp[-\beta e_i \phi(1)] - 1\} \tag{9}$$

Using the definition of C_d and the electroneutrality relation (6) we get the formula for the differential capacitance

$$C_d = \sqrt{\frac{2\pi}{\varepsilon kT}}\ \frac{\sum_i e_i\ \rho_i \exp[-\beta e_i \phi(0)]}{\sqrt{\sum_i \rho_i \{\exp[-\beta e_i \phi(0)] - 1\}}} \tag{10}$$

where $\phi(0) = \phi(z)|_{z=0} = \Delta\phi$ is the potential at the origin, which is equivalent to the total polarization potential of the electrode.

At this point it is convenient to make a variable change

$$\chi = \exp[-\beta e\ \phi(0)] \tag{11}$$

where $e_i = z_i e$, and z_i is the electrovalence of species i.

We integrate equation (9) to get

$$\int_{\chi_0}^{\chi(z)} d\chi \frac{1}{\chi \sqrt{\sum_i \rho_i \chi^{z_i} - \rho_0 A}} = \sqrt{\frac{8\pi e^2}{kT\varepsilon}} \, (z-z_0) \tag{12}$$

where for the general case, χ_0 and A are integration constants[38] [39]. Since the electrovalences z_i are always small numbers, the integration of the left hand side is always possible in terms of elliptic functions[40]. For the $z_1=-z_2=1$ case the radicand of the left hand side is a perfect square and the integral can be performed explicitly.

The result for this case is, for the potential drop $\Delta\phi$

$$\beta e E_0/\kappa\varepsilon=2\sinh[\Delta\phi e\beta/2] \tag{13}$$

The density profile is given by

$$\rho_i(z)=\rho_i\{[1+z_i\alpha e^{-\kappa z}]/[1-z_i\alpha\ e^{-\kappa z}]\}^2 \tag{14}$$

with $\alpha=\tanh[\Delta\phi\ e\beta/4]$. κ is the Debye parameter

$$\kappa^2=4\pi/kT\varepsilon \sum_i \rho_i e_i^2 \tag{15}$$

There are several remarks about the Gouy-Chapman theory. From equations (10) and (14), we see that for any *mixture of ions of equal size* the contact theorem is satisfied.

$$kT \sum_i \rho_i(0)= \varepsilon/8\pi\ E_z^2(0)+kT \sum_i \rho_i \tag{16}$$

Contrarily to what has been assumed in the literature, the contact theorem is not satisfied for mixtures of unequal size ions. This can be seen from equation (16): In the contact theorem all the ions have to be in contact with the wall simultaneously. Since there is only one distance in (16), there is no way that the theorem will be satisfied. However for very high positive or negative fields *when only* one kind of ions is present, and then the Gouy-Chapman theory will satisfy *asymptotically* the all important contact theorem.

The density profiles obtained from the Gouy-Chapman theory are monotonous, that is they show no oscillations. When the contact theorem is satisfied, and also the electroneutrality integral comes out to be correct, $\rho_i(1)$ is pinned at the origin, and has a fixed integral, so that the density profile cannot deviate too much from the correct result. However, when the density is high the profiles will be oscillatory, and we should expect deviations from the GC theory. This is also true for the non-primitive model in which the solvent is a fluid of finite size molecules.

The Gouy Chapman theory has been solved for non-equal size[41] ions. For 1-1 electrolytes the comparison to computer simulations shows good agreement, because in the regime of high electrode charge there is only one ion present in the double layer. The situation should be different when we are dealing with a mixture of anions or cations of different sizes.

INTEGRAL EQUATIONS-THE PRIMITIVE MODEL

The classic Gouy and Chapman[36] theory, is based on the Poisson equation and a closure given by Boltzmann's equation. In this theory the ions in the double layer are *point charges* with *no* exclusion volume, all embedded in a continuum dielectric. There have been a large number of papers dealing with ways to improve this equation. We must remark, however that at least in the regime of low density and high temperature (or large dielectric constant) the GC theory is not really bad in spite of its simplifications because it does satisfy the contact theorem (16) asymptotically for $E \to \infty$, and of course, it also satisfies the electroneutrality condition (6). However, since the electrochemist is really interested in systems in which the solvent is not a continuum the primitive model should not be considered a working model for the interpretation of experimental data, but rather a learning model for the theoretician because of the availability of computer experiments. Indeed as the density and coupling constant increase, significant deviations from the behavior predicted by the GC theory occur.

All of the theories can be formulated as an (integral) equation for the density profile $\rho_i(1)$, or alternatively as a (differential or integrodifferential) equation for the potential $\phi(1)$[42]. Consider first the one particle direct correlation function, which will be the central quantity of our discussion[43] [44], from which the integral equations can be deduced:

$$c_i(1)=\ln[\rho_i(1)/\mathfrak{z}_i]+\beta u_i(1) \qquad (17)$$

where $c_i(1)$ is the one particle direct correlation function, $\mathfrak{z}_i$ is the fugacity of species i, and $u_i(1)$ is the external potential.

The function $c_i(1)$ is a member of the family of direct correlation functions $c(1,2..)$[45], which is the sum of all irreducible graphs with density factors $\rho_i(1)$ for every field point (For a detailed discussion of correlation functions see for example Hansen and McDonald[46]).

ORNSTEIN-ZERNIKE BASED APPROXIMATIONS

At the interface between an electrode and a fluid the density of the fluid is a function of the distance of the point to the surface $\rho_i(z)$. The Ornstein Zernike equation for this system can be obtained from an homogeneous mixture in which there are some large ions, of radius $R_w \to \infty$,such that $\rho_w R_w^3 \to 0$. In this limit the planar HAB (Henderson-Abraham-Barker) OZ equation is[47]

$$h_i(1)-c_i^w(1)=\sum_j \rho_j \int d2\; c^B_{ij}(|r_{12}|)\; h_j(2) \qquad (18)$$

where $h_i(1)$ is defined by

$$h_i(1)=[g_i(1)-1]=[\rho_i(1)-\rho_i]/\rho_i \qquad (19)$$

The function $h_i(1)$ is the density profile function for ion i. The function $c_i^w(1)$ is a much more complicated object, and in general does not admit a simple diagram expansion. To get some insight about the meaning of this function we use functional series expansion[48].

Consider the functional power series expansion of $\ln[\rho_i(1)]$ around the uniform density ρ_i

$$\beta u_i(1)+\ln[\rho_i(1)]=\ln[\rho_i]+\sum_j \rho_j\int d2\; c^B_{ij}(|r_{12}|)h_j(2)$$

$$+\;1/n!\sum_{jk..}\rho_j\,\rho_k..\int d2d3..c^B_{ijk}(1,2,3\,..)\;h_j(2)\;h_k(2).. \qquad (20)$$

the direct correlation functions are defined by the functional derivative

$$c^{B}_{ijk}(1,2,3,..) = \delta^{n} c_{i}(1)/\delta\rho_{j}(2)\delta\rho_{k}(3).. \tag{21}$$

The superscript B stands for the bulk functions. If we now introduce the new function $c^{w}_{i}(1)$, defined by

$$\begin{aligned} c^{w}_{i}(1) = {} & -\beta u_{i}(1) - \ln[g_{i}(1)] + h_{i}(1) \\ & + 1/n! \sum_{ijk} \rho_{j}\, \rho_{k} \cdot\cdot \int d2d3..c^{B}_{ijk}(1,2,3\,..)\; h_{j}(2)\; h_{k}(3) \end{aligned} \tag{22}$$

where the inhomogeneous potential is of the form

$$u_{i}(1) = u^{sr}_{i}(1) + w_{i}(1) \tag{23}$$

where $u^{sr}_{i}(1)$ is short ranged and for a hard, smooth charged electrode. The electrostatic part is

$$w_{i}(1) = -e_{i} E_{z} z_{1}/2 \tag{24}$$

Combining this definition with the functional expansion (20) we get the HNC1 equation for the flat wall electrode

$$-\beta w_{i}(1) - \ln[g_{i}(1)] = \sum_{j} \rho_{j} \int d2 c^{B}_{ij}(|r_{12}|) h_{j}(2) \tag{25}$$

Equation (25) has a deceivingly simple aspect, but in fact because of the long range of $w_{i}(1)$ is not convergent, and therefore not amenable to numerical solution. Using the equation

$$c^{B}_{ij}(|r_{12}|) = -\beta w_{ij}(|r_{12}|) + c^{sr}_{ij}(|r_{12}|) \tag{26}$$

with

$$w_{ij}(|r_{12}|) = e_{i} e_{j}/\varepsilon r_{12} \tag{27}$$

and replacing into (25) yields

$$\beta\phi_{i}(1) + \ln[g_{i}(1)] = \sum_{j} \rho_{j} \int d2\; c^{sr}_{ij}(|r_{12}|)\; h_{j}(2) \tag{28}$$

where $\phi(1)$ is defined by

$$\phi_{i}(1) = E_{z} z_{1} + \sum_{j} e_{j} \int d2\; \rho_{j}(2)/\varepsilon\; r_{12} \tag{29}$$

This equation is now completely defined in terms of short ranged quantities, which is not the case for the first form of the equation (25)[49]. One important observation about the HNC1 is that it does not satisfy the contact theorem (16), but rather[50]

$$kT \sum_i \rho_i(0) = \varepsilon/8\pi\ E_z^2(0) + \rho_0 \partial P/\partial\rho_0 \qquad (30)$$

with

$$\rho_0 = \sum_i \rho_i \qquad (31)$$

However, the HNC1 satisfies automatically the electroneutrality relations and the Stillinger Lovett sum rules. (see below). The HNC is the most accurate theory for bulk electrolytes. It is the theory that has the closure with the largest number of graphs. One would expect that this fact would remain true in the plane electrode limit. However, because of the inaccuracy of the HNC for uncharged hard sphere fluids the HNC1 does no do well in representing the exclusion volume of the ions, and is not on the whole, such a good approximation for the electric double layer.

For high fields and low concentrations the fact that we get the compressibility rather than the pressure is not very important and the HNC1 is still a reasonably good theory, as will be shown below. However for dense systems this is a rather severe shortcoming. Specifically, when we are dealing with a molecular (dipolar) solvent the density is very large and the dielectric constant ε is of the order of one (instead of 80 in water) which makes the electrostatic term in (16) small in comparison to the contact density term. The consequence is that the HNC1 will put more counter ions near the electrode than the exclusion of the hard cores will permit. Eventually thermodynamic stability conditions will be violated, such as the Bogoliubov inequality[51]. For very high charges the HNC1 predicts a decreasing potential drop ϕ_0 with increasing applied external field E_z[52].

The bulk direct correlation function

$$c^B_{ij}(|r_{12}|) \qquad (32)$$

which should be used in solving the HNC1 equation (28) is that obtained from the solution of the bulk HNC equation for the same system. This however yields poor results when compared to computer simulations. Generally better results are obtained if instead of the HNC bulk direct correlation function the corresponding MSA functions are used, the general agreement with computer simulations improves[53].

There have been several calculations with improved versions of this HNC1 equation. Including the next term in the expansion (22) amounts to including the bridge diagram in the bulk HNC1 calculation. This was done by Ballone, Pastore and Tosi, with good success[54]. The density profile for the 1M, 1-1 electrolyte at a surface charge $\sigma^{*}=q_S\sigma^2/e=$ 0.7, which will be the test case used for comparisons. This is the highest surface density simulated, and shows charge oscillations due to the hard core of the electrolyte. In this calculation the bridge diagrams were computed directly from their definition.

$$c_i^w(1) = -\beta u_i(1) - \ln[g_i(1)] + h_i(1) + 1/2 \sum_{ijk} \rho_j \rho_k \int d2d3\, h^B_{ij}(12)\, h^B_{ik}(13)\, h^B_{kj}(32)\, h_j(2)\, h_k(3) \tag{33}$$

where the product of the three bulk pair correlation functions in the second term of the right hand side is first term in the density expansion of

$$c^B_{ijk}(1,2,3) \tag{34}$$

The results of this calculation are shown in figure 2. Since there are no adjustable parameters, the agreement is very good. An alternative less laborious procedure was suggested by Rosenfeld and Blum[55], but actual calculations were not performed.

Another way of inmproving the HNC1 approximation was introduced by Forstmann and co-workers[56]. In their method the HNC1 equation is used as described above, but instead of taking the bulk direct correlation function, as prescribed by (28), a local density dependent $c^B(r,\bar{\rho})$ is taken. The local density is defined by

$$\bar{\rho}_i(x) = \frac{1}{2\sigma\Delta} \int_{x-\Delta}^{x+\Delta} dz \int_{z-\sigma/2}^{z+\sigma/2} dz\, \rho_i(y) \tag{35}$$

where σ is the diameter of the ion and Δ is an adjustable parameter. The bulk correlation function is then

$$c^{B}_{ij}(|r_{12}|)\Big|_{\rho_i=\bar{\rho}_i} \tag{36}$$

For the test case with surface charge $\sigma^*=.7$, the results of this method, as shown in figure 3 are very good.

BGY BASED APPROXIMATIONS

The BGY equation can be derived from the one particle direct correlation function $c_i(1)$. Consider again (20): letting the gradient ∇ act on the f-bonds of the graphical expansion of $c_i(1)^{57}$, we get the BGY equation

$$-kT\,\vec{\nabla}_1\rho_i(1)=\rho_i(1)\vec{\nabla}_1 u_i(1)+\sum_j\int d2\rho_{ij}(1,2)\vec{\nabla}_1 u_{ij}(1,2) \tag{37}$$

Using (23) and (26) to eliminate the long ranged terms, we obtain (37) in a different form

$$\begin{aligned}-kT\vec{\nabla}_1\rho_i(1)=&\rho_i(1)\vec{\nabla}_1 u_i^{sr}(1)+\ \rho_i(1)e_i\ \nabla_1\phi_i(1)\\&+\sum_j\int d2\rho_{ij}(12)\vec{\nabla}_1 u_{ij}^{sr}(12)+\rho_i(1)e_i\sum_j\int d2\rho_j(2)e_j h_{ij}(12)\vec{\nabla}_1(1/\varepsilon r_{12})\end{aligned} \tag{38}$$

This equation can be integrated from ∞ to z, to yield

$$\ln[g_i(z)]=-e_i[\phi(z)+\psi_i(z)]+J_i(z) \tag{39}$$

which together with Poisson equation (3) forms a closed system of equations that is very convenient for numerical solutions.

This equation is of the same type as the one derived from the HNC1 equation (28): The right hand side term consists of three contributions: The potential $\phi(1)$, which is determined by the single particle distribution function $\rho_i(1)$, and the terms $\psi_i(z)$ and $J_i(z)$ which are functions of the pair distribution function $h_{ij}(1,2)$. From (38) we get

$$\begin{aligned}\psi_i(z)&=\int_z^\infty dz_1\ \rho_i(1)\sum_j\int d2\rho_j(2)e_j h_{ij}(1,2)\vec{\nabla}_1(1/\varepsilon r_{12})\\ J_i(z)&=\int_z^\infty dz_1\sum_j\int d2\ \rho_{ij}(12)\vec{\nabla}_1 u_{ij}^{sr}(1,2)\end{aligned} \tag{40}$$

We remark that in (38) (and also in (39)), if the fluctuation terms $J_i(z)$ and $\psi_i(z)$ are neglected, then we get back the Gouy Chapman theory, which has a known analytical solution .

