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THE LIQUID STATE OF MATTER: Fluids, Simple and Complex
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ON THE EQUILIBRIUM THEORY OF FLUIDS:
AN INTRODUCTORY OVERVIEW*

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Abstract

This article is intended to serve as a general introduction to aspects of the subject of fluids which are discussed in this volume. It is written primarily for the non-specialist and is based in part on material contained in the reviews of Lebowitz and Waisman (1980) and Lebowitz (1981). The knowledgeable reader is therefore advised to sample only lightly this hors d'oeuvre and go on to the main articles so excellently prepared by the experts. Each of these articles has its own distinct flavor yet they all blend well together to present a fairly detailed review of the current state of our understanding of the fluid state of matter.

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PREFACE

The ancient Greeks thought that the basic constituents of matter were earth, water, air and fire. At the present time we would say instead that the common forms of matter are solid, liquid, gas and plasma. The crucial difference between the two statements is not the names but the substitution of "common forms" for "basic constituents." While we are still far from knowing what are the basic constituents of matter--perhaps the question does not even have a well defined answer--we do know that, for practical purposes all macroscopic matter (the kind we touch, smell and eat) is made up of electrons and nuclei. Indeed in many applications we can start with a higher level of organization--atoms and molecules. The objective of statistical mechanics is to explain and predict the properties of macroscopic matter from the properties of these microscopic constituents. The articles in this volume concern the fluid state of matter.

The study of fluids has, in addition to its theoretical interest, many important practical applications. It would be very useful to be able to predict the properties of fluids, especially those composed of many different species of complex molecules. Chemical engineers designing large plants, mechanical engineers designing propulsion systems need to know equations of state, boiling points, heats of vaporization, etc. On the other hand, the structure of real fluids even the simplest ones, is too complex for a complete treatment from first principles. One of the main goals of fluid research has, therefore, been the development of simple, useful approximate descriptions of dense fluids. This research has been very successful for simple fluids--those composed of approximately spherical, neutral atoms or molecules with negligible dipole moments. The emphasis of research has therefore shifted in recent years to the study of more complex fluids--molecular, dipolar and ionic--as well as to nonuniform fluids. It is these subjects which are the focus of the technical articles in this volume.

To give some background to those works, this introductory article consists of two parts. The first part describes the main ingredients which enter into the successful theories for simple fluids. It traces these ideas back to van der Waals and discusses some limit cases in which they are exact. The second part deals with Coulomb systems. It sketches some of the known exact results and the still unsolved fundamental problems in this field. An attempt is made, in both parts, to at least indicate the current directions of research in these areas. For more detailed background and additional references we mention here a few recent books and reviews on the subject of fluids: Hansen and McDonald (1976), Barker and Henderson (1976), Anderson, Chandler and Weeks (1976), S.G. Brush (1976), B. Berne (1977), Hilderbrand (1915) and (1978).

I. STATISTICAL THERMODYNAMICS OF SIMPLE FLUIDS

Dense fluids, defined to include both dense gases and liquids, have the reputation of being especially difficult to deal with theoretically. This reputation is not undeserved. Unlike dilute gases and crystalline solids which can be thought of as deviants from a well understood ideal state, the ideal gas and the ideal harmonic crystal, the dense fluid lies far from any recognizable landmark. This rules out the use of straightforward, convergent or asymptotic expansions--the all purpose tool of the theoretical physicist and makes even the hardy winee.

In recent years there have, nevertheless, been some significant advances in the theory, particularly in the region of large fluid density where we now have approximations to the free energy and structure function that are accurate to a few percent. This progress has come about from the recognition that while there is no analytically simple reference system there does exist a practical reference system for dense fluids. To arrive at this ideal fluid one starts with what has been a common theme of almost all successful liquid theories: the separation of the intermolecular forces into a short ranged and long ranged part which are treated differently. Simplifying the form of the interaction between molecules to keep only their essential features, a strong repulsion when the molecules are close together and a much weaker longer range attraction when they are further apart, leads to the desired reference system. It is a model fluid of hard spheres. This is a system of little billiard balls having the same density ρ as the real fluid and a diameter d which is a prescribed but rather complicated function of the density ρ and temperature T of the real fluid. This reference system adequately describes the basic structure of the real dense fluid. The effect of the attractive interactions, which are responsible for the condensation of a vapour into a liquid when the temperature is lowered or the pressure is increased, are then treated in a quasi-perturbative way.

While these ideas go back over a century to van der Waals and even earlier, the tractability of the hard sphere fluid and the realization that it can serve as a quantitatively useful reference system, owe a great deal to the availability, in recent times, of high speed computers. This will become amply evident in this volume where references to "computer experiments" abound.

Description of System

We shall assume here that, for the range of temperatures and densities we are interested in,

(a) It is permissible to consider our system as consisting of electrically neutral particles interacting through pair potentials which depend only on the distance r between their centers, and

(b) A macroscopic system of such particles can be described by classical statistical mechanics.

The justification of this description, i.e., its deduction from an analysis of a system consisting of electrons and nuclei obeying quantum mechanics, will be discussed briefly in part II--it is far from resolved at the present time, c.f. Chandler (1981). Indeed, we expect that a full description would involve very complicated many body interactions between the atoms. Any pair potential is therefore best thought of as an "effective" interaction. Remarkably enough this potential can be adequately represented over a wide range of temperatures and densities by a simple analytic formula. A typical form of such a pair potential, commonly used for simple fluids, is the Lennard-Jones 6-12 potential,

$$v(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{-12} - \left(\frac{\sigma}{r}\right)^{-6} \right], \quad (1)$$

which is sketched in Figure 1. Evidence for this potential is based on a comparison of deductions made from such an assumption with those obtained by experiment.

In this comparison computers play a central part. By computer simulation we can, at selected temperatures and densities, solve "exactly" the classical many body problem. The result of these "computer experiments" can then be compared with

(a) experiments on real fluids to test the adequacy of the classical description and of the assumed inter-particle potential. (See Fig. 2 as an example. The "appropriate" values of ϵ and σ for different simple fluids determined either from comparisons such as Figure 2 or from low density properties are remarkably consistent.)

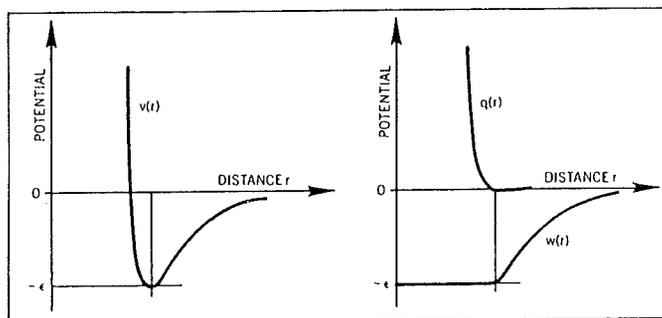
(b) theoretical predictions to test the validity of the (unavoidable) approximations.

The intermediary role of the computer is important since direct comparison of results obtained from a theoretical approximation scheme with experiment tests simultaneously both the basic description and the approximation scheme and frequently leaves in doubt the sources of discrepancy. Equally important, the computer permits experiments on idealized test systems, e.g., hard spheres, not available on nature's shelf. Such models play a very important role in the development of useful theories of real real fluids.

The important features of the pair potential (1) are the strong, short range repulsion at small r and the relatively weak, longer range attraction at larger r . As a consequence each particle in a dense fluid feels simultaneously the attractive (but not repulsive) part of the interaction of many other particles. This suggests that it may be useful to separate the effects of the different parts of $v(r)$: the short range part keeps the particles apart and is responsible for the local correlations while the long range part sees only the gross (macroscopic) density profile of the fluid and provides an attractive potential well (mean field) for the fluid particles. The latter is also responsible for the condensation from the gas into the liquid below the critical temperature T_c . We shall discuss later how this separation can be implemented formally by writing $v(r)$ as a sum of two parts, (see Fig. 1), a short range repulsive part, $q(r)$, and a long range attractive part, $w(r)$:

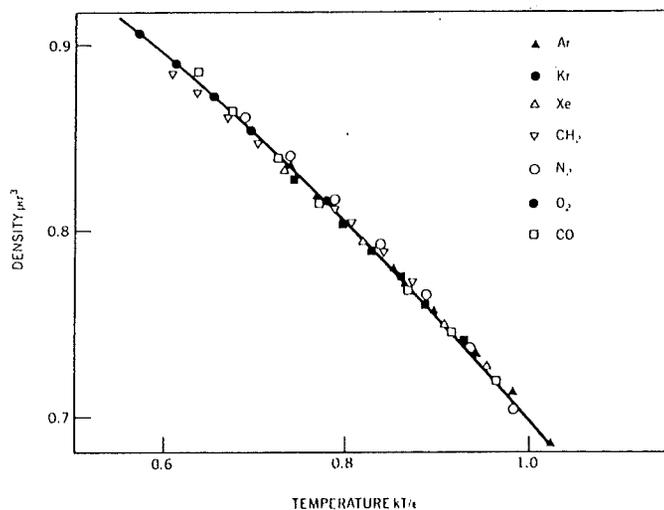
$$v(r) = q(r) + w(r). \quad (2)$$

The different roles which $q(r)$ and $w(r)$ play in determining the structure of a dense fluid is essential to the development of useful approximation schemes.



The separation of the Lennard-Jones potential, $v(r)$, into a part $q(r)$ containing all the repulsive interactions of the potential (and no attractions), and a part $w(r)$ containing all the attractive interactions (and no repulsions). After Andersen, Chandler and Weeks.

Figure 1



Zero-pressure densities of some simple liquids. The curve shows the results of Monte Carlo calculations for the Lennard-Jones potential; the points are experimental data reduced by values of ϵ and σ chosen to give the best fit to the curve. After McDonald and Singer.

Figure 2

VAN DER WAALS'-MAXWELL THEORY

The recognition of the separability of the interparticle potential dates back at least to van der Waals who utilized it in 1873, to develop an equation of state for dense fluids which bears his name,

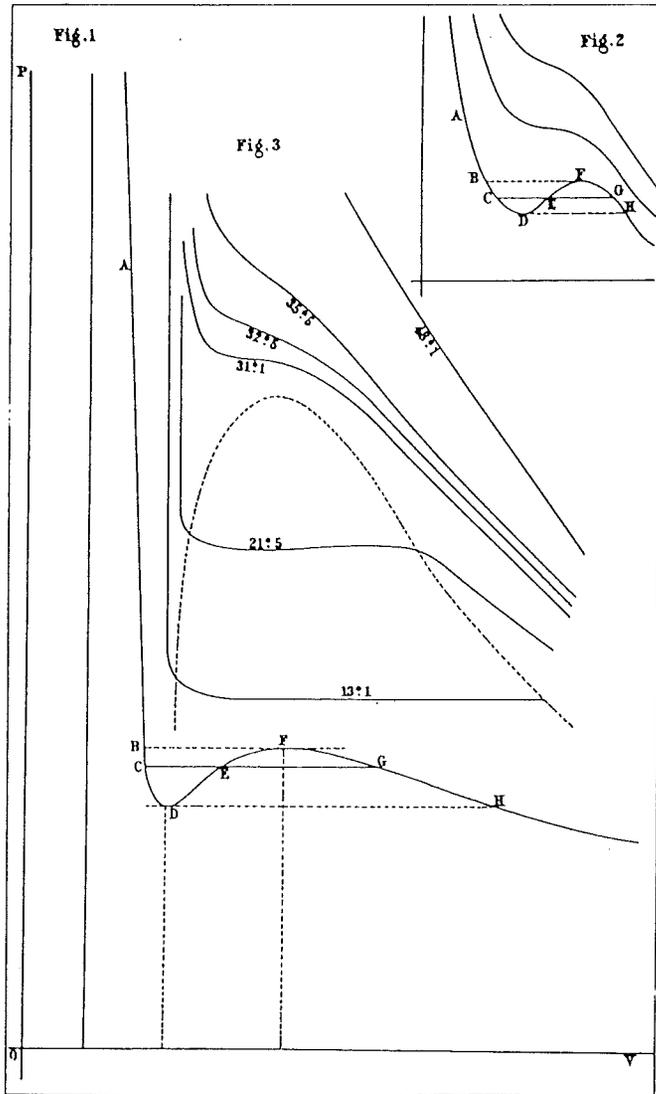
$$p(\rho, T) = k T \rho / (1 - \rho b) - a \rho^2. \quad (3)$$

Figure 3 shows van der Waals' graphs of this relationship. (A centennial conference, whose proceedings were published in *Physica* (1974), celebrating this discovery by van der Waals was held in Amsterdam in 1973.) In Eq. (3) the positive parameters a and b are related to the attractive and repulsive parts of the potential. As described in any number of textbooks, b is the "volume" taken up by a molecule in "excluding" other molecules from it. This increases the effective density and thus increases the pressure to $kT\rho/(1-\rho b)$ from the ideal gas value $p = kT\rho$. The term $-a\rho^2$, which also appears in van der Waals approximation for the free energy, represents the energy per unit volume of the attractive part of the potential. This potential acts to hold the system together and thus decreases the external pressure needed to maintain the fluid in a given volume.

The van der Waals equation gives a good qualitative representation of the isotherms of a real fluid at "high" temperatures. For T less than the critical temperature $T_c = 8a/27bk$, however, each isotherm contains a part in which $\partial p/\partial \rho < 0$, i.e., the equation predicts that a decrease in pressure results in a decrease in the volume of the system. Such a situation is thermodynamically unstable and was later proven, c.f. Ruelle (1969), Thompson (1972), never to arise from a correct statistical mechanical computation of the equilibrium pressure of a macroscopic system whose particles interact via reasonable potentials. Maxwell read and appreciated van der Waals' paper, his thesis, immediately after its publication. (Maxwell's interest can be gauged from his statements, c.f. Klein (1974), that the thesis "has certainly directed the attention of more than one inquirer to the study of the Low-Dutch language in which it is written.") He interpreted parts of the van der Waals isotherms at low temperatures as representing metastable and unstable states of matter (rather than equilibrium states) and amended the van der Waals equation of state at $T < T_c$ by the well-known Maxwell equal area construction, Fig. 3. This construction is designed to yield equality of the chemical potentials in the two phases. With this amendment the van der Waals equation, with suitably chosen constants a and b , gives a qualitatively reasonable equation of state for many fluids: better than some purely empirical equations of state with many more adjustable parameters. Indeed, G.E. Uhlenbeck has complained that the successes of the van der Waals equation "were so remarkable that they practically killed the subject for more than fifty years," BHush (1972).