In the BGY based theories the pair correlation function $h_{ij}(1,2)$ must be given by some approximation. The interesting feature of the BGY equation is that for no matter which closure, the contact theorem (16) is satisfied. However, the electroneutrality conditions (see below) are not satisfied, in general. The simplest approximation one could think which is equivalent to Kirkwoods superposition consists in writing

$$h_{ij}(1,2)=h^{B}_{ij}(r_{12}) \tag{41}$$

where $h^{B}_{ij}(r_{12})$ are the bulk pair correlation functions, fails to satisfy the important electroneutrality condition (see below),

$$-e_i=\sum_j\int d2\rho_j(2)e_j h_{ij}(1,2) \tag{42}$$

and gives very poor results when compared to the computer simulations. The approximation[58] [42]

$$h_{ij}(12) = f_i(1)f_j(2)h^{B}_{ij}(r) \quad r_{12}>\sigma_{ij} \tag{43}$$

$$=-1 \qquad r_{12}<\sigma_{ij}$$

where

$$\sigma_{ij}=(\sigma_i+\sigma_j)/2 \tag{44}$$

is constructed so that the functions $f_i(z)$ are required to satisfy the electroneutrality condition (42) for the inhomogeneous pair distribution function. This yields an integral equation for those functions. This construct of the inhomogeneous pair correlation function can give negative values of $g_{ij}(1,2)$. The problem is specially severe for dense systems, beyond 2 M of salt concentration or also for the test case of high surface density charge. A simple way to circumvent this problem was suggested by Caccamo, Pizzimenti and Blum[59]

$$h_{ij}(1,2) = f_i(1)f_j(2)h^{B}_{ij}(r)+A_{ij}(1,2) \qquad r_{12}>\sigma_{ij}$$
$$= -1 \qquad r_{12}<\sigma_{ij} \qquad (45)$$

where

$$A_{ij}(1,2)=Ah^{PY}_{ij}(r_{12}) \qquad z_1,z_2<2\sigma_{ij} \qquad (46)$$

the parameter A is adjusted to eliminate negative correlations from $h_{ij}(1,2)$. The results are, however not very sensitive to the exact value of A. The comparison to the Monte Carlo simulations is again good, this method yields for the test case with $\sigma^{*}=E_z/e\sigma^2=.7$ the density oscillations in the profile of the counterions. Figure 4 shows the comparison to the computer simulations of Torrie and Valleau[34].

The inhomogeneous pair correlation function $h_{ij}(1,2)$ can be obtained from the inhomogenous OZ equation

$$h_{ij}(1,2)-c_{ij}(1,2) = \sum_{k}\int d3 \;\; h_{ik}(1,3)\rho_k(3)\; c_{kj}(3,2) \qquad (47)$$

and a suitable closure for the direct correlation function.

$$c_{ij}(1,2)=-\beta\; u_{ij}(1,2) \qquad r_{12}>\sigma_{ij} \quad \text{(MSA2 approximation)} \qquad (48)$$

$$c_{ij}(1,2)=-\beta\; u_{ij}(1,2) + h_{ij}(1,2)-\ln[g_{ij}(1,2)] \qquad (49)$$
$$r_{12}>\sigma_{ij}$$

(HNC2 approximation)

The MSA2 approximation cannot be integrated explicitly, as is the case of the homogeneous MSA. When the ions are approximated by charged points then for some specific form of the density profiles $\rho_i(1)$ the OZ equation can be integrated, and series solutions have been given (Blum, Hernando and Lebowitz[42] and Carnie and Chan[60]). The numerical solution of the MSA2 and HNC2 has been extensively studied by Henderson and Plischke[61]. Approximate solutions of this kind will satisfy the contact theorem (16) as well as the electroneutrality and dipole sum rules[62]

The BGY-HNC2 equation has been solved numerically by Nieminen, Ashcroft and collaborators[63], however for systems with neutral molecules.

WLMB BASED EQUATIONS

Yet another integral equation is derived from the one particle direct correlation function $c_i(1)$ (22) by introducing relative coordinates for all field in the diagram representation and taking the derivatives with respect to those coordinates[57 64]. This yields and exact hierarchy of equations that is related to thy BGY hierarchy. The first member of the Wertheim-Lovett-Mou-Buff (WLMB) equation is

$$\vec{\nabla}_1\rho_i(1)+\beta\,\rho_i(1)\,\vec{\nabla}_1 u_i(1) = \rho_i(1)\sum_j \int d2\ c_{ij}(1,2)\ \vec{\nabla}_2\rho_j(2) \qquad (50)$$

This equation contains long range, divergent terms. Introducing the local potential $\phi(1)$ (29), we have[65 66]

$$\vec{\nabla}_1 \ln[\rho_i(1)]+\beta\,\vec{\nabla}_1\phi(1)+\ \beta\,\vec{\nabla}_1 u_i^{sr}(1) = \sum_j\int d2\ c_{ij}^{sr}(1,2)\ \vec{\nabla}_2\rho_j(2) \qquad (51)$$

This equation has been studied by Henderson and Plischke[66] in detail. As can be seen in the figure 5, it yields very good results for the test case of σ^*=.7. The calculations were performed solving both the HNC2 closure for the inhomogeneous pair correlation function, and also the MSA2 closure in a few cases.

A simplified version of the WLMB equation that produces reasonably good results was studied by Colmenares and Olivares[67]

KIRKWOODS EQUATION

An interesting approach has been suggested by Kjellander and Marcelja[68], based on the observation that for the HNC approximation the chemical potential can be obtained explicitly as a function of the pair potential $h_{ij}(r_{12})$ for an homogeneous fluid. Then, within the HNC the function $c_i(1)$ can be explicitly evaluated.

The central idea is to slice the three dimensional space into two dimensional layers that are homogeneous. The three dimensional OZ equation can be mapped into coupled set of N two dimensional OZ equations for a mixture of N components, each component is an ion in a different layer. The particles interact with a species dependent interaction pair potential. In the limit of an infinite number of layers this procedure yields the correct inhomogeneous OZ equation. The chemical potential $\mu_i(\alpha)$ of the ith ion in the αth layer is given by Kirkwoods equation:

$$\mu_i(\alpha) = kT \ln \rho_i(\alpha) + kT \ln \Lambda_0/\Delta z + V_i(\alpha)$$

$$+ \sum_{\beta, j} \rho_i(\beta) \int_0^1 d\lambda \int d\vec{R} \; g_{ij}(R,\alpha\beta;\lambda) \frac{\partial g_{ij}(R,\alpha\beta;\lambda)}{\partial\lambda} \tag{52}$$

where λ is the coupling parameter, Δz is the thickness of the layer, Λ_0 is the ideal gas fugacity, $V_i(\alpha)$ is the interaction between a particle in layer α and the wall; R is the two dimensional distance. In the HNC closure

$$c_{ij}(R,\alpha\beta) = h_{ij}(R,\alpha\beta) - u_{ij}(R,\alpha\beta)/kT - \ln[g_{ij}(R,\alpha\beta)] \tag{53}$$

Kirkwoods equation can be integrated to yield

$$\rho_i(\alpha) = \Delta z/\Lambda_0 \exp\left\{ \beta\mu_i(\alpha) + \sum_{\beta, j} \rho_i(\beta) \int d\vec{R} \left[1/2\, h_{ij}^2(R,\alpha\beta) - c_{ij}(R,\alpha\beta) \right.\right.$$

$$\left. - u_{ij}(R,\alpha\beta)/kT \right] - 1/2 \ln \left[g_{ij}(R,\alpha\beta)/\exp[u_{ij}(R,\alpha\beta)/kT] \right]_{R=0} - \Phi_i(\alpha) \tag{54}$$

where $\Phi_i(\alpha)$ is the average potential for layer α.

$$\Phi_i(\alpha) = 2\pi e^2/\varepsilon \sum_{\beta} \rho_i(\beta) |z_\alpha - z_\beta| \tag{55}$$

The results for the same case of $\sigma^* = .7$ is shown in figure 6. The agreement is also excellent.

II- SUM RULES FOR THE CHARGED INTERFACE

The sum rules for the charged interfaces can be classified in two categories:

1) the dynamic sum rules which are derived from balance of forces considerations,

2) the screening sum rules, which are specific to Coulomb forces. Because of the very long range of the electrostatic forces, the stability of the system requires that all charges surround themselves with a neutralizing cloud.

DYNAMIC SUM RULES

Consider the Born Green Yvon (BGY) equation[33 69 70]

$$-kT\ \vec{\nabla}_1\rho_i(1)=\ \rho_i(1)\ \vec{\nabla}_1 u_i(1)+\sum_j\int d2\ \rho_{ij}(1,2)\ \vec{\nabla}_1 u_{ij}(1,2) \qquad (56)$$

where k is Boltzmann's constant, T is the absolute temperature, $\rho_i(1)$ is the density of species i at position $\mathbf{r}_1\equiv x_1, y_1, z_1$. If species i is non spherically symmetric then the integration should also include the rotational coordinates, the Euler angles $\Omega_1\equiv\ \alpha_1\beta_1\gamma_1$. $u_i(1)$ is the single body potential acting on i. The pair potential is represented by $u_{ij}(1,2)$. Similarly $\rho_{ij}(1,2)$ is the pair density function, which can be written in the form

$$\rho_{ij}(1,2)=\rho_i(2)\rho_j(2)g_{ij}(1,2) \qquad (57)$$

where $g_{ij}(1,2)$ is the pair distribution function.

For charged particles it is convenient to separate the electrostatic from the nonelectrostatic contributions. For the singlet potential we have

$$u_i(1)=e_i\phi(1)+u_i^{sr}(1) \qquad (58)$$

where $\phi(1)$ is the local potential at $\mathbf{r}_1$, e_i is the electric charge of species i and $u_i^{sr}(1)$ is the sum of all nonelectrostatic forces, which includes the hard repulsion from the wall. Similarly, the two body contribution is

$$u_{ij}(1,2)=e_i e_j/\varepsilon r_{12}+u_{ij}^{sr}(1,2) \qquad (59)$$

where $u_{ij}^{sr}(1,2)$ is the nonelectrostatic interaction of the pair ij, and the first term is the electric potential between the charges of i and

j. Furthermore we use the function

$$h_{ij}(1,2)=g_{ij}(1,2)-1 \tag{60}$$

and the potential

$$\psi\ (1)=\phi(1)+\sum_j e_j \int d2\rho_j(1)/\varepsilon r_{12} \tag{61}$$

where $r_{12}=|\mathbf{r}_1-\mathbf{r}_2|$. The BGY equation is then transformed to

$$-kT\vec{\nabla}_1\rho_i(1)=\rho_i(1)\vec{\nabla}_1 u_i^{sr}(1)+\rho_i(1)e_i\vec{\nabla}_1\psi_i(1)$$

$$+\sum_j\int d2\rho_{ij}(1,2)\vec{\nabla}_1 u_{ij}^{sr}(1,2)+\rho_i(1)e_i\sum_j\int d2\rho_j(2)e_j h_{ij}(1,2)\vec{\nabla}_1(1/\varepsilon r_{12}) \tag{62}$$

We consider a system which is limited by an arbitrarily rough planar, but charged surface. The precise mathematical requirement is that there is a prism with an arbitrarily large cross section area S , and height L (the volume V=SL), such that the force through the walls parallel to z is of $O(S^{1-\delta})$, where $\delta>0$, as $S\to\infty$.

We integrate now over the whole prism of volume V. This is a generalization of the case of a decorated surface recently discussed in the literature[71], and is of interest in the discussion of the electrochemistry of rough surfaces.

We integrate the BGY equation in the volume of a prism of the same section S but smaller height $L_1<L$. Summing over all species i, we get

$$-kT\sum_i\int d1\vec{\nabla}_1\rho_i(1)=\sum_i\int d1\left[\rho_i(1)\vec{\nabla}_1 u_i^{sr}(1)+\rho_i(1)e_i\vec{\nabla}_1\psi_i(1)\right]$$

$$+\sum_i\int d1\sum_j\int d2\left[\rho_{ij}(1,2)\vec{\nabla}_1 u_{ij}^{sr}(1,2)+\rho_i(1)\rho_j(2)\,h_{ij}(1,2)\,\vec{\nabla}_1(e_ie_j/\varepsilon r_{12})\right] \tag{63}$$

Since in our system $\vec{\nabla}_1=\partial/\partial z_1$ the integral of the left hand side term can be easily performed

$$\int d\mathbf{r}_1 \vec{\nabla}_1 \rho_i(1) = \int_S dx_1 dy_1 \int_{z_s(x_1,y_1)}^{L_1} dz_1 \quad \partial\rho_i(1)/\partial z_1$$

$$= S\left[\ \rho_i(L_1) \ - 1/S\int dx_1 dy_1 \ \rho_i(x_1,y_1,z_s)\right]$$

$$\int d\mathbf{r}_1 \vec{\nabla}_1 \rho_i(1) = S\left[\ \rho_i(L_1) \ - \ \bar{\rho}_i(S)\ \right] \tag{64}$$

where we have defined the average contact value as

$$\bar{\rho}_i(0) = 1/S\int dx_1 dy_1 \ \rho_i(x_1,y_1,z_s) \tag{65}$$

To integrate the second term in the right hand side we use Poisson's equation

$$\nabla_1^2\psi(1) = -4\pi/\varepsilon \sum e_i\rho_i(1) = -\vec{\nabla}_1.\mathbf{E}(1) \tag{66}$$

where we have used the electric field

$$\mathbf{E}(1) = -\vec{\nabla}_1\psi(1) \tag{67}$$

Substitution into the second term of the right hand side leads to

$$\int d\mathbf{r}_1\left[\sum e_i\rho_i(1)\right]\left[E_z(1)\right] = -\ \varepsilon/4\pi\int d\mathbf{r}_1 \ \nabla_1^2\psi(1)\ E_z(1)$$

$$= \ \varepsilon/4\pi\int d\mathbf{r}_1\left[\vec{\nabla}_1 \ . \ \mathbf{E}(1)\right] \ E_z(1) \tag{68}$$

where $\mathbf{E}(1)$ is the electric field at position $\mathbf{r}_1$, and $E_z(1)$ is the z component. Integrating by parts, we get

$$\int d\mathbf{r}_1\left[\sum e_i\rho_i(1)\right]\left[E_z(1)\right] = \varepsilon/8\pi\int_S dx_1 dy_1\int_{z_s(x_1,y_1)}^{L_1} dz_1 \quad \partial E_z^2(1)/\partial z \tag{69}$$

$$+\ \varepsilon/4\pi\int dx_1 dy_1 dz_1\left[E_z(1)\ \partial E_x(1)/\partial x_1 + E_z(1)\ \partial E_y(1)/\partial y_1\right]$$

The second term of the right hand side is zero: For a periodic interface in the x and y directions, if we take S to be the surface of a unit cell, then the terms like $\partial E_x(1)/\partial x_1$ will be equal but with opposite sign for neighboring cells. For the general random interface we conjecture that this term is finite: then in the limit $S \to \infty$ the contribution vanishes. We have

$$1/S \int dr_1 \left[\sum e_i \rho_i(1)\right] \left[E_z(1)\right] = -\varepsilon/8\pi \, \langle E_z^2 \rangle_S \tag{70}$$

where the average square field in the z direction is

$$\langle E_z^2 \rangle_S = 1/S \int_S dx_1 dy_1 \; E_z^2(x_1,y_1,z_s) \tag{71}$$

The first term yields

$$1/S \int d1 \; \rho_i(1) \vec{\nabla}_1 u_i^{sr}(1) = \langle \rho_i(1) \; \partial u_i^{sr}(1)/\partial z_1 \rangle_S \tag{72}$$

where

$$\langle \rho_i(1) \; \partial u_i^{sr}(1)/\partial z_1 \rangle_S = 1/S \int_S dx_1 dy_1 \int_{z_s(x_1,y_1)}^{\infty} dz_1 \;\; \rho_i(1) \; \partial u_i^{sr}(1)/\partial z_1 \tag{73}$$