Rigorous Derivation

The Maxwell amendment of the original van der Waals equation is an ad hoc addition to an approximation which is qualitatively correct above T_c but leads to non-physical, certainly non-equilibrium, isotherms below T_c . The reason for this failure lies in the assumption that all particles of the fluid see the same average attractive interaction $-a\rho$. This necessarily requires the system to be in a single phase of density ρ ; it does not



Plots of Isotherms from van der Waals's thesis, showing van der Waals's curves (labeled Fig. 1), unstable Isotherms according to James Thomson (Fig. 2) and experimental curves from Thomas Andrews (Fig. 3). While van der Waals's recognized that the isotherm DEF represents unstable states, it remained for Maxwell to show exactly where to draw the line CEG that represents the stable states, namely, so as to equalize the areas CDE and EFG.

Figure 3

allow for the possibility of coexisting liquid and vapor phases at different densities in different regions of the container. Clearly when these regions have linear dimensions larger than the range of $w(r)$ the energy density will be different in different regions. Letting α be the fraction of volume occupied by the liquid (density ρ_L) and $(1-\alpha)$, the fraction of volume occupied by the vapor (density ρ_V), the attractive energy per unit volume would be not $-a(\alpha\rho_L + (1-\alpha)\rho_V)^2 = -a\rho^2$ but the lower value $-a[\alpha\rho_L^2 + (1-\alpha)\rho_V^2]$. It is precisely this latter value which corresponds to Maxwell's construction or the equivalent Gibbs double tangent construction for the free energy.

A very interesting derivation of van der Waals equation of state with Maxwell's rule was given by van Kampen in 1964. In this derivation the volume occupied by the system is divided into a large number of cells, each small compared with the range of the long range attractive force, but large enough to contain many particles. Avoiding the pitfall of assuming a uniform distribution of particles over cells van Kampen obtained the distribution over cells by minimizing the free energy. His method leads to the Maxwell modified van der Waals equation of state, which implies a first-order phase transition.

An entirely different, mathematically rigorous, approach to the van der Waals equation of state was taken by Kac, Uhlenbeck and Hemmer (1963a, 1963b, 1964). Their work concerned a one-dimensional system for which the repulsive potential $q(r)$ in Eq. (2) is infinite for $r < d$ and vanishes for $r > d$ (hard rods of diameter d). We shall call this potential $q_d(r)$. The attractive potential $w(r)$ has a range $1/\gamma$,

$$w(r, \gamma) = -a\gamma e^{-\gamma r}. \quad (4)$$

Kac, Uhlenbeck and Hemmer were able to prove the validity of the van der Waals equation of state, together with the Maxwell rule, in the van der Waals limit $\gamma \rightarrow 0$: a limit first considered by Baker (1961) for lattice systems.

The limit $\gamma \rightarrow 0$ provides a clear distinction between the short range of $q(r)$ and the long range of $w(r, \gamma)$. Since this limit is taken after the thermodynamic limit (in which the size of the system becomes infinite), the range of $w(r, \gamma)$ is independent of and small compared to the size of the system or the size of coexisting liquid and vapor regions. By contrast, the usual mean-field theory (in which each particle moves in the average field due to the whole system) does not produce the Maxwell construction.

Lebowitz and Penrose (1966) combined the ideas of Van Kampen with the use of the van der Waals limit. They considered systems with interparticle potential of the form given in equation (2) with $w(r)$ a "Kac potential"

$$w(r, \gamma) = \gamma^v \phi(\gamma r)$$

where γ is a positive parameter and v is the dimensionality of the space considered. This potential reduces to that given in equation (4) when $v = 1$ and $\phi(x) = -ae^{-x}$. By imposing certain conditions on $q(r)$ and $\phi(r)$ Lebowitz and Penrose showed that in the limit $\gamma \rightarrow 0$, taken so that

the range γ^{-1} remains small compared to the size of the system, one obtains the Maxwell equation of state.

$$p(\rho, T, \epsilon_+) = \lim_{\gamma \rightarrow 0} p(\rho, T, \gamma) = MC \{p^0(\rho, T) - a\rho^2\}. \quad (5)$$

Here MC stands for the operation involved in Maxwell's construction and $p^0(\rho, T)$ is the pressure of a reference system defined by $w(r, \gamma) = 0$, which may itself have a transition of its own. The van der Waals parameter a is given by

$$\begin{aligned} a &= 1/2 \int w(r, \gamma) d^3r \\ &= 1/2 \int \phi(x) d^3x. \end{aligned} \quad (6)$$

For a review of work in this field see Hemmer and Lebowitz (1975).

Metastable and Critical Regions

Penrose and Lebowitz (1971) also showed that the correct equation of state for a system that is constrained to have uniform density on a scale large compared to the interparticle spacing but small compared to γ^{-1} is given in the limit $\gamma \rightarrow 0$ by that part of the curve $p^0(\rho, T) - a\rho^2$ that falls between the densities ρ_v and ρ_u . They further showed that for densities in the metastable region--but ρ_u not in the unstable (spinodal) region--of the phase diagram, the lifetime of such a uniform state goes to infinity as $\gamma \rightarrow 0$. This latter property of theories of the van der Waals type appears to depend crucially on the length scale, γ^{-1} , of the attractive potential (which is responsible for the phase transition) going to infinity. It is generally accepted that the lifetime of the metastable state is finite for systems with realistic potentials. There is no general agreement, however, on whether the possibility of analytic continuation of the pressure into the coexistence region that is exhibited by the van der Waals equation also holds for real systems. Most workers feel it does not, see Fischer (1967), Langer (1967), Klein (1980), Baker and Kim (1980).

A similar situation exists also for the behavior of the system in the vicinity of the critical point. Near the critical point, many of the system's parameters vary with temperature according to some power of $|T - T_c|$. The behavior given by Eq. (5) and its analog for magnetic systems yields classical values for the critical exponents. This is in disagreement with experiments on real systems and with calculations on systems with fixed finite range (or rapidly decaying) potentials. The reason is the intrinsic long-range correlations in the neighborhood of the critical point. An equation of the van der Waals type is a reliable approximation only when the range of the attractive potential is large compared to the scale of the relevant correlations. Improved approximations that are like van der Waals' (such as those we describe below) therefore cannot be expected a priori to be useful for the immediate vicinity of the critical point.

In some very recent work Bricmont and Fontaine (1981) have considered from a fresh point of view the expansion, about $\gamma = 0$, of the free energy and correlation functions of a lattice gas interacting via the pair potential

$$w(\underline{r}, \gamma) = a(2\pi)^{-3} \gamma^2 \int_{-\pi}^{\pi} d^3k e^{ik \cdot r} [2 \sum_{\alpha=1}^3 (1 - \cos k_{\alpha}) + \gamma^2]^{-1} \\ + \text{Const. } \gamma^3 \exp[-\gamma r] / (\gamma r) \quad (7)$$

$r \rightarrow \infty$

The short range potential $q(\underline{r})$ is here simply hard core exclusion of two particles at the same lattice site. Unlike previous expansions, in γ , reviewed in Hemmer and Lebowitz (1976), which were entirely uncontrolled, they are able, for this particular system at the critical density $\rho = 1/2$ and $T \geq T_c$, to put rigorous bounds on the remainder in the expansion. Remarkably enough their results hold also in the vicinity of the critical temperature T_c at $\gamma = 0$. Indeed they find an expansion for $T_c(\gamma)$,

$$T_c(\gamma) = T_c(0) + \lambda \gamma^2 + o(\gamma^2), \quad (8)$$

where $T_c(0) = T_c = (a/k_B)$ is the mean field critical temperature and

$$\lambda = (2\pi)^{-3} \int_{-\pi}^{\pi} d^3k / [2 - \sum_{\alpha=1}^3 (1 - \cos k_{\alpha})]. \quad (9)$$

This new expansion may suggest ways on how to improve our otherwise good approximation schemes in the vicinity of the critical temperature. This would certainly be most welcome for, as shown recently, Jones *et al.* (1981); Fisher and Fishman (1981), Fishman (1981), the "critical behavior" predicted by the Kirkwood superposition and by the hyper-netted-chain approximations are no more correct than the mean field type results given by the approximate theories discussed here.

BEYOND VAN DER WAALS

We now outline the steps used in obtaining a good approximation to the properties of a classical fluid whose atoms interact via the Lennard-Jones potential given in equation 1.

The most useful decomposition of the potential appears to be the one due to Chandler and Weeks (1970). It is shown in figure 1. The minimum energy of the Lennard-Jones potential is $-\epsilon$; it attains this value at $r = r_0 = 2^{1/6}\sigma$. One defines $q(r) = v(r) + \epsilon$ for $r < r_0$ and zero otherwise; and $w(r) = v(r) - q(r)$. Thus q corresponds to a purely repulsive force while w corresponds to a purely attractive one. The reason for the success of this decomposition lies presumably in the fact that both q and w and their derivatives are continuous.

The properties of the "reference system," one for which $v(r) = q(r)$, are obtained most conveniently by a perturbation about a "zero order reference system" of hard spheres of diameter d . The "correct" choice of d depends on the temperature and density of the fluid and is extensively discussed in the literature, c.f. Verlet and Weiss (1972). Suffice it to say that a good choice for d can be obtained from knowing only the form of the hard-sphere radial distribution function for r near d , at density ρ .

Once the properties of the reference fluid are obtained the attractive part $w(r)$ becomes a weak perturbation, which is treated either in a straightforward expansion or in some self-consistent scheme.

Radial Distribution and Direct Correlation Functions

The actual procedure for obtaining an approximate theory goes via the radial distribution function. This is for many purposes a useful--and often sufficient--description of the microscopic structure of the fluid. It is given by the correlation function of molecular distances, that is by the variation of the fluid density with distance from a given molecule.

Let $\Delta N(r)$ be the average number of molecular centers within a spherical shell of thickness Δr at distance r from the center of the given molecule. We define the "radial distribution function" of a uniform isotropic system by:

$$g(r) = \Delta N(r) / (4\pi r^2 \rho \Delta r) \quad \text{as } \Delta r \rightarrow 0. \quad (10)$$

Because ρ is the average density, $g(r) = 1$ corresponds to no correlation between the particles. It is always assumed that $g(r)$ approaches unity as r becomes infinite in a single phase fluid; this is essentially a definition of a pure phase.

The radial distribution function determines the average value of all pair functions in a uniform fluid, including, in particular, the energy and pressure of a fluid with central pair potentials. Moreover, the Fourier transform of the function $h(r) = g(r) - 1$ is an experimental observable: the elastic scattering intensity of x rays and neutrons depends on it. The scattering is, in fact, proportional to the "structure factor" of the fluid $\hat{S}(k)$, which is defined as

$$\hat{S}(k) = 1 + \frac{4\pi}{k} \rho \int_0^{\infty} r h(r) \sin(kr) dr = 1 + \rho \hat{h}(k). \quad (11)$$

The direct correlation function, $C(r)$, introduced by Ornstein and Zernike plays an important role in the modern theory of dense fluids. It is defined in terms of $h(r)$ as

$$h(r) = C(r) + \rho \int h(|r-r'|) C(|r'|) d^3r' \quad (12)$$

or in terms of Fourier transforms:

$$\hat{C}(k) = \hat{h}(k) / (1 + \rho \hat{h}(k)) \quad (13)$$

The functions $C(r)$ and $h(r)$ contain, in principle, the same amount of information: given one of them for all r the other can be obtained from equations (12) or (13). It turns out, however, that $C(r)$ is simpler and therefore easier to approximate (guess) than $g(r)$. In terms of Mayer graphs with density vertices $C(r)$ contains only graphs with no nodal points, c.f. articles by Percus and Stell in Frisch and Lebowitz (1964).

There are two ways of obtaining the equation of state from $g(r)$:

(i) from the virial theorem

$$p/kT = \rho - \frac{2}{3} \pi \rho^2 \int_0^\infty \frac{dv(r)}{dr} g(r) r^3 dr \quad (14)$$

(ii) from the compressibility relation

$$\frac{1}{kT} \frac{\partial p}{\partial \rho} = [1 + \rho \int h(r) d^3 r]^{-1} = 1 - \rho \hat{c}(0). \quad (15)$$

The two relations give the same results for the pressure with the exact $g(r)$ but will generally disagree for approximate distribution functions $g(r)$ (see other articles in this volume). There have been many attempts to build into the approximation scheme the requirement that (14) and (15) yield consistent results. These yields improved approximations at the cost of extra work, see in particular recent work by Verlet (1980, 1981).

The Hard-sphere Fluid

The hard-sphere potential $q(r)$, is infinite whenever r is less than the hard-core diameter d , and zero otherwise. Sad to say, even for this simple zero-order reference system there are no exact results useful at high (or even moderate) densities, available at present. In the last twenty years, however, following the early computer studies of hard spheres by Rosenbluth and Rosenbluth (1954), Alder and Wainwright (1957), Wood and Jacobson (1957), some very good simple approximations have been found for this system. The computer results provide the radial distribution function and the equation of state as a function of η , the volume fraction occupied by the hard spheres: $\eta = \pi \rho d^3 / 6$. The hard-sphere system has a maximum close packing density, $\eta = \pi / (3\sqrt{2})$.

One of the most surprising findings of these computer studies is the presence of a fluid-solid phase transition at density corresponding to a value of η near 0.5, a value we shall call $\bar{\eta}$. A theoretical description of the fluid-solid phase transition remains an open challenge. Since there is no energy in the problem the transition must be entirely entropic. This does not, however, explain how there can be a dynamic coexistence of the two phases in a container. Despite this theoretical uncertainty the transition seems well established. There is even reason to believe, c.f. Longuet-Higgins and Widom (1964), that this hard-sphere phase transition "underlies" the fluid-solid transition for simple fluids. This shows again the dominant influence of the repulsive short-range forces in determining the structure of simple dense fluids. For the liquid state we are describing in this article, it is sufficient to consider densities smaller than $\bar{\eta}$.