The last term in the right hand side of equation (63) is the average of the pair forces. We write

$$\begin{aligned} I_p &= \int_S dx_1 \, dy_1 \int_S dx_2 dy_2 \int_{z_s(x_1,y_1)}^{L_1} dz_1 \int_{z_s(x_2,y_2)}^{L} dz_2 \; \sum_{ij} F_{ij}(1,2) \\ &= \int_S dx_1 \, dy_1 \int_S dx_2 dy_2 \int_{z_s(x,y)}^{L_1} dz_1 \left[\int_{z_s(x,y)}^{L_1} dz_2 + \int_{L_1}^{L} dz_2 \right] \sum_{ij} F_{ij}(1,2) \end{aligned} \tag{74}$$

where

$$F_{ij}(1,2) = \left[\rho_{ij}(1,2) \vec{\nabla}_1 u_{ij}^{sr}(1,2) + \rho_i(1)\rho_j(2) \; h_{ij}(1,2) \; \vec{\nabla}_1 (e_i e_j / \varepsilon r_{12}) \right] \tag{75}$$

clearly

$$F_{ij}(1,2) = -F_{ji}(2,1) \tag{76}$$

from where the first double integral in (74) vanishes. Since the interactions are short ranged, the second double integral yields the virial contribution to the bulk pressure P

$$\begin{aligned} P &= 1/S \int_S dx_1 dy_1 \int_S dx_2 dy_2 \int_{z_s(x,y)}^{L_1} dz_1 \int_{L_1}^{L} dz_2 \sum_{ij} F_{ij}(1,2) \\ &= 2\pi/3 \sum_{ij} \rho_i \rho_j \int_0^{\infty} dr\ r^3 \left[e_i e_j h_{ij}(r)/\varepsilon r^2 + g_{ij}(r)\ \partial u_{ij}(r)/\partial r \right] \end{aligned} \tag{77}$$

Putting it all together yields the general contact theorem for a surface that is planar on the average, but not necessarily smooth:

$$kT \sum_i \bar{\rho}_i(0) = P + \varepsilon/8\pi \langle E_z^2 \rangle_S - \sum_i \langle \rho_i(1)\ \partial u_i^{sr}(1)/\partial z_1 \rangle \tag{78}$$

This theorem is a generalization of the previously derived contact theorems to the realistic case of non smooth electrode surfaces. It contains the previous results as particular cases. If the interface is a smooth hard wall then the surface averages become the surface values of the parameters and we get

$$kT \sum_i \rho_i(0) = P + \varepsilon/8\pi\ E_z^2(0) - \sum_i \langle \rho_i(1)\ \partial u_i^{sr}(1)/\partial z_1 \rangle \tag{79}$$

where the last term is now

$$\langle \rho_i(1)\ \partial u_i^{sr}(1)/\partial z_1 \rangle = \int_0^{\infty} dz_1\ \ \rho_i(1)\ \partial u_i^{sr}(1)/\partial z_1 \tag{80}$$

when $u_i^{sr}(1)$ is zero then we recover the previously obtained results

$$kT \sum_i \rho_i(0) = P + \varepsilon/8\pi\ E_z^2(0) \tag{81}$$

for the primitive model with a continuum solvent of dielectric constant ε, and

$$kT\left[\sum_{i} \rho_{i}(0)+\sum_{n} \rho_{n}(0)\right]= P + 1/8\pi\ E_{z}^{2}(0) \tag{82}$$

for the molecular solvent case. Here the second sum in the left hand side is over all the neutral molecules in the system, while the first is over all the ions present.

When the surface has an array of sticky adsorption sites, such as in the case of the SSM model discussed below, then the adsorption potential has the form

$$\exp[-\beta u_{a}(\mathbf{r})]= 1 + \lambda_{a}(\mathbf{R})\delta(z) \tag{83}$$

with

$$\lambda_{a}(\mathbf{R})= \sum_{n_1 n_2} \lambda_{a}\ \delta(\mathbf{R}-n_1\mathbf{a}_1-n_2\mathbf{a}_2) \tag{84}$$

Here $\mathbf{R}$=x, y is the position at the electrode surface, and z the distance to the contact plane, which is at a distance σ/2 from the electrode. In (84), n_1,n_2 are natural numbers, and $\mathbf{a}_1,\mathbf{a}_2$ are lattice vectors of the adsorption sites on the surface. The number λ_a represents the fugacity of an adsorbed atom of species a. Define now the regular part of the *density function*

$$\rho_{i}(1)=y_{i}(1)\exp[-\beta u_{i}^{sr}(1)] \tag{85}$$

Replacing into the general contact theorem (78) yields

$$kT\sum_{i} \bar{\rho}_{i}(0)= P + \varepsilon/8\pi<E_{z}^{2}>_{S} + kT\lambda_{a} \sum_{i}<\partial y_{i}(1)/\partial z_{1}> \tag{86}$$

This theorem has been verified recently by F.Cornu, for the exactly solved model of a one component plasma in two dimensions[72]

THE SCREENING SUM RULES

In systems that are electrically neutral, any fixed arrangement of charges is screened by the mobile charges of the system. In homogeneous bulk phase this is an intuitively natural fact, because if the long ranged Coulomb forces would not be screened then the partition function would not exist (it would diverge), and matter would not be stable.

This is expressed by the fact that the charge distribution around a given charge e_i is of equal value but opposite sign.

In the homogeneous bulk phase this is a natural fact:

$$-e_i=\sum_j \int d2\rho_j(2)\ \ e_j\ h_{ij}(1,2) \tag{87}$$

Rotational invariance in bulk fluids require that not only charges but also multipole of arbitrary order should be screened by the mobile charges of the media[73]. This fact is much less intuitive in the neighborhood of charged objects, in particular in the neighborhood of a charged electrode. However the theorems hold and in classical mechanics, at least, perfect screening of all multipoles occurs, in the homogeneous or inhomogeneous systems.

These conclusions are supported by the results of the exactly solved Jancovici model[74]. However, perfect screening of all multipoles does not occur in quantum systems or in systems out of equilibrium[75].

As a consequence of the screening the second moment of the pair distribution function must be normalized. This is the Stillinger-Lovett moment relation[76]. As was shown by Outhwaite[77], it can be written in the form of a normalization condition for the electrostatic potential

$$\psi_i(\mathbf{r})= 1/\varepsilon\ \left[e_i/r+\sum_j \rho_j e_j \int dr_1\ \ h_{ij}(r_1)/(|\mathbf{r}-\mathbf{r}_1|)\right] \tag{88}$$

We have then that the second moment relation is

$$1/kT\left[\ \sum_j \rho_j e_j \int dr_1\ \ \psi_i(1)\right]=1 \tag{89}$$

Carnie and Chan[78] have shown that this normalization condition is also valid for the inhomogeneous systems of charged particles: Consider the inhomogeneous Ornstein-Zernike (OZ) equation

$$h_{ij}(1,2)-c_{ij}(1,2) = \sum_k \int d3\ \ h_{ik}(1,3)\rho_k(3)\ \ c_{kj}(3,2) \tag{90}$$

where $c_{ij}(1,2)$ is the direct correlation function and the singlet density function $\rho_i(1)$ satisfies the electroneutrality condition

$$\sum_j e_j \int dr_1\ \rho_i(1) = -q_s S \tag{91}$$

where q_s is the surface charge density and S is the area of the interface. The pair distribution function satisfies the sum rule

$$-e_i = \sum_j \int d2 \rho_j(2)\ e_j\ h_{ij}(1,2) \tag{92}$$

From the diagram expansion we write the direct correlation function as

$$c_{ij}(1,2) = c^o_{ij}(1,2) - \beta u^{el}_{ij}(1,2) \tag{93}$$

where

$$u^{el}_{ij}(1,2) = e_i e_j / \varepsilon r_{12} \tag{94}$$

is the electrostatic part of the interaction and $c^0_{ij}(1,2)$ is the short ranged part of the direct correlation function. in the dense media

$$\phi_i(1,2) e_j = -u^{el}_{ij}(r_{12}) + \sum_k \int dr_3 u^{el}_{ik}(r_{13}) \rho_k(r_3) h_{kj}(3,2) \tag{95}$$

and from the OZ equation (90) we get

$$h_{ij}(1,2) = -\beta \phi_j(1,2)\ e_i\ - c^0_{ij}(1,2)\ +\ \sum_k \int d3\ \ c^0_{ik}(1,3) \rho_k(3)\ h_{kj}(3,2) \tag{96}$$

Multiplying this equation by $e_j \rho_j(2)$, integrating over $\mathbf{r}_2$ and summing over j , yields after use of the electroneutrality condition (92)

$$1/kT \sum_i e_i \int dr_1 \rho_i(1) \phi_i(1,2) = 1 \tag{97}$$

which is the generalization of the Outhwaite formula of the Stillinger Lovett sum rule for inhomogeneous charged systems.

OTHER SUM RULES

For flat hard electrode surfaces there are number of other sum rules. A complete review of these rules was recently made by Ph.A.Martin[79]. We will just mention a few of the more relevant to the calculation of density profiles in the electric double layer[80].

$$kT\ \partial \ln \rho_i(1)/\partial E_0 = \sum_j \int d2\rho_j(2)\ e_j\ h_{ij}(1,2)\ (z_2-z_1) \tag{98}$$

where E_0 is the bare field at the electrode surface. The differential capacity, which is defined by

$$C_d = \partial\ q_s/\partial\ \phi_i(1) \tag{99}$$

where q_s is the surface charge, $q_s=E_0\varepsilon/4\pi$, and $\phi(1)$ is the potential drop, satisfies the sum rule

$$1/C_d = 8\pi^2/\varepsilon^2 S \sum_{ij} \int d1d2\rho_j(2)\ \rho_i(1)\ e_j e_i h_{ij}(1,2)\ (z_2-z_1)^2 \tag{100}$$

The surface tension γ obeys relations that can be given in terms of the direct correlation function[81 82]

$$\gamma = (\pi kT/2)\sum_{ij}\int dz_1 dz_2\ \partial\rho_i(1)/\partial z_1\ \partial\rho_j(1)/\partial z_2 \int dr_{12} r_{12}^3\ c_{ij}(1,2) \tag{101}$$

Using the Ornstein Zernike equation we get the form that contains the pair correlation function

$$\gamma = (\pi/2kT)\sum_{ij}\int dz_1 dz_2\ \rho_i(1)\partial u_i(1)/\partial z_1\ \rho_j(2)\ \partial u_j(1)/\partial z_2 \int dr_{12} r_{12}^3\ h_{ij}(1,2) \tag{102}$$

These sum rules provide ways of asserting the accuracy of the different approximations used to compute the charge and ion density near charged walls.

III- THE STICKY SITE MODEL

The theoretical discussion of smooth surfaces is considerably simpler than that of a realistic surface, in which the solid, usually a metal, has a well defined crystal structure. The reason is that in the case of a smooth surface the problem is one dimensional, rather than three dimensional. The analysis of a realistic metal surface potential in contact with an ionic solution is extremely difficult, and requires the use of very large computers. We would like to discuss a simple model of a structured interface which predicts surface phase behavior, for the adsorbed layers, and which is mathematically tractable. In fact, if the correlation functions of the smooth surface model are known to all orders, then the properties and correlation functions of our model can be computed exactly, at least in principle.

The model[83 84] combines two ideas that have been used a very long time ago : Boltzmann's sticky potential[85], and the adsorption site model of Langmuir[86]. The elegant work of Baxter[87] in which the Percus-Yevick approximation of the sticky hard sphere model is solved and discussed, shows that this model has a particularly simple mathematical solution. In Baxter's work the potential has the form

$$\exp\,[-\beta u_a(\mathbf{r})] = 1 + \lambda\delta(r-\sigma^-) \qquad (103)$$

where $\beta=1/kT$ is the usual Boltzmann thermal factor, $u(\mathbf{r})$ is the intermolecular potential, λ is the stickiness parameter, $\mathbf{r}=(x,y,z)$ is the relative position of the center of the molecules, and σ is the diameter of the molecules. The right hand side term represents the probability of two molecules being stuck by the potential $u_a(\mathbf{r})$: this occurs only when the two molecules actually touch, and for this reason we use the Dirac delta function $\delta(r-\sigma^-)$, which is zero when the molecules do not touch, is infinity when they do, but the integral is normalized to one. The stickiness is represented by the parameter λ, which except for a normalization factor, can be considered as the fugacity of the formation of the pair.

The Langmuir adsorption sites can be represented by a collection of sticky sites of the same form as was suggested by Baxter. Only that now we do not have a sphere covered uniformly by a layer of glue, but rather a smooth, hard surface with sticky points, which represent adsorption sites where actual chemical bonding takes place. For this model, equation (103) has to be changed to

$$\exp[-\beta u_a(\mathbf{r})] = 1 + \lambda_a(\mathbf{R})\delta(z) \tag{104}$$

with

$$\lambda_a(\mathbf{R}) = \sum_{n_1 n_2} \lambda_a \, \delta(\mathbf{R} - n_1\mathbf{a}_1 - n_2\mathbf{a}_2) \tag{105}$$

Here $\mathbf{R}=(x,y)$ is the position at the electrode surface, and z the distance to the contact plane, which is at a distance $\sigma/2$ from the electrode. In (105), n_1,n_2 are natural numbers, and $\mathbf{a}_1,\mathbf{a}_2$ are lattice vectors of the adsorption sites on the surface. The number λ_a represents the fugacity of an adsorbed atom of species a, onto the surface which has a perfectly ordered array of adsorption sites. While this is not a requirement of the model, it makes the mathematical discussion much simpler.

Consider now a fluid consisting of only one kind of particles of diameter σ , near a smooth, hard wall with sticky sites. The fluid has N particles and the volume of the system is V. The Hamiltonian of the system is

$$H = H^0 + H^2 \tag{106}$$

where H^0 is the hamiltonian of the system in the absence of the sticky sites on the hard wall, and H^2 is the sticky sites interaction

$$H^2 = \sum_{i=1}^{N} u_a(\mathbf{r}_i) \tag{107}$$

where $u_a(\mathbf{r}_i)$ is the sticky interaction of eq.(104).

The canonical partition function of this model is[83]

$$Z = \frac{1}{\prod_a N_a!} \int \exp[-\beta H^0] \prod_{i=1}^{N} \prod_a [\, 1 + \lambda_a(\mathbf{R}_i)\delta(z_i)] \, d\mathbf{r}_i \tag{108}$$

Expanding the product in (108) and integrating the Dirac delta functions we get, using the single component notation to avoid heavy and unnecessarily complex equations, with the understanding that in the multi component case λ is a vector quantity with components $\lambda_1..\lambda_a$, and the necessary modifications of N! and the integrations have to be made.

$$Z = Z^0 \sum_{\substack{\text{all sites} \\ \text{on the surface}}} (\lambda^s/s!)\, \rho_s^0(\mathbf{r}_1 \ldots \mathbf{r}_s) \tag{109}$$

where $\mathbf{r}_i = \mathbf{R}_i, 0$ is the position of the i^{th} adsorbing site on the surface. $\rho_s^0(\mathbf{r}_1 \ldots \mathbf{r}_s)$ is the s-body correlation function of the smooth interface model.

$$\rho_s^0(\mathbf{r}_1 \ldots \mathbf{r}_s) = \frac{1}{(N-s)!Z^0} \int \exp[-\beta H^0] \prod_{i=s+1}^{N} d\mathbf{r}_i \tag{110}$$

$$= g_s^0(\mathbf{r}_1 \ldots \mathbf{r}_s) \prod_{i=1}^{s} \rho^0(\mathbf{r}_i) \tag{111}$$

Equation (111) defines the s-body correlation function $g_s^0(\mathbf{r}_1 \ldots \mathbf{r}_s)$ while $\rho^0(\mathbf{r}_i)$ is the singlet density of the smooth wall inhomogeneous problem. The smooth wall partition function is

$$Z^0 = \frac{1}{N!} \int \exp[-\beta H^0] \prod_{i=1}^{N} d\mathbf{r}_i \tag{112}$$

The important observation is that in our sticky sites model (SSM), the excess properties of the interface depend only on the correlation functions of the smooth interface model. In fact, introducing the potentials of mean force $w_s^0(\mathbf{r}_1 \ldots \mathbf{r}_s)$

$$g_s^0(\mathbf{r}_1 \ldots \mathbf{r}_s) = \exp\left[-\beta\, w_s^0(\mathbf{r}_1 \ldots \mathbf{r}_s)\right] \tag{113}$$

$$Z/Z^0 = \sum_{\substack{\text{all sites}\\ \text{on the surface}}} \frac{\lambda^s \prod_{i=1}^{s} \rho^0(\mathbf{r}_i)}{s!} \exp\left[-\beta \sum w_s^0(\mathbf{r}_1 \ldots \mathbf{r}_s)\right] \tag{114}$$

The left hand side of (114) is closely related to the excess free energy of the sticky site model as compared to the smooth wall problem. In fact, from standard thermodynamics the excess free energy is

$$\Delta F^S = -1/\beta \ln(Z/Z^0) \tag{115}$$

It is clear that in (114) the right hand side is the grand canonical partition function of the two dimensional lattice gas in which the fugacity is $z_a = \lambda\rho_a^0(\mathbf{r}_i) = \lambda\rho_a^0(0)$, where we have used the fact that the single particle density of the smooth wall problem depends only on the distance to the electrode z, and not on the position of the adsorbed particle on the interface. The SSM is a model that decouples the structure of the interface from the inhomogeneous charged fluid problem, which in itself is a very difficult one, even for the smooth interface. The excess properties of the lattice surface are formally the same as two the dimensional lattice gas problems that have been extensively investigated, notably in connection with the Ising model[88]. If the area of the interface is S , and the number of sites is M, the number of sites per unit area is

$$\omega = M/S \tag{116}$$

Define also the excess free energy per unit area

$$\Delta f^S = \Delta F^S/S \tag{117}$$

and the fraction of occupied sites $\theta_a = N_a/M$ of particles of species a. If we compare (109) to the grand canonical partition function of a lattice gas on the sites of our model, we see that the number of sites occupied by particles of species a is

$$\langle N_a \rangle = \partial \ln Z_N / \partial \ln \lambda_a \tag{118}$$

and using (116) the fraction of occupied sites is

$$\theta_a = (1/M)\partial \ln Z_N / \partial \ln \lambda_a \tag{119}$$

The excess free energy Δf^S is also the excess pressure due to the presence of the discrete sites structure on the interface.

EXACT RELATIONS FOR THE SSM

SUM RULES FOR THE FLUID DENSITY FUNCTIONS

The SSM for a charged interface satisfies a number of exact relations: The first one is the analog to the Gibbs absorption equation: If we define the surface excess in the SSM of species a[83]

$$\Delta\Gamma_a=\int_0^\infty dz[\rho_a(z)-\rho_a^0(z)] \tag{120}$$

where $\rho_a^0(z)$ is the density profile of the smooth wall, and $\rho_a(z)$ is that of the SSM, then we must have

$$\Delta\Gamma_a=-\beta\partial\Delta f^S/\partial\ln\lambda_a \tag{121}$$

Because of the singularity in the f-function, the distribution functions also must have a singularity. They must be of the form

$$\rho_a(\mathbf{r})=\left[1+\lambda_a(\mathbf{R})\delta(z)\right]y_a(\mathbf{r}) \tag{122}$$

where $y_a(\mathbf{r})$ is the regular part of the distribution function. The average number of adsorbed particles is given by the integral of the singular part of the density $\rho_a(\mathbf{r})$

$$<N_a>=\int\lambda_a(\mathbf{R})\delta(z)y_a(\mathbf{r})d\mathbf{r} \tag{123}$$

since this integral is actually a sum over the sticky sites m, we get the relation

$$\theta_a=\lambda_a y_a(\mathbf{r}_m) \tag{124}$$

which is exact : The stickiness parameter λ_a is the ratio between the number of adsorbed and non adsorbed particles at site $\mathbf{r}_m$ of the lattice. Integrating (122) over all space yields

$$N=<N_a>+\int y_a(\mathbf{r})d\mathbf{r} \tag{125}$$

which can be rewritten as

$$<N_a>=-\int d\mathbf{r}[y_a(\mathbf{r})-\rho_a] \tag{126}$$

Because of the analogy of the partition function to the grand canonical partition function, a relation similar to the compressibility relation holds

$$\langle N_a^2\rangle - \langle N_a\rangle^2 = \lambda_a \frac{\partial \langle N_a\rangle}{\partial \lambda_a} \qquad (127)$$

EXACT RESULTS FOR THE ADSORBED LAYER

Consider the case of a simple salt dissolved in water, near a metallic electrode: in the SSM there will be three components, the anion, the cation and the solvent, and the lattice atoms. In the limiting case of the SSM, the sizes of the different species play a crucial role in the possible ordering of the ad layers at the interface. It will be convenient to picture the ions as having a hard sphere core with a diameter σ_a, σ_b, and the solvent as having a hard core with diameter σ_n. The lattice spacing of the metal surface is d, and because it is the most stable surface, we will restrict ourselves to discussing the (111) surface of the fcc crystals, or the (100) face of the hcp crystal, that is, the triangular lattice. In the most general case, all three components can be adsorbed competitively and this situation can give raise to very complex phase diagrams[89]. This most general case can be modeled by the spin S=1 Ising model, has a very rich phase diagram, involving first and second order phase transitions and multi critical points. However, in most electrochemical situations the electrode surface is polarized either positively or negatively, which means that either the cation or the anion is strongly repelled from the surface, and therefore we need to consider the adsorption of either a or b and the solvent n on the electrode. This implies a drastic simplification in the model, because now we can discuss at least the case of commensurate adsorption in terms of models that have been solved analytically, such as the spin S=1/2 Ising model and the hard hexagon gas model. The phase transitions predicted for these models seem to be reasonable in terms of the currently available experimental evidence. Consider

$$Z/Z^0 = \sum_{\substack{\text{all sites}\\ \text{on the surface}}} \frac{\lambda^s \prod_{i=1}^{s} \rho^0(\mathbf{r}_i)}{s!} \exp\left[-\beta \sum w_s^0(\mathbf{r}_1 \ldots \mathbf{r}_s)\right] \qquad (114)$$

Here the sum has two kind of factors, the fugacity of the adsorbed molecules

$$\mathfrak{z}_a = \lambda_a \rho_a^0(\mathbf{r}\ ) \tag{130}$$

and another factor which corresponds to the interaction of the adsorbed particles

$$g_s^0(\mathbf{r}_1 \ldots \mathbf{r}_s) = \exp\left[-\beta \sum w_s^0(\mathbf{r}_1 \ldots \mathbf{r}_s)\right] \tag{131}$$

Equation (114) is the grand canonical partition function for a lattice gas with arbitrary interactions. In the most general case, the adsorbate could occupy one or more than one single adsorption site, and any adsorbed molecule could interact with an arbitrary number of neighbors. This problem is however quite untractable, and therefore not very useful. The first approximation that comes to mind is the Kirkwood superposition approximation

$$g_s^0(\mathbf{r}_1 \ldots \mathbf{r}_s) = \prod_{1<i,\, j<s} g_2^0(\mathbf{r}_i, \mathbf{r}_j) \tag{132}$$

Because of geometrical considerations, this approximation is probably a good one for molecules with short range interactions such as hard spheres, and not a very good one for unscreened charged particles. In terms of the effective potentials, we have

$$w_s^0(\mathbf{r}_1 \ldots \mathbf{r}_s) = \sum_{1<i\, j<s} w_2^0(\mathbf{r}_i, \mathbf{r}_j) \tag{133}$$

With this approximation the problem can be mapped onto the lattice gas problem with arbitrary interactions, which is still a difficult problem. If we restrict the interactions to nearest neighbors only, then not only is the problem a tractable one, but there is a rather extensive literature on cases that are of physical interest, for which the phase diagram of the two dimensional lattice gas is known, and hence the adsorption isotherm can be deduced.

Consider the case of a simple salt dissolved in water, near a metallic electrode: in the SSM there will be three components: the anion, the cation and the solvent, and the lattice atoms. In the limiting case of the SSM, the sizes of the different species play a crucial role in the possible ordering of the ad layers at the interface. It will be convenient to picture the ions as having a hard sphere core with a diameter σ_a, σ_b, and the solvent as having a hard core with diameter σ_n. The lattice spacing of the metal surface is d, and because it is the most stable surface, we will restrict ourselves to the (111) surface of the fcc crystals, or the (100) face of the hcp crystal, that is, the triangular lattice. In the most general case, all three components can be adsorbed competitively, and this situation can give rise to very complex phase diagrams. In most electrochemical situations the electrode surface is polarized either positively or negatively, which means that either the cation or the anion is strongly repelled from the surface, and therefore we need to consider the adsorption of either a or b and the solvent n on the electrode. This implies a drastic simplification in the model, because now we can discuss at least the case of commensurate adsorption in terms of models that have been solved analytically, such as the spin s=1/2 Ising model and the hard hexagon gas model. The phase transitions predicted for these models seem to be reasonable in terms of the currently available experimental evidence.

There are two cases of chemisorption of electrochemical interest: In the first one, the charge of the adsorbate is neutralized by the electrons in the metal, and this means that the interactions between neighbors on the surface is attractive. If we are far from the point of zero charge, and the metal is negatively charged, the contact probability of the anions a is zero for all practical purposes and we have only the cation b or the solvent n on the adsorption sites. The problem is then reduced to a spin s=1/2 Ising model with ferromagnetic interactions. In the second case there is no discharge of the adions by the metal. The interactions between the ions of the same sign is clearly repulsive, so that the nearest neighbor sites to an occupied site are not going to be occupied.

The possible existence of phase transitions was discussed in the work of Huckaby and Blum[90]. The observation is that the SSM model maps the three dimensional interface onto a two dimensional lattice problem. The phase behavior in the interphase is determined by the mapping of the parameters, and exact conditions on the existence of phase transitions can be given.

The simplest electrolyte has three components that can be adsorbed onto the sites of the metal: the anion, the cation and the solvent. The possible phase behavior of such a system has been discussed in the literature and although there are some exact results on the phase behavior of the adsorbed layer, the study of this system remains an open problem. The simpler case of two component adsorption is discussed in more detail.

THE THREE STATE ADSORPTION MODEL

This is the case of a simple salt dissolved in a solvent like water. We call the ions a and b, and the solvent n. since this is a dense system, then the sticky sites will never be empty, they will be occupied by either by a, b or n. Now there are various possibilities, because the size of adsorbate may be bigger or smaller that the site-site separation. In the first case the adsorbate will exclude not only its own site but also the neighboring ones, and the problem becomes the hard hexagon problem of Baxter when the interactions of the neighboring sites are ignored altogether. If the adsorbate is smaller than the lattice site separation then it can been shown that the problem can be reduced to the two component lattice gas: This case was recently studied by Rikvold[89]. In fact we have, by direct comparison of the partition function and the hamiltonian of the three state lattice gas

$$-(1/\beta)\ \ln \Xi = -\phi_{aa} \sum_{<i,j>} c_i^a c_j^a \;-\; \phi_{ab} \sum_{<i,j>} \left(c_i^a c_j^b + c_i^b c_j^a \right)$$

$$-\; \phi_{bb} \sum_{<i,j>} c_i^b c_j^b \;-\; \mu_a \sum_i c_i^a \;-\; \mu_b \sum_i c_i^b \tag{134}$$

where we have used Rikvold's notation: the operators c_i^x are 1 when site i is occupied by x, and 0 otherwise. In our case x is either a or b, and the solvent n counts as the empty site. The interactions are

$$\phi_{aa} = w_{aa} - w_{nn} = -(1/\beta)\ \ln \left(g^{0}_{aa}(\mathbf{r}_i,\mathbf{r}_j) \Big/ g^{0}_{nn}(\mathbf{r}_i,\mathbf{r}_j) \right) \qquad (135)$$

i,j are neighboring
sites

and similar relations for ϕ_{ab} and ϕ_{bb}. The last two sums in (134) correspond to the single occupation of a site by x :

$$\mu_a = (1/\beta)\ \ln\ \mathfrak{z}_a/\mathfrak{z}_n = (1/\beta)\ \ln \left[\frac{\lambda_a \rho^{0}_{a}(\mathbf{r}_i)}{\lambda_n \rho^{0}_{n}(\mathbf{r}_i)} \right] \qquad (136)$$

and a similar expression for μ_b.

The possible arrangements on the triangular lattice of a three component mixture is quite complicated and has been studied recently by Collins et al.[91](see also Y.Saito[92]). There are 10 different ordered phases on the surface, when only next nearest neighbors are interacting. Of course the picture is even more complicated for longer ranged interactions. The geometrical arrangement is either (1x1), and there are three phases of this kind which correspond to pure a, pure b and pure solvent n. These are dense phases and correspond to total coverage (θ=1) for each of these components. These are limiting cases when there is very strong adsorption of any of the components and attractive interaction between atoms of the same kind. If we consider ions with their charge, then because of the Coulombic repulsion the interaction is repulsive or antiferromagnetic and the dense phases with either pure a or pure b are to be excluded. In the case of the underpotential deposited dense monolayers. This is explained by the fact that the metal cations are not charged at the surface, and therefore do not repell each other.

The remaining 7 phases are mapped on the ($\sqrt{3}$x$\sqrt{3}$) lattice. The unit cell of this lattice contains three sites of the original triangular lattice, and appears rotated by 30° with respect to it. Each of the three sites can be occupied by either of the components of the mixture, but because of the symmetry (geometrical degeneracy) of the phases, the number of distinct coverings is reduced from 24 to 7. In table 1, which is taken directly from Collins's work we show the coverage, energy and degeneracy of each of the ordered phases.

There are two cases chemisorption of electrochemical interest: In the first one, the charge of the adsorbate is neutralized by the electrons in the metal, and this means that the interactions between neighbors on the surface is attractive. If we are far from the point of zero charge, and the metal is negatively charged, the contact probability of the anions a is zero for all practical purposes and we have only the cation b or the solvent n on the adsorption sites. The problem is then reduced to an spin s=1/2 Ising model with ferromagnetic interactions, which will be discussed in the next section.

In the second case there is no discharge of the adions by the metal. The interactions between the ions of the same sign is clearly repulsive, and that of opposite sign is attractive: we have then

$$\phi_{ab} < 0, \text{ and } \phi_{aa}, \phi_{bb} > 0 \tag{137}$$

This is definitely the antiferromagnetic case. Let us assume for simplicity that we are dealing with the symmetric case in which

$$\phi_{aa} = \phi_{bb} \tag{138}$$

Then there are two possible situations: either the repulsive interactions predominate and

$$- \phi_{aa} > \phi_{ab} \quad \text{(case I)} \tag{139}$$

or the ab attractions predominate

$$- \phi_{aa} < \phi_{ab} \quad \text{(case II)} \tag{140}$$

The phases in case I for a possible set of parameters is pictured in figure 7. Here we may have phases ranging from pure a, for very large negative μ_a to pure b for very large negative μ_b. In the example of case II the ab attraction predominates so as to render the dilute phases with θ_b=1//3, 2/3 thermodynamically unstable. This case is pictured in figure 8.