We now describe briefly one of the most successful attempts to approximate the hard-sphere system in this fluid regime. It is a non-linear integral equation for the radial distribution function of fluids introduced by Percus and Yevick in 1958. While this equation is not

restricted to hard spheres it is most successful for this system for which the approximation consists of assuming that the direct correlation function $C(r)$ vanishes outside the core. This happens to be exact in the one-dimensional fluid of hard rods, Lebowitz (1964), but fails in higher dimensions. What is remarkable is that in 1963 Wertheim and Thiele independently obtained the exact solution of the Percus-Yevick equation in three dimensions. The solution gives $C(r)$ as a cubic polynomial in r , for $r < d$, with coefficients that are simple rational functions of η . The exact $C(r)$ in one dimension is linear in r . The solution of the Percus-Yevick equation is known to be unique at low densities, Groeneveld (1966), and is not expected to show the transition to a crystalline state.

Using the Wertheim-Thiele solution we can obtain explicitly the equation of state either from the virial theorem, Eq. (14),

$$p^{(v)}/\rho kT = (1+\eta+\eta^2-3\eta^3)/(1-\eta)^3 \quad (16)$$

or from the compressibility relation, Eq. (15),

$$p^{(c)}/\rho kT = (1+\eta+\eta^2)/(1-\eta)^3. \quad (17)$$

As expected the pressures do not agree with $p^{(v)} < p^{(c)}$ for all η . For $\eta < \bar{\eta}$ the pressure obtained from the computer studies falls between $p^{(v)}$ and $p^{(c)}$. Carnahan and Starling (1969) found an equation of state which interpolates between $p^{(v)}$ and $p^{(c)}$ and is essentially indistinguishable from the computer results for $\eta < \bar{\eta}$:

$$p/\rho kT = (1+\eta+\eta^2-3\eta^3)/(1-\eta)^3. \quad (18)$$

From equation (18) it is easy to obtain the excess free energy a_d , that is, the free energy above that of an ideal gas at the same temperature and density:

$$a_d(\eta)/kT = \eta(4-3\eta)/(1-\eta)^2. \quad (19)$$

Interestingly enough, the pressure obtained from the Percus-Yevick equation via the compressibility coincides exactly with an equation of state obtained earlier by means of an entirely different method--the scaled particle theory. This theory is sufficiently simple that its basic ideas can and will be given here.

SCALED PARTICLE THEORY

We describe here briefly the basic idea of the method developed by Reiss, Frisch and Lebowitz (1959) for treating a fluid of hard spheres. Since the analysis is equally simple for a mixture of hard spheres we shall present it in that context. The one component result is obtained by setting all densities but one equal to zero. The coincidence between the scaled particle equation of state with that obtained, via the compressibility relation, from the solution of the Percus-Yevick equation is valid also for mixtures of hard spheres.

As already noted, the reasons for the coincidence of the two equations of state, which holds in odd but not even dimensions, are obscure--the

starting point of the R.F.L. and the P.Y. approximation appear unrelated. It is our feeling that a resolution of this mystery would shed some valuable light also on other problems, e.g. why does the P.Y. equation for hard spheres coincide also with the continuum limit of the mean spherical approximation for a lattice gas with extended hard cores, Lebowitz and Percus (1966).

The basic idea of the R.F.L. theory is to consider the work $w(R, \rho_1, \dots, \rho_m, R_1, \dots, R_m)$ of putting in a single particle of diameter R into an m -component mixture of hard spheres of diameters R_1, \dots, R_m and densities ρ_1, \dots, ρ_m . R has the meaning that the 'R-particle' can come only as close as $(R+R_i)/2$ to a particle of the i th species. Hence R can be negative; it has only to be greater than $-R_1$, where $R_1 \leq R_2 \leq \dots \leq R_m$. Now w is equal to the change in the configurational part of the Helmholtz free energy upon adding an R -particle to the system. This can be readily computed for $R \leq 0$, (in which case the exclusion spheres for the R -particle, centered on each fluid particle, do not overlap),

$$w(R) = -\beta^{-1} \ln \left[1 - \sum_{i=1}^m \frac{4}{3} \pi \frac{(R+R_i)^3}{2} \rho_i \right], \quad R \leq 0. \quad (20)$$

It is also easy to show that $w(R)$ and its first two derivatives are continuous at $R = 0$. Furthermore for R very large, $R \gg R_m \geq \dots \geq R_1$, the leading term in $w(R)$ must be the pressure-volume term $\frac{4}{3} \pi p \frac{R^3}{2}$. The R.F.L. approximation now consists in assuming that $w(R)$ can be approximated for all values $R > 0$ by a cubic polynomial,

$$w(R) = w_0 + w_0' R + \frac{1}{2} w_0'' R^2 + \frac{\pi}{6} p R^3, \quad R \geq 0 \quad (21)$$

where w_0 , w_0' and w_0'' are the values of w and its first two derivatives at $R = 0$. When $R = R_i$, $i = 1, \dots, m$, then the R -particle is just another particle of the i th species and $w(R_i)$ is therefore equal to the configurational part of the chemical potential μ_i . We therefore have,

$$\begin{aligned} \beta \mu_i(\rho_1, \dots, \rho_m) &= \ln[\rho_i h^3 / 2\pi m_i kT]^{3/2} + w(R_i) \\ &= \ln[\rho_i h^3 / 2\pi m_i kT]^{3/2} - \ln(1-\xi) + \frac{3X}{(1-\xi)} R_i \\ &\quad + \frac{3}{2} \frac{3X^2}{(1-\xi)^2} + \frac{2Y}{(1-\xi)} R_i^2 + \frac{\pi}{6} \beta p R_i^3, \end{aligned} \quad (22)$$

where

$$\xi = \frac{\pi}{6} \sum_i \rho_i R_i^3, \quad X = \frac{\pi}{6} \sum_i \rho_i R_i^2, \quad Y = \frac{\pi}{6} \sum_i \rho_i R_i.$$

Combining (22) with the thermodynamic relation,

$$\frac{\partial p}{\partial \rho_j} = \sum \rho_i \frac{\partial \mu_i}{\partial \rho_j}, \quad (23)$$

yields

$$\beta p = \left\{ \rho(1+\xi+\xi^2) - \frac{\pi}{2} \sum_{i < j} \rho_j \rho_i (R_j - R_i)^2 [R_i + R_j + R_i R_j X] \right\} / (1-\xi)^3 \quad (24)$$

with $\rho = \sum_{i=1}^m \rho_i$. When all the spheres have the same radii, $R_i = d$ then (24) reduces to (18).

For recent developments in scaled particle theory the reader is referred to the work of Reiss (1977), Barbay and Gelbart (1980) and Reiss and Merry (1981).

Real Fluids

There are several, more or less equivalent, prescriptions available in the literature for calculating the properties of single-phase fluids, once the properties of the reference hard-sphere system are known. The most straightforward of these are the high-temperature expansion method of Zwanzig (1954) and its self-consistent formulation by Barker and Henderson (1954) and its self-consistent formulation by Barker and Henderson (1967). We present here, in outline form, a more refined method due to Andersen, Chandler and Weeks (1970, 1971, 1972, 1976). (The authors' names appear in various permutations; see also article by Chandler in this volume.)