Complicated phase diagrams may exist in the neighborhood of the point of zero charge for systems in which there is strong chemisorption of some of the species. In the absence of specific adsorption one would expect that either μ_a or μ_b is large , but not both at the same time. In these cases we are in the asymptotic regime where the system can be treated by two state models. This will be done in the next section.

THE TWO STATE ADSORPTION MODEL

We specialize now to the case in which only one of the ionic species of the solution or the solvent is adsorbed. In this case the structure of the phase diagrams is simpler, which at the same time allows for a more general discussion, because we can include the cases in which the size of the adsorbate is variable.

The following discussion is taken from the work of Huckaby and Blum[90]. We consider a system in which we have a triangular lattice of sticky sites on a hard plane surface. The spacing between the sites of the lattice is d. This surface is in contact with a solution. Only two states of occupation are allowed: the sites are either occupied by an ion or by the solvent, or alternatively in the case of a pure fluid, by a fluid particle or none. The fluid particles have an exclusion diameter σ, which may or may not be associated with a hard core potential. Otherwise the interactions are arbitrary. We assume however that the pair correlations on the surface decay sufficiently fast so that we need to take into account first neighbor interactions only. There are two possible situations: If the adsorbate diameter σ is smaller than the lattice spacing d, then there are two possible phases, a dense, crystalline one and a dilute disordered one. Three is a first order transition between them. If the adsorbed particles exclude all next nearest neighbors, that is when

$$d<\sigma<\sqrt{3}d \qquad (141)$$

then the problem is exactly analogous to the hard hexagon problem[93] of Baxter. In this case there is a second order phase transition between an ordered $\sqrt{3}\times\sqrt{3}$ phase and a disordered one.

SINGLE SITE OCCUPANCY

Consider again equation (114) together with the superposition approximation (133):

$$Z/Z^0 = \sum_{\substack{\text{All sites} \\ \text{on the surface}}} \frac{\lambda^s \prod_{i=1}^{s} \rho^0(\mathbf{r}_i)}{s!} \quad \exp\left[-\beta \sum_{nn} w_2^0(\mathbf{r}_i,\mathbf{r}_j)\right] \tag{142}$$

where the subscript nn means that the pairs $(\mathbf{r}_i,\mathbf{r}_j)$ in the sum inside the square brackets are nearest neighbors. As was done before (see eq.134), we can write (142) as a lattice gas partition function[94]

$$Z/Z^0 = \sum_{\{t_i\}} \exp\left[-\beta w \sum_{nn} t_i\, t_j + \beta\mu \sum_i t_i \right] \qquad t_i=0,1 \tag{143}$$

where t_i is the occupation number of site i which can be either 0 for the site when it is occupied by the solvent (or empty) and 1 when it is occupied. Furthermore

$$\beta w = -\ln g_2^0(d) \tag{144}$$

$$\beta\mu = \ln\left[\lambda \rho^0(0)\right] \tag{145}$$

This partition function can be mapped onto an Ising model with spin variables $s_i=\pm 1$ by means of the transformation

$$s_i=2t_i-1 \qquad \text{or} \qquad t_i=(s_i+1)/2 \tag{146}$$

In this case (143) becomes the partition function for the Ising model

$$Z/Z^0 = C \sum_{\{t_i\}} \exp\left[-\frac{\beta w}{4} \sum_{nn} (s_i s_j - 2s_i - 2s_j) + \frac{1}{2}\beta\mu \sum_i s_i \right] \qquad s_i=\pm 1 \tag{147}$$

where C is a constant that is irrelevant to our calculation. $w/4=J$ is the Ising parameter, which is bigger than zero in the ferromagnetic case, and smaller than zero in the antiferromagnetic case. The variable that plays the role of the external magnetic field is h, given by

$$2h = \mu - wq/2 \qquad (148)$$

where q is the coordination number of the lattice. In the case of the triangular lattice q=6. The two state ferromagnetic Ising model has a first order phase transition when h=0 . From (148) this means

$$\mu = wq/2 \qquad (149)$$

and using the definitions (144) and (145) we get the exact condition for phase transitions when w>0

$$\mathfrak{z} = \lambda\rho^0(0) = [g_2^0(d)]^{-3} \qquad (150)$$

The preceding analysis can be illustrated by a fluid of hard spheres in contact with a sticky triangular lattice of spacings d=σ. In this case a good estimate of both the contact density and the pair distribution function are obtained from the Percus Yevick theory

$$\rho^0(0) = \rho\,\frac{(1+2\eta)}{(1-\eta)^2} \qquad (151)$$

$$g_2^0(\sigma) = \frac{(1+\eta/2)}{(1-\eta)^2} \qquad (152)$$

$$\eta = (1/6)\pi\rho\sigma^3 \qquad (153)$$

where η is the fraction of occupied volume. Replacing into (150) we get

$$\lambda = (1/6)\pi\sigma^3 \frac{(1-\eta)^8}{\eta\,(1+2\eta)\,(1+\eta/2)^3} \qquad (154)$$

This relation is a necessary but not sufficient condition for the occurrence of phase transitions.

A sufficient condition for the occurrence ot a phase transition can be obtained from the classic work of Potts on the magnetization of the ferromagnetic Ising model on the triangular lattice[95]. The magnetization in the Ising model is the difference in the number of spins up ρ_u and spins down ρ_d

$$I(x) = \rho_u - \rho_d \qquad (155)$$

or using (146)

$$I(x) = 2\theta - 1 \qquad (156)$$

where θ is the fraction of occupied sites. Following Potts we use the variable

$$x = e^{-\beta w/2} = 1 \Big/ \left(g_2^0(d) \right)^{1/2} \qquad (157)$$

The result for the spontaneous magnetization is

$$I(x)= \left[1- \frac{16\ x^6}{(1+3x^2)(1-x)^3}\right]^{1/8} \qquad (158)$$

Using (156) and (157) yields the fraction of occupied sites as a function of the pair interaction function

$$\theta = 1/2 -(1/2)\left[\ 1\ -\ \frac{16\ \ g_2^0(d)}{(g_2^0(d)+3)(\ g_2^0(d)-1)^3}\right]^{1/8} \qquad (159)$$

The critical value of θ occurs when $\theta=1/2$. Solving (159) for the contact pair correlation function yields

$$g_2^0(d)=3 \qquad (160)$$

From (150) we get the value for the critical sticky parameter λ

$$\lambda\ \rho^0(0)=1/27 \qquad (161)$$

In our example of hard core fluid in the Percus Yevick approximation, we get using these equations together with (151) and (152) we get the critical value of the excluded volume fraction

$$\eta_{crit}=0.3712 \qquad (162)$$

and the sticky parameter

$$\lambda_{crit}=0.01185\sigma^3 \qquad (163)$$

This system undergoes a first order phase transition. The isotherms for various values of the parameter λ are shown in figure 9. These exact results are in qualitative agreement with the mean field theory of Badiali et al.[84], where the first order phase transition is also predicted. But the quantitative agreement is not good, which illustrates the pitfalls of mean field theory. In the computer simulations of Caillol et. al.[96] the conditions for the occurrence of a first order phase transition are not met, because the adsorption sites are of finite size, and for that reason the occupancy of a site may prevent nearest neighbor occupation. In this case we expect a second order phase transition to occur.

When there are longer ranged interactions, beyond the nearest neighbor interactions, Dobrushin[97] has shown that the first order phase transition still occurs. However, an exact relation such as (150) is not available.

As was mentioned already in the electrochemical case the contact pair correlation function of ions of equal sign is practically zero, because of the Coulomb repulsion which prevents ions of equal sign to approach each other. However condensed phases in the adlayers are observed in electrochemistry. In particular the underpotential deposition of some metals on electrodes occurs at certain very well defined values of the potential bias[98]. For example the deposition of Cu on the Au (111) face forms two phases according to the deposition potential[99]. These phases have been observed ex-situ[100] and in situ[101]. At a lower potential a dilute ordered $\sqrt{3}\times\sqrt{3}$ phase is formed. At a higher potential a dense commensurate phase is formed.(see figure 10). It is clear from the above considerations that in the dense adlayer case the ions must be discharged, because then they would form a metallic bond, which makes w positive , and therefore ferromagnetic. This is supported by the features of the EXAFS spectra. In the high density phase the near edge structure corresponds to that of metallic copper, which has a characteristic double peak (figure 11). The dilute $\sqrt{3}\times\sqrt{3}$ phase has the white line characteristic of the charged ions. We may assume then that in this case the Cu retains part of its charge, so that the interactions are in this case repulsive, which corresponds to the antiferromagnetic case.

MULTIPLE SITE OCCUPANCY: THE HARD HEXAGON CASE

If the occupation of one site in the triangular lattice also excludes the nearest neighbors, then the problem is equivalent to the hard hexagon problem of Baxter[87]. This problem can be solved when the interactions between the hard hexagons are neglected.

The thermodynamics of the hard hexagon model was recently worked out by Joyce[102]. In terms of the lattice fugacity

$$\mathfrak{z}=\lambda\rho^{0}(0) \qquad (130)$$

The system undergoes a second order phase transition between an ordered solidlike phase and a disordered one. The transition occurs when

$$\mathfrak{z}_{crit}=(11+5\sqrt{5})/2=11.09 \qquad (164)$$

The fraction of occupied sites is

$$\theta_{crit} = (5-\sqrt{5})/10 = 0.2764 \qquad (165)$$

We remark that in the limit of highest possible density the occupied sites fraction is $\theta=1/3$.

For the low density phase the equation of state is

$$\gamma = \frac{1}{4\theta^6(1-\theta)} \left[Q_0^2 Q_1^{1/2} + Q_2 - Q_0 \left(2Q_3 + 2Q_2 Q_1^{1/2} \right)^{1/2} \right] \qquad (166)$$

$$Q_0 = 1-5\theta+5\theta^2$$

$$Q_1 = Q_0(1-\theta+\theta^2)$$

$$Q_2 = (1-2\theta)(1-11\theta+44\theta^2-77\theta^3+66\theta^4-33\theta^5+11\theta^6)$$

$$Q_3 = 1-16\theta+106\theta^2-378\theta^3+803\theta^4-1080\theta^5+962\theta^6 -576\theta^7+219\theta^8-50\theta^9+10\theta^{10}$$

while for the ordered phase

$$\gamma = \frac{2(2-3\theta)(1-\theta)^3}{\left\{-1+12\theta-45\theta^2+66\theta^3-33\theta^4-\left[(1-5\theta+5\theta^2)^3(1-9\theta+9\theta^2)\right]^{1/2}\right\}} \qquad (167)$$

Consider the case of an electrolyte in the neighborhood of a charged electrode. The simplest model is the restricted primitive model of a continuum dielectric and a smooth imageless surface. The contact probability is computed from the Gouy-Chapman theory discussed in section I.

$$g_2^0(d) = \rho_i(0)/\rho_i = \exp[-z_i\psi_i(0)] \qquad (168)$$

where we are using (7) together with the definition

$$\psi_i(0) = \beta e \phi_i(0) \qquad (169)$$

we get

$$\gamma = \lambda\rho_i \exp[-z_i\psi_i(0)] \qquad (170)$$

where $\psi_i(0)$ is the reduced potential at the inner Helmholtz plane. Equating (170) to either (166) or (167) produces a suggestive form of an adsorption isotherm that is shown in figure 12.

From (164) and (170) we deduce that in reduced units there is a critical potential at which a phase transition occurs between an ordered and a disordered phase

$$z_i \psi_{crit}(0)=\ln[\lambda\rho_i]-2.406 \tag{171}$$

At this point a second order phase transition occurs in the surface, which is also seen in the adsorption isotherm.

ACKNOWLEDGEMENTS

The author is indebted to Dr. D.A.Huckaby and Dr. J.G.Gordon for useful discussions. This work was supported by the Office of Naval Research.

TABLE 1

Configuration	θ_a	θ_b	θ_n	Energy	Degeneracy
Dense Phases (1x1)					
a a a	1	0	0	$3\phi_{aa}+\mu_a$	1
b b b	0	1	0	$3\phi_{bb}+\mu_b$	1
n n n	0	0	1	0	1
Diluted Phases ($\sqrt{3}$x$\sqrt{3}$)					
b a a	2/3	1/3	0	$\phi_{ab}+(\frac{1}{2})\phi_{bb}+(\frac{3}{2})\phi_{aa}$ $+(\frac{1}{3})\mu_b+(\frac{2}{3})\mu_a$	3
a b b	1/3	2/3	0	$\phi_{ab}+(\frac{1}{2})\phi_{aa}+(\frac{3}{2})\phi_{bb}$ $+(\frac{1}{3})\mu_a+(\frac{2}{3})\mu_b$	3
n a a	2/3	0	1/3	$\phi_{aa}+(\frac{2}{3})\mu_a$	3
n b b	0	2/3	1/3	$\phi_{bb}+(\frac{2}{3})\mu_b$	3
a n n	1/3	0	2/3	$(\frac{1}{3})\mu_a$	3
b n n	0	1/3	2/3	$(\frac{1}{3})\mu_b$	3
a b n	1/3	1/3	1/3	$\phi_{ab}+(\frac{1}{3})\mu_a+(\frac{1}{3})\mu_b$	6

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FIGURE CAPTIONS

Figure 1: The primitive model of the electric double layer. The metal side is represented by a smooth hard wall. The ions are charged hard spheres. The solvent is a dielectric continuum.

Figure 2: Density profile for the test case with $\sigma^*=0.7$ (ref.34,$\sigma^*=\sigma^2E/e$). The line is the result of Ballone, Pastore and Tosi, ref.54.

Figure 3: same as fig.2. Results from Nielaba and Forstmann , ref.56.

Figure 4: same as fig.2. Results from Caccamo, Pizzimenti and Blum, ref.59.

Figure 5: same as fig.2. Results from Plischke and Henderson, ref.66.

Figure 6: same as fig.2. Results from Kjellander and Marcelja, ref. 68.

Figure 7: Phase diagram for the three state adsorption model case I (from Rikvold et al. ref. 89).

Figure 8: same as figure 7. case II.

Figure 9: Adsrption isotherms for hard spheres in the mean field approximation for a triangular lattice of sticky sites. (ref.84).

Figure 10: Cyclic potential curves for underpotential deposition of Cu on Au(111). The first peak (low density phase), corresponds to a coverage $\theta=0.3$. The second peak corresponds to a dense, commensurate adlayer (ref.99).

Figure 11: Comparison of the near edge adsorption peaks for the underpotential deposited Cu on Au (111). (a) spectra of the low density phase. The near edge structure has a single high peak, similar to that of $CuSO_4$, shown in (b). The high density phase spectrum (c) has a double peak, similar to that of Cu foil (d).

Figure 12: The fraction of occupied sites θ as a function of the applied potential. The units are adimensional. There is a second order phase transition at $\theta=0.2764$.