We start from the decomposition of the Lennard-Jones potential shown in figure 1. The next step is to select a hard-sphere system with a temperature- and density-dependent diameter $d(\rho, T)$ to approximate the Lennard-Jones system with potential $q(r)$. (We shall call this system the reference system and denote its properties with subscripts 0.) A good (but not unique) choice used by Andersen, Chandler and Weeks is the condition, introduced by Percus and Yevick (1964), that

$$\int [e^{-q(r)/kT} - e^{-q_d(r)/kT}] y_d(r) d^3r = 0. \quad (25)$$

The function $y_d(r)$ is defined as the hard-sphere limit of the function $\exp[v(r)/kT]g_v(r)$, where $g_v(r)$ is the radial distribution function of a fluid whose pair potential $v(r)$ approaches the potential $q_d(r)$ as a limit. It is also possible to define $y_d(r)$ directly for a hard-sphere system by means of Mayer graphs. Since $y_d(r)$ is equal to $g_d(r)$, the distribution function for hard spheres, for $r \geq d$ and is smooth at $r = d$, one can in practice obtain $y_d(r)$ by extrapolating the function $g_d(r)$ from $r > d$ into the small region $r < d$ where it is needed.

Having determined the effective hard-core diameter $d(\rho, T)$, which is generally quite close to σ (near the triple point of the Lennard-Jones fluid, for example, d is 1.02σ), one approximates the properties of the reference fluid by,

$$g_0(r) = e^{-q(r)/kT} y_d(r), \quad (26)$$

$$a_0(\rho, T) = a_d(n). \quad (27)$$

The next and final step is to obtain an approximation for the full system. For that, we note first that there are exact upper and lower bounds on the free energy $a(\rho, T)$ given by the Gibbs-Bogoliubov inequalities, c.f. Isihara (1968),

$$a_0 + \frac{1}{2} \rho \int g(r) w(r) d^3r \leq a \leq a_0 + \frac{1}{2} \rho \int g_0(r) w(r) d^3r \quad (28)$$

where $g(r)$ is the radial distribution function of the full system. When the fluid is very dense $g(r)$ is very close to $g_0(r)$ (within 2 or 3%). Therefore one can accurately approximate the free energy per particle at these high liquid densities, using equations (26) and (27), by

$$a(\rho, T) = a_d(n) + \frac{1}{2} \rho^2 \int g_0(r) w(r) d^3r. \quad (29)$$

Equation (29) represents the first two terms in a high-temperature series (in powers of $1/kT$) for a system in which $q(r) = q_d(r)$, with d fixed. It is clear that this approximation is very close in spirit to van der Waals' analysis of the different roles played by $q(r)$ and $w(r)$ in determining the structure and thermodynamics of the very dense fluid. Indeed, eq. (29) would agree with the van der Waals approximation for the free energy when $q(r) = q_d(r)$ and $w(r)$ is sufficiently weak and long range for $g_0(r)$ to be approximately unity over most of the range of the integration. We remark that the actual computation of the right side of equation (29) is nowadays a relatively simple, desk-calculator task, due to the availability of very compact fits for the relevant quantities.

When we consider lower fluid densities, $\rho\sigma^3 < 0.65$, the effect of $w(r)$ on the radial distribution function must be included to obtain quantitative agreement with laboratory and computer experiments. For example, Andersen, Chandler, and Weeks have obtained a non-linear integral equation for a "renormalized potential" $\xi(r)$ that is very similar in structure to the integral equation in the Percus-Yevick approximation for hard spheres. In the simplest version of their scheme, called the exponential approximation, $g(r)$ is obtained from $\xi(r)$ through

$$g(r) = g_0(r) e^{-\xi(r)/kT}. \quad (30)$$

At low densities $\xi(r)$ is close to $w(r)$ but at large fluid densities it is smaller and has a shorter range than $w(r)$. In particular, if $g(r) \approx g_0(r)$ (which is true for very large fluid densities) then $\xi(r)$ vanishes.

The exponential approximation, and the corresponding thermodynamic functions, are found to give an accurate description of the dense single-phase Lennard-Jones fluid. In fact, for $\rho\sigma^3 > 0.65$ the radial

distribution function obtained from this approximation scheme is within the "experimental" accuracy of the computer simulations; the accuracy is a few percent for $\rho\sigma^3$ between 0.65 and 0.1 as long as $T < 3T_c$. For very high temperatures the approximation of $q(r)$ by $q_d(r)$ is not so accurate, because the high kinetic energy of the particles permits them to penetrate deeper into the repulsive part of the potential.

Remarks

(i) As mentioned earlier there are various other schemes similar to the one described here which do about as well in the same situations, c.f. Barker and Henderson (1975). (Indeed the "super" accuracy of the exponential approximation for Lennard-Jones fluids may be somewhat fortuitous, Stell (1977)). All these approximations start from the recognition of the different roles played by the repulsive and attractive parts of the interactions. The former determines the microscopic structure of the fluid and may be idealized by a hard-sphere interaction while the latter can be treated by refined approximations of the mean-field type. It is the emphasis on this separation which sets these works apart from the earlier approximation schemes, such as the superposition or hyper-netted-chain approximation.

(ii) These approaches generalize in a natural way to mixtures of simple fluids. Here again the solution of the Percus-Yevick equation for mixtures of hard spheres with different diameters, Lebowitz (1964), discussed earlier plays an important role.

(iii) These types of approximations have also been applied with reasonable success to not-so-simple fluids in which the interparticle interactions are only roughly spherical, Hansen and McDonald (1976), such as methane. For highly asymmetrical molecules further work is needed to obtain an accurate description of a zero-order reference system, e.g. a system of hard ellipsoids, c.f. Barboy and Gelbart (1980), Wertheim (1981).

(iv) As already mentioned, a topic of current interest described in detail in the article by Percus in this volume, is the structure of non-uniform fluids, particularly the interface between gas and liquid. So far the type of approach described in this article has been only partially successful for these problems. The reason for this appears to lie in the lack of any simple reference system for such an interface. Unlike the situation in the bulk fluid, the width and structure of the interface at temperatures away from the critical temperature are strongly affected by both the repulsive and the attractive parts of the interaction potential and there is no simple way to disentangle them.

(v) This brings us to the final point we wish to make here: even in the case of simple dense fluids there is still much to do to understand why the schemes described here work as well as they do. After all, the effective range of the attractive part of the Lennard-Jones potential is not really all that large compared to σ , as one can see in figure 1. Why then should van der Waals', and similar theories, exactly valid for very weak, very long-range potentials work so well for Lennard-Jones fluids? George Stell (1977) calls this "the principle of unreasonable utility of asymptotic estimates" and it bears further investigation. An understanding

of this point will, we hope, also lead to new, useful and simple approximation schemes for systems that are not covered by the present methods.

II. FREE ENERGY AND CORRELATION FUNCTIONS OF COULOMB SYSTEMS

As already noted in the introduction, all of statistical mechanics, which is the microscopic theory of macroscopic matter, deals in some sense with Coulomb systems. The properties of the materials we see and touch are almost entirely determined by the nature of the Coulomb force as it manifests itself in the collective behavior of interacting electrons and nuclei. In many applications of statistical mechanics, however, such as those described in the previous sections, this fact is not explicit at all. One starts with an "effective" short range microscopic Hamiltonian appropriate to the problem at hand, e.g., we describe simple fluids as a collection of neutral atoms represented by point masses interacting via Lennard-Jones pair potentials. Statistical mechanics of Coulomb systems therefore usually refers to those investigations in which the Coulomb potential is explicitly considered as a part of the starting microscopic Hamiltonian. (Appropriate quantum statistics are always assumed.)