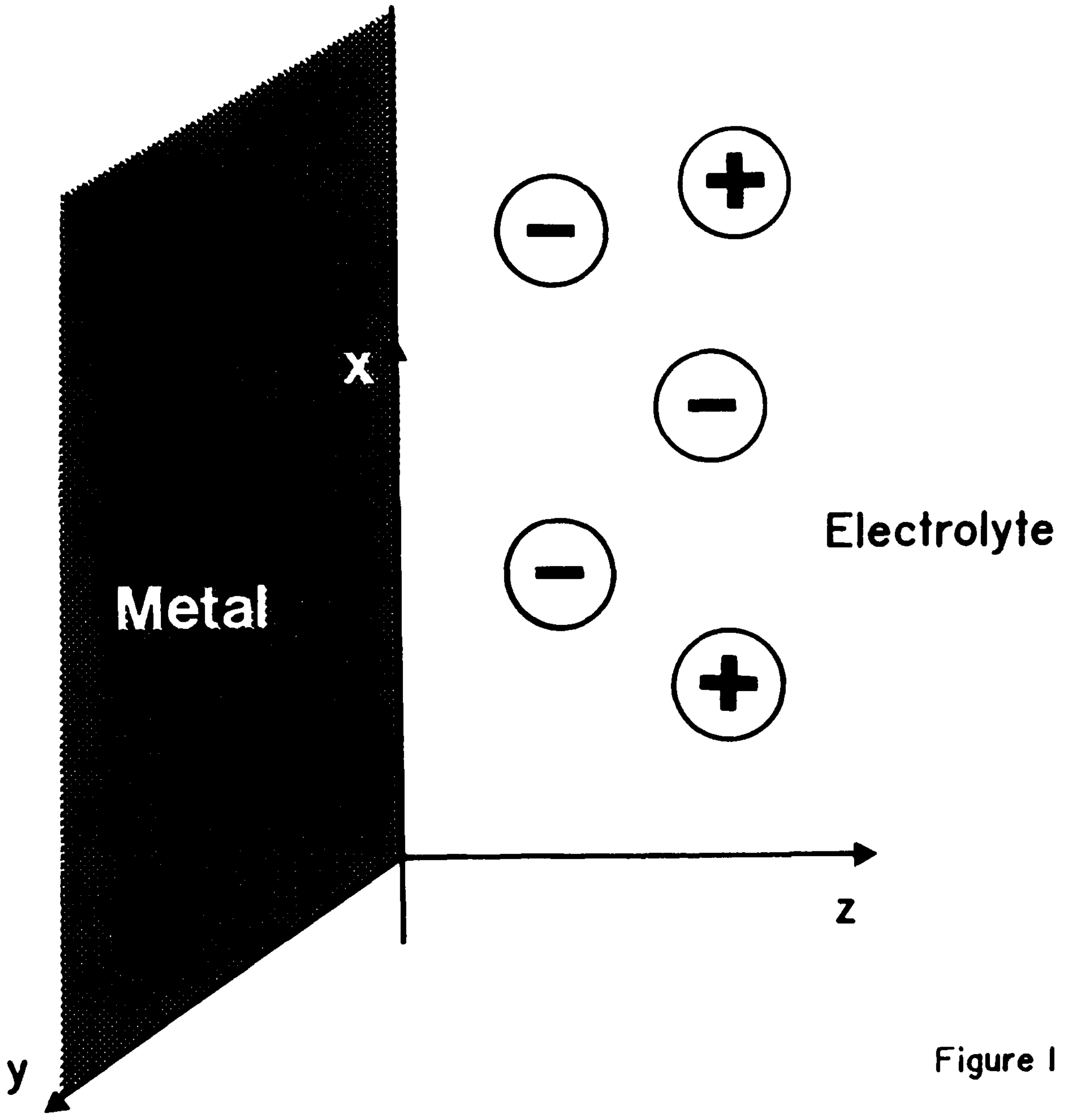

Figure I

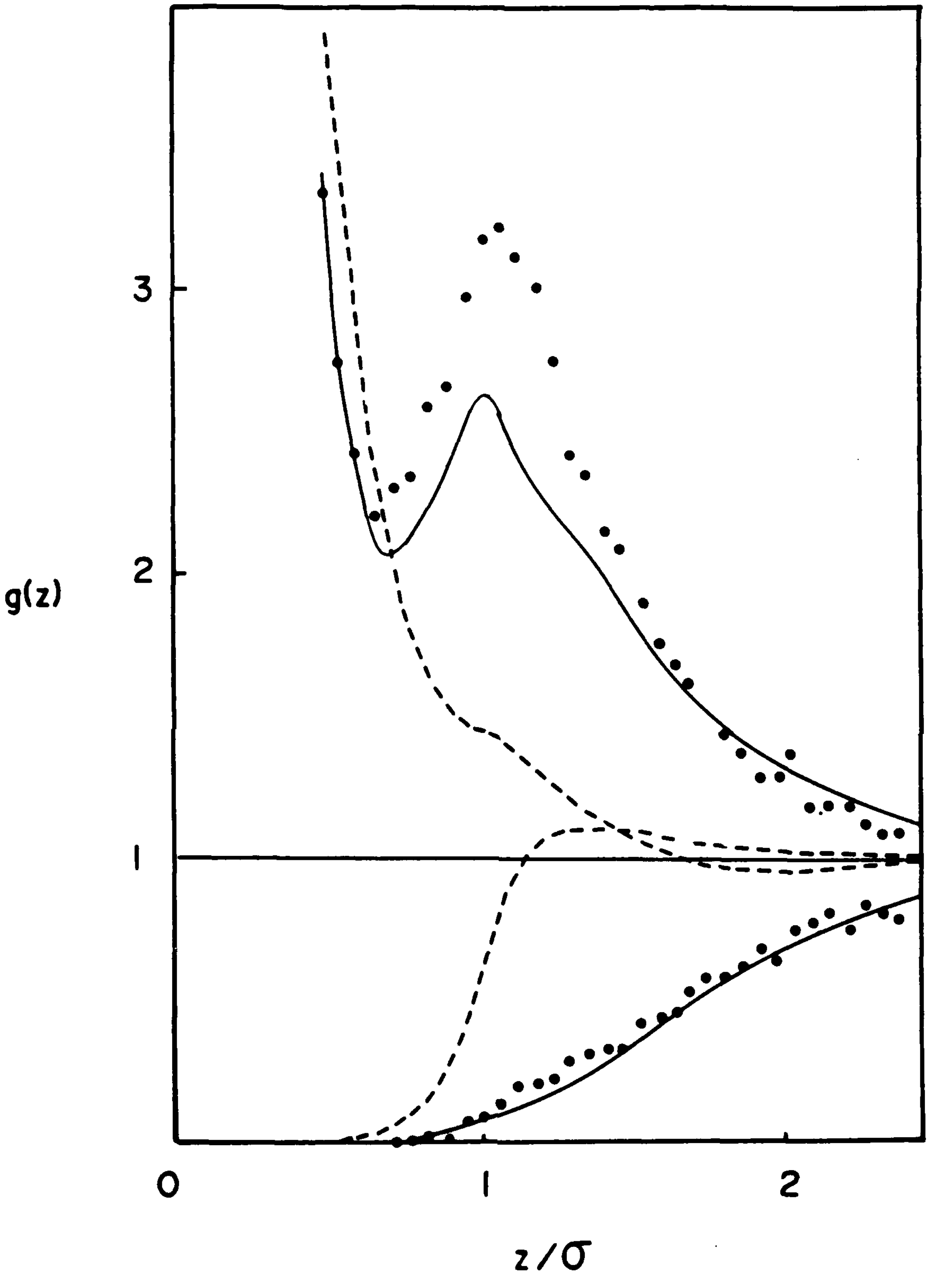

Figure 2

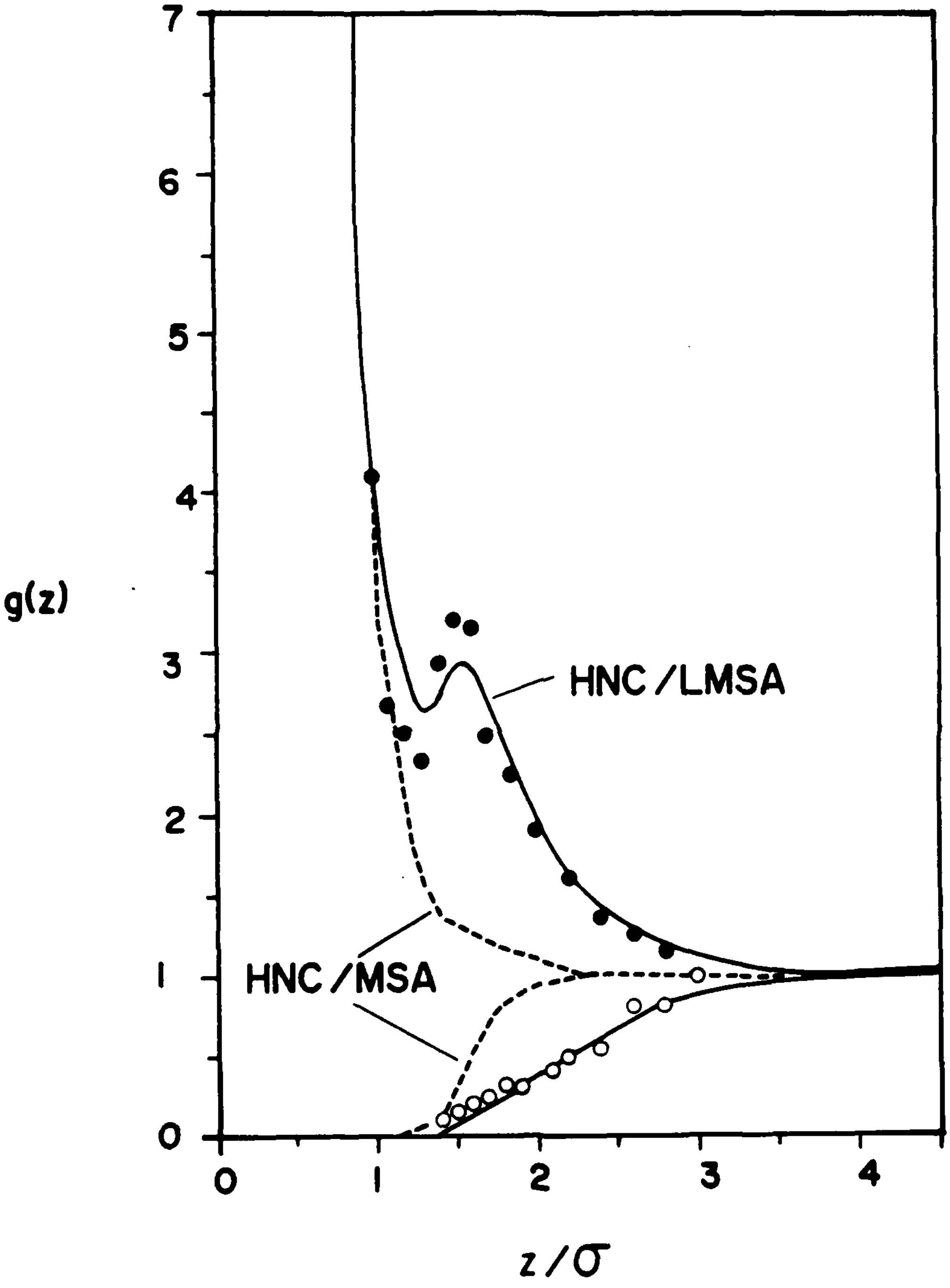

Figure 3

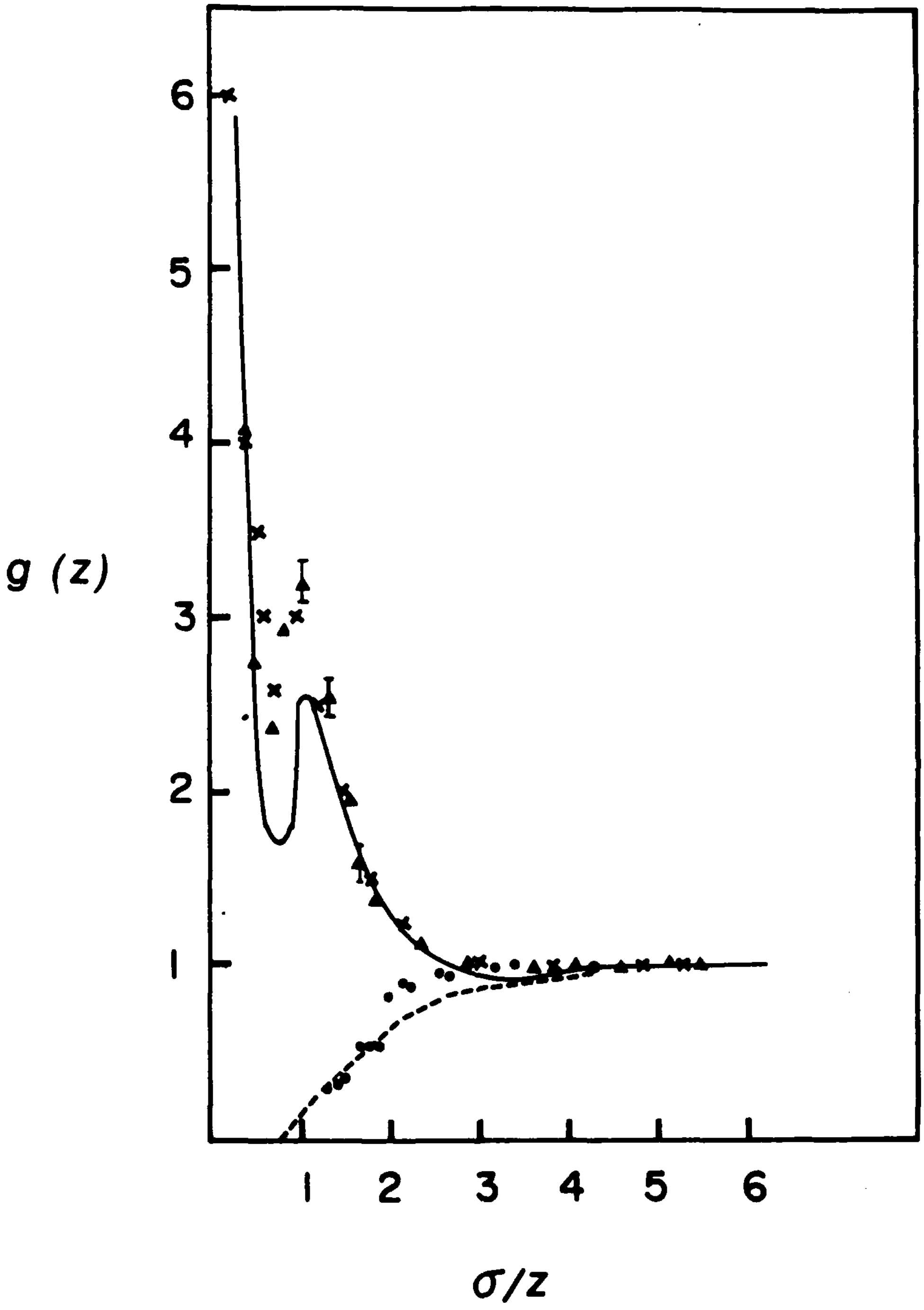

Figure 4

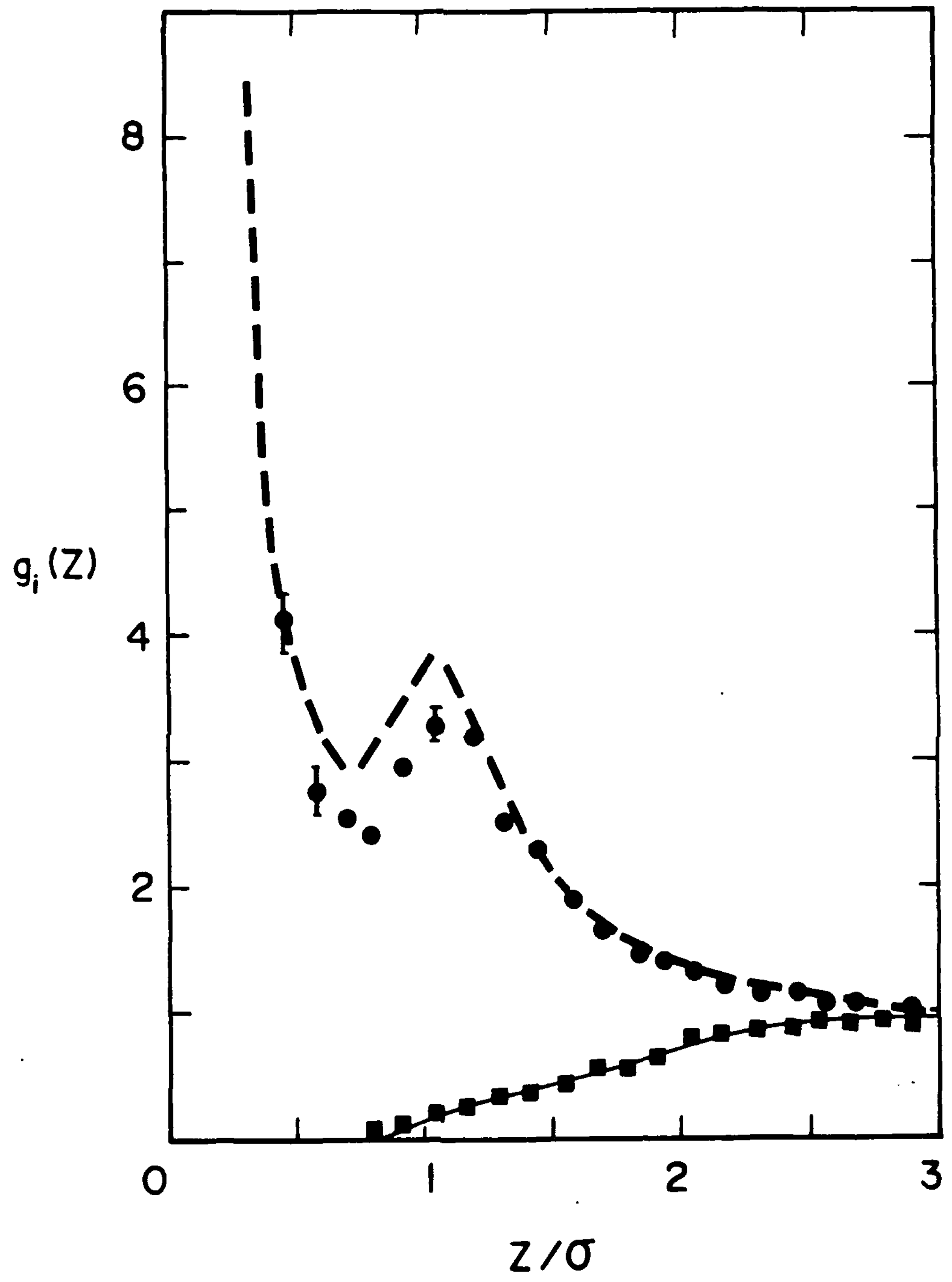

Figure 5

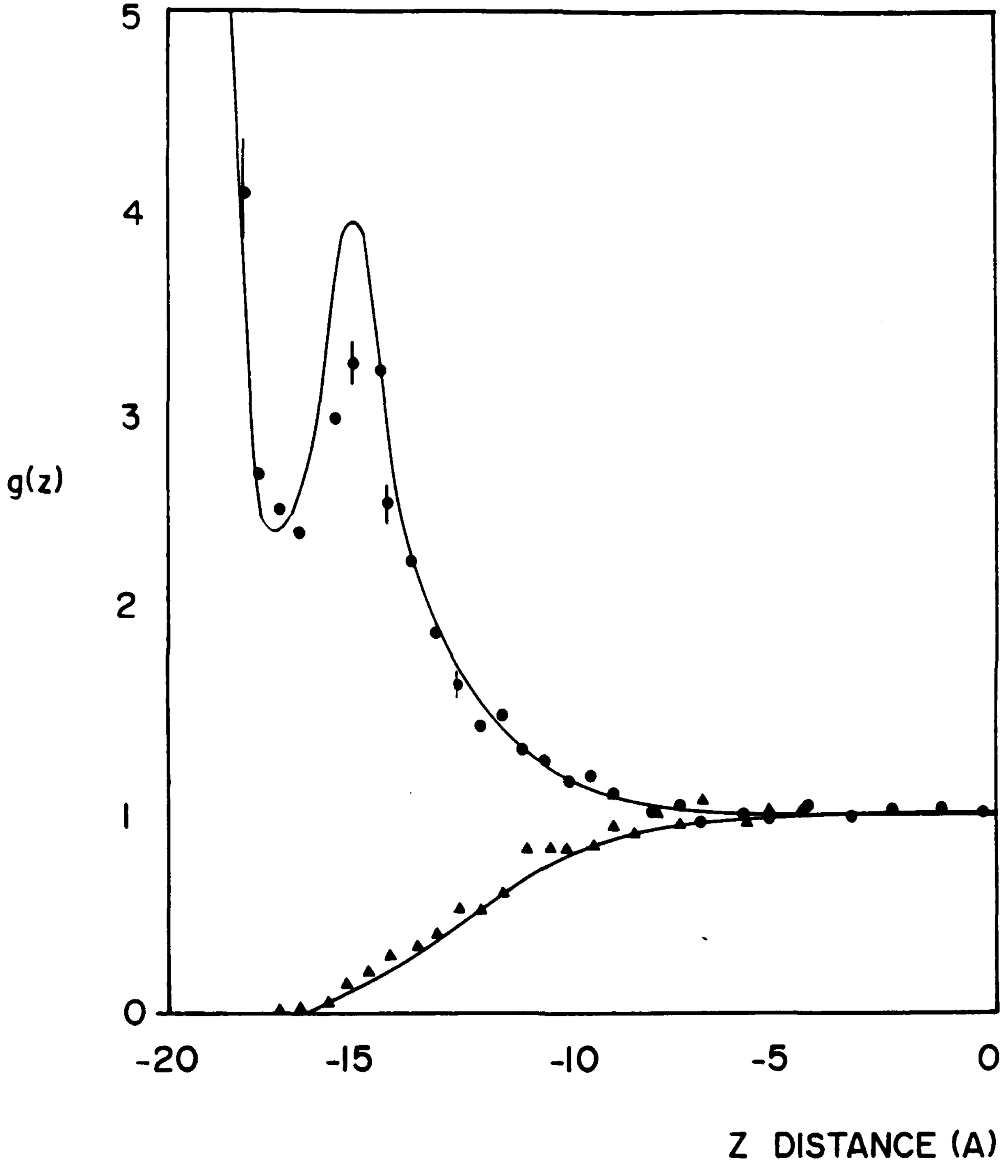

Figure 6

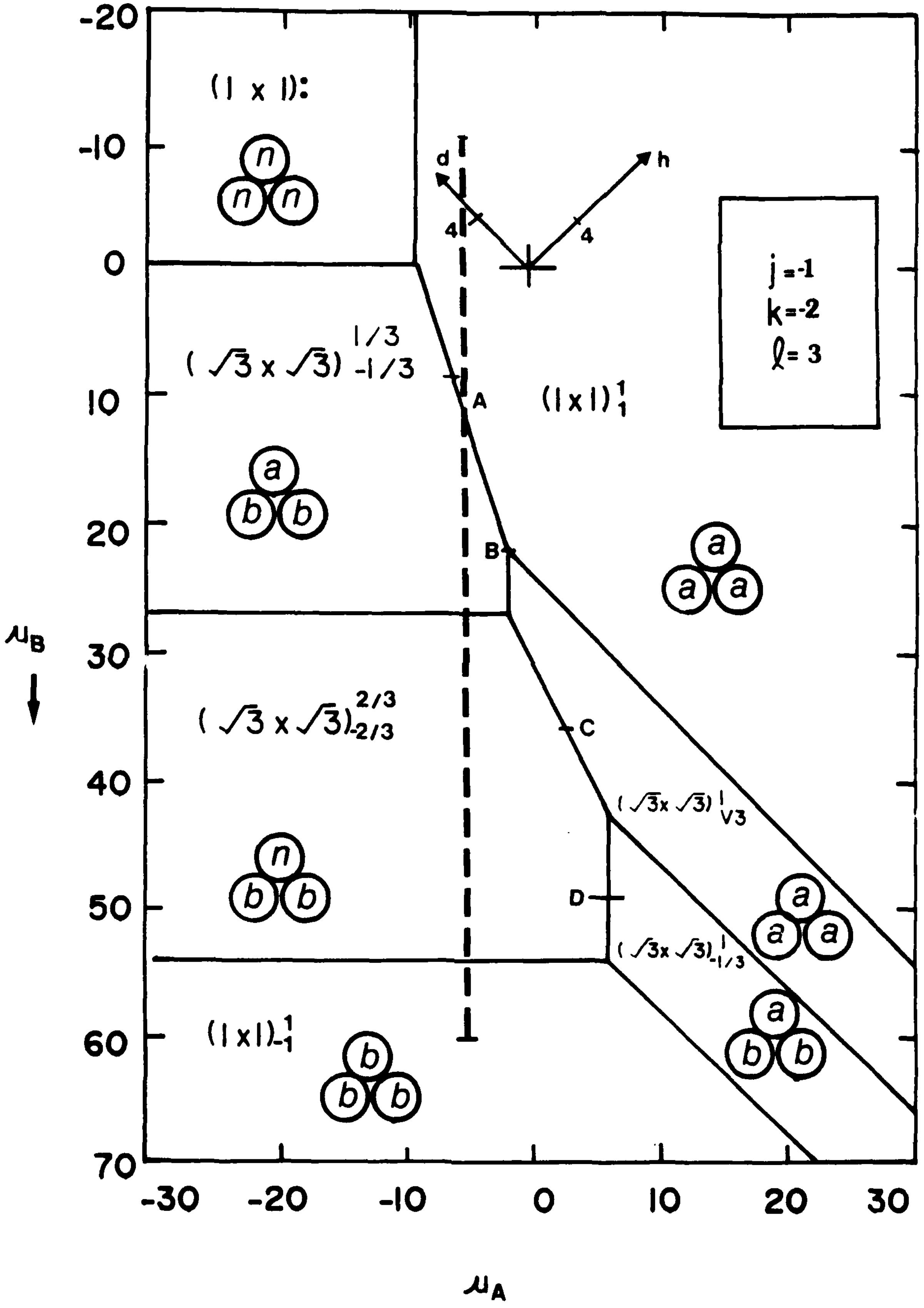
(1 x 1):
n n n
(√3 x √3) 1/3 -1/3
a b b
(√3 x √3) 2/3 -2/3
n b b
(1x1) 1 -1
b b b
(1x1) 1 1
a a a
(√3x √3) 1 1/3
(√3x √3) 1 -1/3
a a a
a b b
d
h
4
4
A
B
C
D
j = -1
k = -2
ℓ = 3
μB
μA
-20
-10
0
10
20
30
40
50
60
70
-30
-20
-10
0
10
20
30

Figure 7

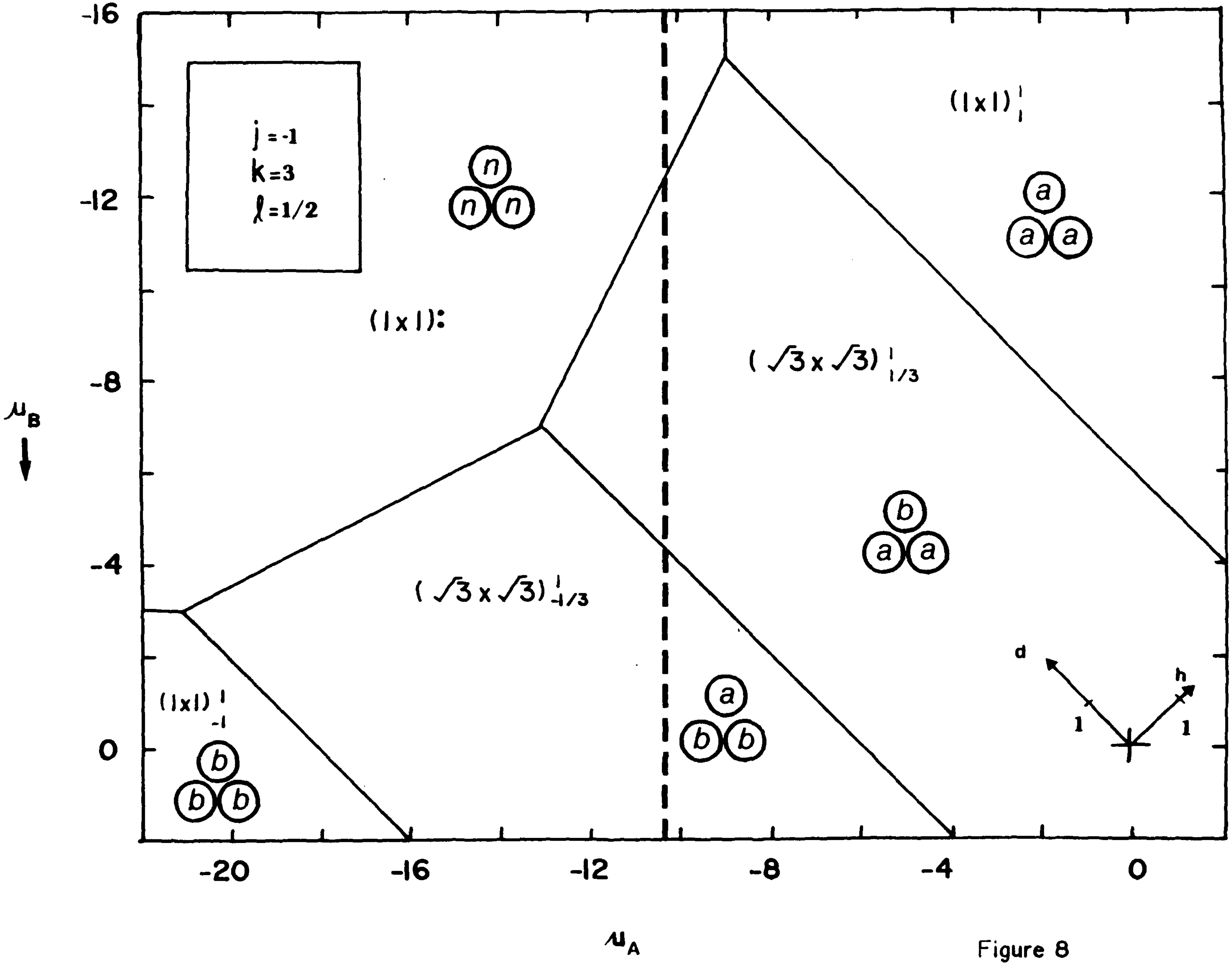
j=-1
k=3
ℓ=1/2
(1x1)⁰
(1x1)¹₁
(√3x√3)¹₁/₃
(√3x√3)¹₋₁/₃
(1x1)¹₋₁
n n n
a a a
b a a
a b b
b b b
d
h
1
1
-16
-12
-8
-4
0
-20
-16
-12
-8
-4
0
μB
μA