There are two reasons for considering explicitly systems with such Hamiltonians. The first is primarily a theoretical one--we would like to understand in a more precise way how the Coulomb forces give rise to the effective interactions. The second reason is more practical. There are many systems, e.g. plasmas, molten salts, ionic crystals, etc. where bare Coulomb interactions are part of the appropriate effective Hamiltonian. We shall review here, very briefly, the rigorous mathematical status of some selected topics in the first of these categories. (This is based on lectures given at a summer school in 1980, Lebowitz (1981).) The second aspect is very adequately represented by the articles of Ashcroft, Hafskjold and Stell, and of Stillinger in this volume.

THERMODYNAMIC LIMIT OF FREE ENERGY

The problem here is to prove that the most basic fact of macroscopic thermodynamics, extensivity and stability of the free energy of neutral systems, follows from the prescriptions of statistical mechanics for computing this free energy, $- \beta a(\beta, \rho)$

$$a(\beta, \rho) = \lim_{|\Lambda| \rightarrow \mathbb{R}^3} |\Lambda|^{-1} \ln \{ \text{tr} \exp[-\beta H(\underline{N}; \Lambda)] \}. \quad (1)$$

Here $H(\underline{N}; \Lambda)$ is the Coulomb Hamiltonian of k species of charged particles with charges e_α and numbers N_α , $\alpha = 1, \dots, k$ contained in a box $\Lambda, \Lambda \subset \mathbb{R}^3$ with volume $|\Lambda|$. The thermodynamic limit $\Lambda \rightarrow \mathbb{R}^3$ is taken along a "reasonable" sequence of boxes Λ_j and particle numbers \underline{N}_j such that

$$\sum_{j=1}^k N_j e_\alpha = 0, \quad N_j \geq 0, \quad (2)$$

and

$$N_j^\alpha / |\Lambda_j| = \rho_j^\alpha + \rho^\alpha \quad (3)$$

The existence and thermodynamic stability of the limit function $a(\beta, \rho)$ was proven by Lebowitz and Lieb (1969, 1972) (see also Lieb and Lebowitz (1973), Lieb (1976)) under the assumption that at least one type of charge, the positive or negative ones, obey Fermi statistics--as indeed electrons do. This condition was proven by Dyson (1967) to be necessary and by Dyson and Lenard (1967, 1968) to be sufficient for the extensivity of the ground state energy of the system, i.e. for H-stability,

$$\text{Min } H(\underline{N}; \Lambda) \geq -bN, \quad b < \infty \quad (4)$$

$N = \sum_{\alpha=1}^k N^\alpha$. A simple elegant derivation of (4) with a greatly improved constant b was later given by Lieb and Thirring, cf. Lieb (1976).

The actual Hamiltonian for which the existence of $a(\beta, \rho)$ was proven is

$$H(\underline{N}; \Lambda) = \sum_{i=1}^N \frac{p_i^2}{2m_i} + \frac{1}{2} \sum_{i \neq j} e_i e_j / |x_i - x_j| + U(x_1, \dots, x_N) \quad (5)$$

where $e_i = e_\alpha$ and $m_i = m_\alpha$ when particle i is of species α . Dirichlet boundary conditions were used for the wave functions on the boundary of Λ and the negative charges are Fermions. U is any "standard" short range ℓ -body interaction, $\ell = 2, 3, \dots$ finite, which satisfies classical H-stability, Ruelle (1969).

$$\text{Min}_{\{x_i\}} U(x_1, \dots, x_N) \geq -bN \quad (6)$$

U is essentially such that if $e_\alpha = 0 \forall \alpha$, then the thermodynamic limit in (1) would exist without any restrictions on the statistics. In fact the system could then be treated by classical statistical mechanics with the trace in (1) replaced by the appropriate symmetrized integrals. Indeed, if U contains a hard core, i.e. $U(x_1, \dots, x_N) = \infty$ whenever $|x_i - x_j| < d, d > 0$, then classical and hence also quantum mechanical H-stability for $H(N)$ in (5) was proven by Onsager in 1939. The existence of the thermodynamic limit for the free energy of Coulomb systems then also hold for such classical systems (a suitable representation in many cases).

Onsager's proof is based on the observation that in the presence of hard cores the charge on each particle can be considered (as far as the interactions are concerned) to be smeared out on the surface of a sphere of radius d . This has a self energy $\epsilon(d)$. It is then a basic fact of electrostatics that

$$\begin{aligned} \frac{1}{2} \sum_{i \neq j} e_i e_j / |x_i - x_j| &= \frac{1}{2} \int_{\mathbb{R}^3} E^2(x) d^3x - \sum (\text{self energy}) \\ &\geq -N\epsilon(d), \quad |x_i - x_j| \geq d. \end{aligned} \quad (7)$$

Here $E(x)$ is the electric field at the point x and the integral is obviously non-negative.

Onsager was the first one to consider the problem of H-stability which expresses the "saturation" of the interactions between a particle and the "rest of the universe." This is an absolute necessity for the existence and extensivity of the free energy in macroscopic matter. Onsager's proof is not conceptually satisfactory because it requires the existence of a hard core. Even if such a hard core (or something equivalent to it) were to be true in nature as a consequence of other non-Coulombic (strong, weak) interactions, the lower bound $\epsilon(d)$ in (7) would be, for any reasonable d , orders of magnitude larger than the actually observed energies of real matter. Thus Fermi statistics of electrons are a central ingredient of the stability of matter.

Once we have H-stability there still remains the problem of how to deal with the long range nature of the Coulomb potential: if all the charges were of the same sign then clearly the energy would be non-negative but the system would "explode"--all particles going to the surface of Λ . The reason this does not happen for neutral systems is of course screening. Just because the Coulomb forces are long range they are also very strong (their integral diverges at infinity) and cause the system to be locally neutral. The "effective" interaction between different regions of a macroscopic system is therefore greatly attenuated. This idea was turned (with some effort) into a formal proof of (1) for such systems.

Remarks

(i) We note that the results described above are for the three dimensional Coulomb system specified by the non-relativistic Hamiltonian (5). It is not clear at present how to deal with inclusion of relativistic effects. H-stability is the basic problem here--magnetic dipolar forces behave as $|x|^{-3}$ and their inclusion makes even the hydrogen atom unstable against collapse. Until this is resolved--which might involve getting a good theory of all the forces in nature--there seems little incentive to consider the thermodynamic limit problem for relativistic Hamiltonians.

(ii) The rigorous derivation of effective Hamiltonians from first principles is at the present time in a far from satisfactory state. We do not even have a precise "in principle" scheme for showing that the Lennard-Jones description of He^4 is a good approximation, in certain ranges of temperature and density, to an overall neutral system of α -particles and electrons interacting via the Coulomb potential and satisfying the proper statistics, Bose for the α -nuclei, Fermi for the electrons with spins.