Figure 8

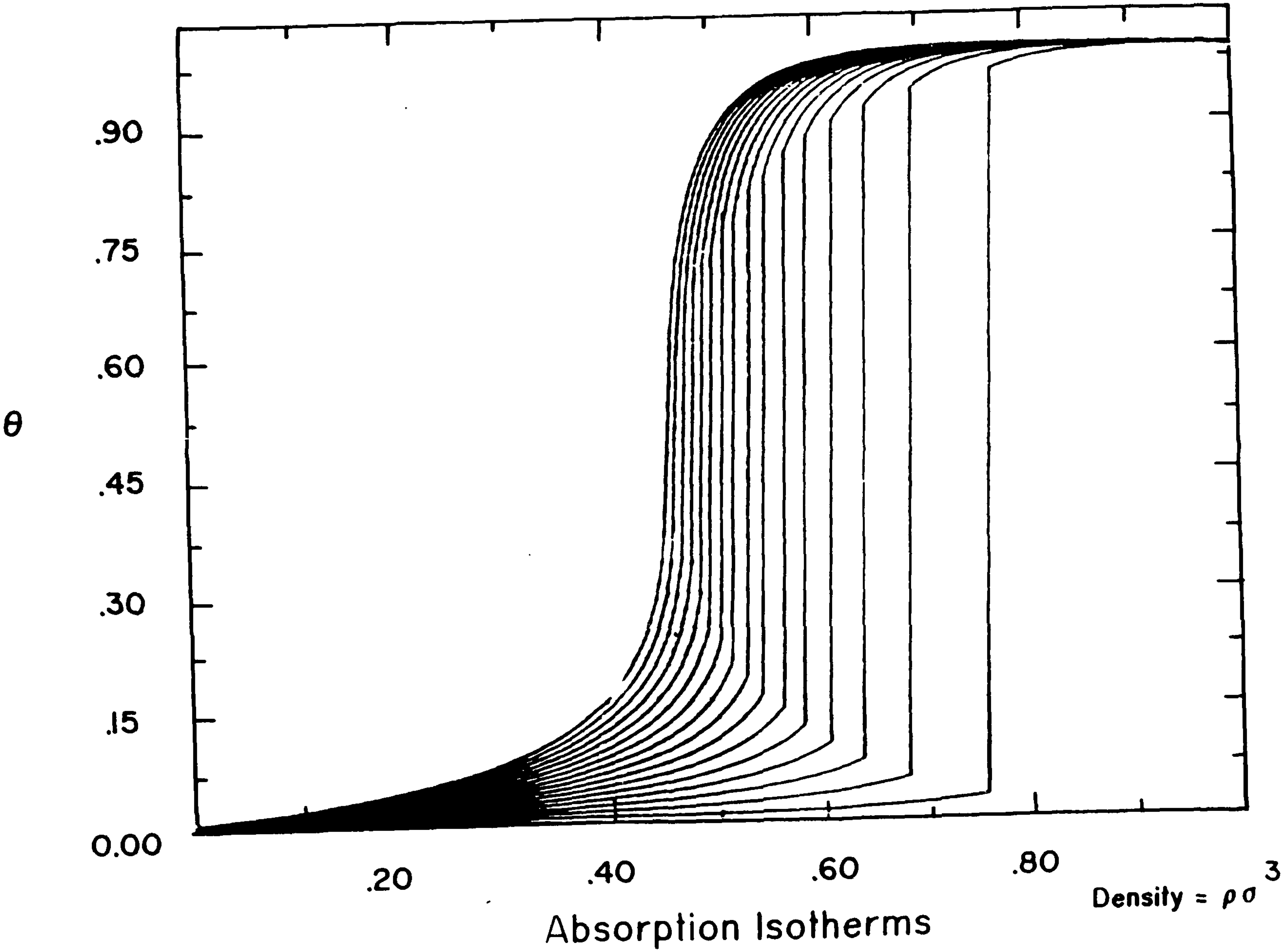
θ
.90
.75
.60
.45
.30
.15
0.00
.20
.40
.60
.80
Density = $\rho\sigma^3$
Absorption Isotherms

Figure 9

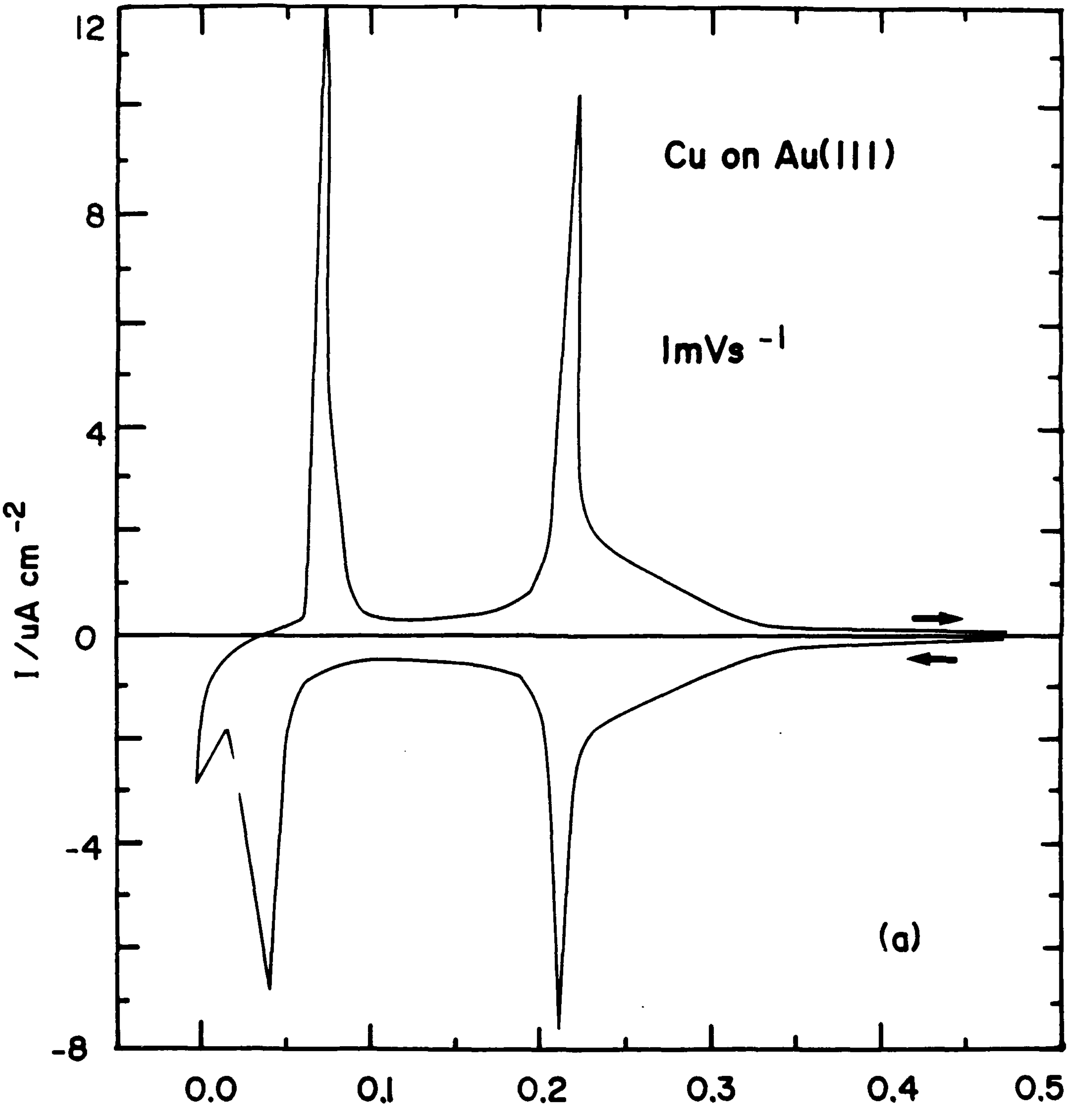

Figure 10

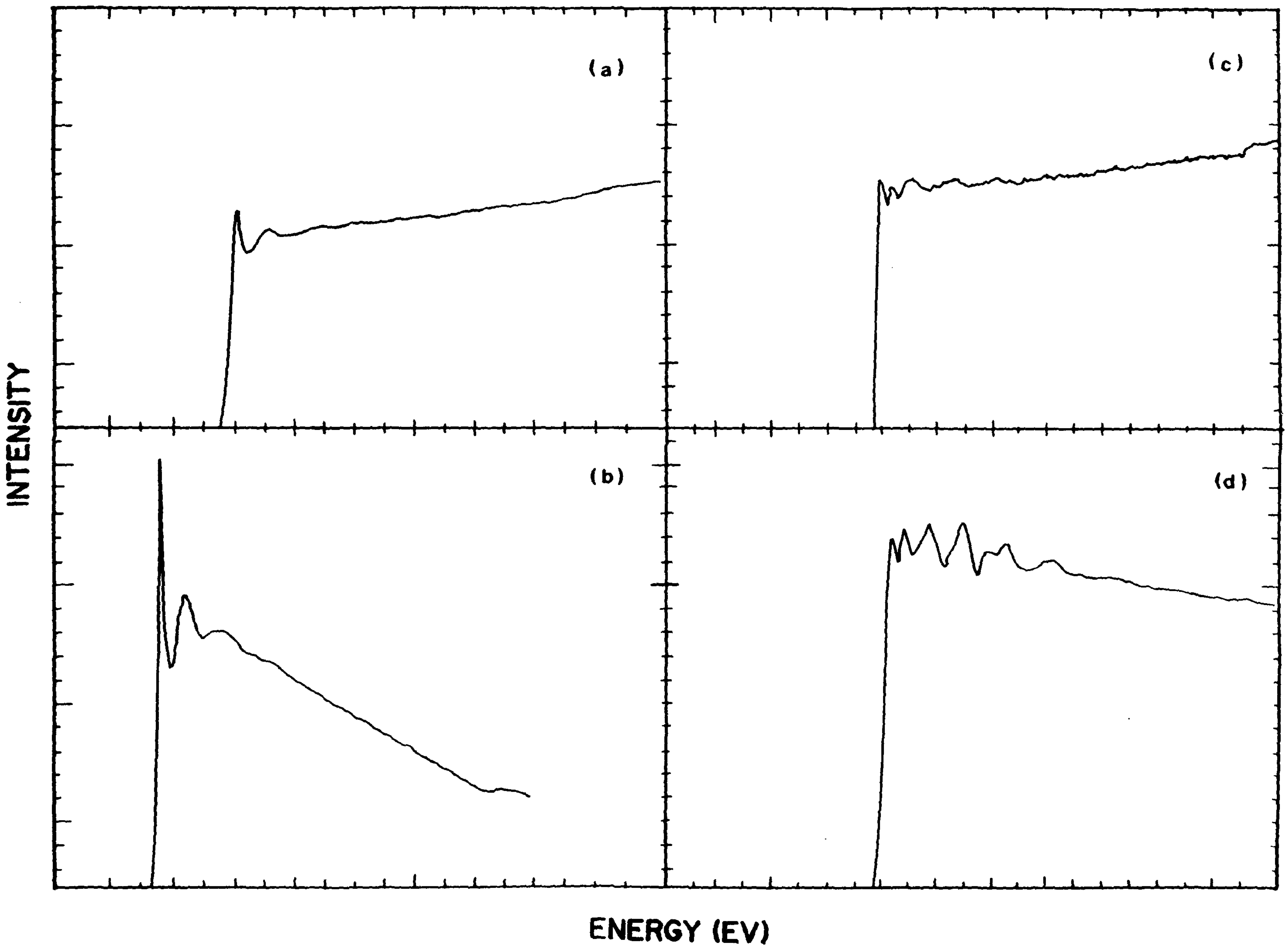

Figure 11

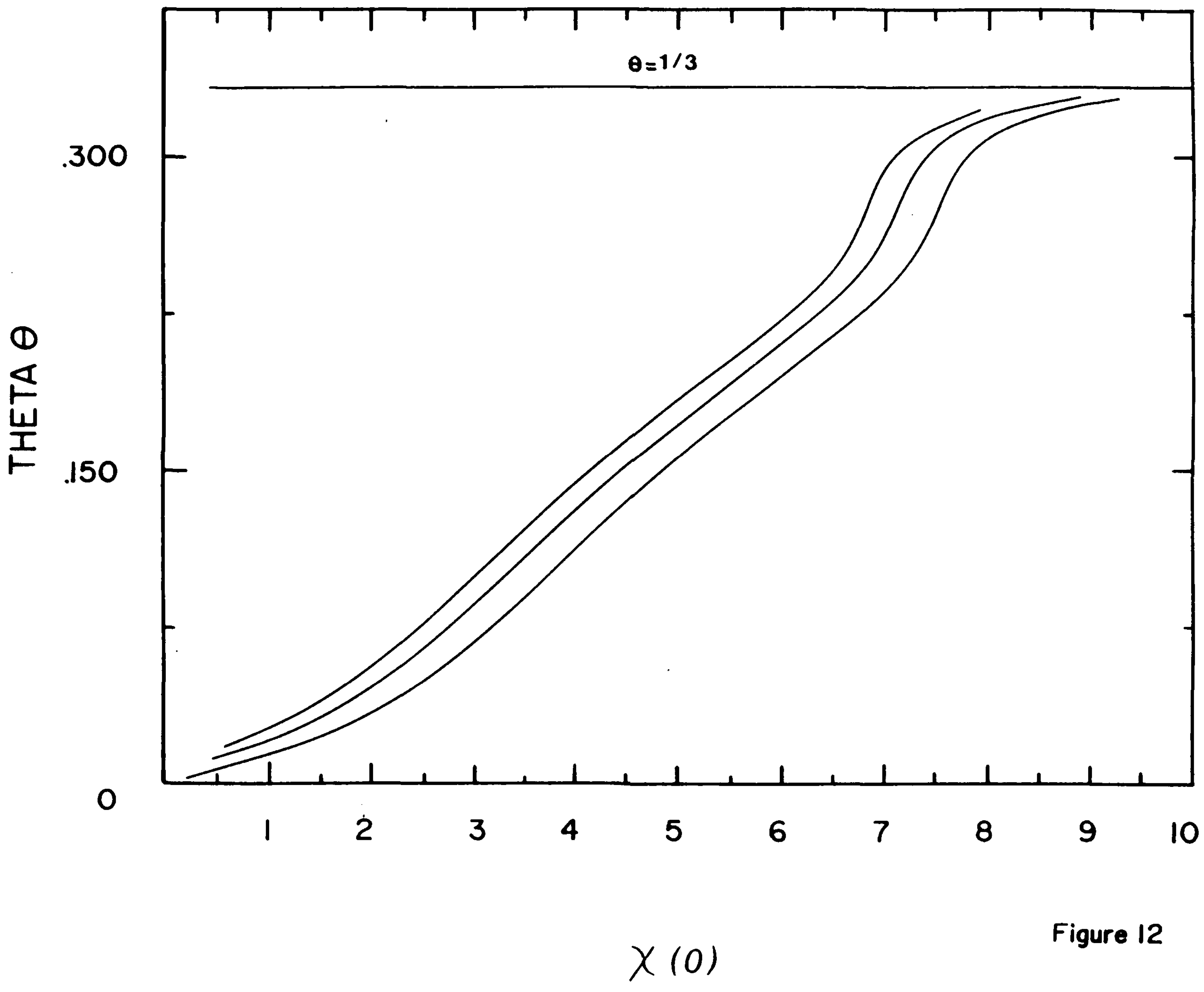

Figure 12