It is our belief (or hope) that this problem, while very difficult, may not be entirely hopeless. I regard the work by Fröhlich and Spencer (1981) on the two dimensional charged lattice gas as having (despite its being two-dimensional and entirely classical) the right flavor for this problem. They show, in a precise way, that in a certain range of temperature and density the weight of the Gibbs measure is concentrated entirely on "neutral molecules of finite extent." We don't expect this to happen in three dimensions where the Coulomb force is weaker and there

should always be a finite density of loose charges (electrons and ions) around--we do expect that these play a negligible role at low temperatures and moderate densities. (For a more heuristic approach to this problem see article by Chandler in this volume.)

(iii) The Hamiltonian (5) corresponds to the box Λ having insulating boundaries. The existence of the thermodynamic limit for a Coulomb system in three dimensions with super-conducting boundary conditions was proven by Penrose and Smith (1972). Unlike the case for systems with short range potential, it is not known whether the free energy is the same in both cases.

Jellium

A model often used to describe certain kinds of plasmas or solids is the so-called jellium system. In this model one of the charges, say electrons, are assumed to form a uniform background of constant negative charge density in which the ions move. We shall not go into the justification of this model, which neglects fluctuations in the density of one of the species, or into any details of its properties referring the reader to the article by Ashcroft in this volume and the review by Baus and Hensen (1980). The Hamiltonian for this model is obtained from (5) by adding the potential produced by the uniform background of charge density $\bar{\rho}$.

$$H'(N, \Lambda) = H(N,) + \sum_{i=1}^N e_i \bar{\rho} v(x_i) + \frac{1}{2} \bar{\rho} \int_{\Lambda} v(x) d^3x \quad (8)$$

with

$$v_{\Lambda}(x) = \int_{\Lambda} d^3y / |x-y|. \quad (9)$$

Charge neutrality is now given by the relation

$$\sum_{\alpha=1}^k N^{\alpha} e_{\alpha} + \bar{\rho} |\Lambda| = 0. \quad (10)$$

Lieb and Narnhoffer (1975) proved the existence of the thermodynamic limit for the free energy of this system in three dimensions. In two dimensions the electrostatic potential is, of course, $\ln|x|$ rather than $|x|^{-1}$ and the proof needs changing. This was done by Sari and Merlini (1976).

In one dimension the Jellium model with electrostatic potential $|x|$ can be solved exactly classically as can the two component (no background) charged system, Lenard (1961), Edwards and Lenard (1962). When $k = 1$ in (10) the system, also known as the one component plasma, OCP, is known to form a crystal, at all temperatures $\beta > 0$. This is true in both the classical and quantum description, Kunz (1974), Brascamp and Lieb (1979) and is the only system for which crystalline Gibbs states are known to exist. There is strong theoretical and numerical (computer simulation) evidence that in three (and two) dimensions the OCP forms a crystal at low

temperatures (Wigner crystal) which melts as the temperature is raised, Baus and Hansen (1980), Ashcroft (1981), this volume.

The OCP is in some sense both simple and interesting--since its interactions are exact rather than approximate or modeled--and therefore presents a challenge to the theorist. It would be particularly interesting to know whether its behaviour in three dimensions is "physical" despite the suppression of fluctuations in one component. As already noted, the behaviour in one-dimension is artificial. In two dimensions the system is exactly solvable at one temperature, $\beta\epsilon = 2$, where the truncated correlation functions are found to be Gaussian, Jancovici (1980), a much faster than "typical" decay.

H-stability

As mentioned earlier, classical H-stability, Eq. (6), can be proven for more or less all potentials commonly used to describe the interactions between neutral molecules. There is a little known simple proof of this fact in a very complicated paper by Morrey (1959) for pair potentials $v(r)$ satisfying the inequalities

$$v(r) \geq C_1 r^{-(v+\epsilon)}, \quad r < r_0 \quad (11a)$$

$$v(r) \geq -C_2 r^{-(v+\epsilon)}, \quad r > r_0 \quad (11b)$$

where n is the dimension of space considered and C_1, C_2, ϵ are finite positive numbers. It seems worthwhile presenting his argument here. The Lennard-Jones potential clearly satisfies these conditions.

Consider a configuration $\{x_1, \dots, x_N\}$. Let λ be the smallest distance between any pair, $\lambda = \text{Min}|x_i - x_j|$, $i \neq j$. If $\lambda > r_0$ then (11b) assures that (6) is satisfied. If $\lambda < r_0$ call the pair for which this minimum is achieved x_1 and x_2 . Write then

$$U(x_1, \dots, x_N) = \frac{1}{2} \sum_{i \neq j} v(x_i - x_j) = [v(x_1 - x_2) + \sum_{j=3}^N v(x_1 - x_j)] + U(x_2, \dots, x_N). \quad (12)$$

Since the spacing between x_i and x_j is at least λ and so the density is less than $1/\lambda^v$, we have by (11) that

$$V_1 = v(x_1 - x_2) + \sum_{j=3}^N v(x_1 - x_j) \geq A_1 / \lambda^{v+\epsilon} - A_2 / \lambda^v = G(\lambda) \quad (13)$$

where $0 < A < \infty$. Let now $-b = \text{Min}_{\lambda} G(\lambda) > -\infty$ and repeat the procedure on the interaction between the $N-1$ particles $\{x_2, \dots, x_N\}$ to obtain (6). N.B. The theorem does not give a lower bound for the interaction energy of

any particle with the rest of the system. This is clearly impossible if $v(r) < 0$ for some r and there is no hard core, e.g. for the Lennard-Jones potential.

Historical Note

The paper by Morrey sets out to prove that in a certain limit the Liouville equation leads to the Euler equations of hydrodynamics. It is not clear whether the paper ever achieves this goal (I doubt it), but it does prove on the way the convergence of the Mayer expansion for the pressure at small fugacities for potentials satisfying (11). This is a remarkable achievement since the author had apparently never heard of the Mayer expansion before, so he derives it as an aside (in fifty pages) from the BBGKY hierarchy. His proof of convergence ante-dates by many years the proofs of Groeneveld, Ruelle, and Penrose; see Ruelle (1969).

CORRELATION FUNCTIONS AND SUM RULES

So far we have dealt only with the thermodynamic limit of the free energy. We now wish to consider the behavior of the correlation functions (c.f) in this limit. This problem is intrinsically more difficult. Unlike the free energy the c.f do not always have a unique limit. When the system can exist in more than one phase, i.e. at a first order phase transition, the c.f. depend on the boundary conditions used to go to the infinite volume limit. For systems composed of neutral molecules, e.g. those with potentials satisfying (11), there are several ways of dealing directly with the probability distributions of local configurations in infinite systems. This is not only esthetically satisfying but also greatly facilitates the rigorous investigation of phase transitions--a phenomena which is well defined only in the thermodynamic limit. These approaches do not readily work for Coulomb systems. The most promising approach at present appears to be that of Gruber and Martin (1979, 1980) in which the infinite volume equilibrium c.f. are assumed to satisfy the stationary BBGKY hierarchy. This leads to some interesting sum rules for inhomogenous charged systems, Gruber, Lebowitz and Martin (1981), which we now describe briefly.

We consider a system consisting of k species of charged particles which move either in the whole v -dimensional space R^v , or in a restricted domain \mathcal{D} defined by appropriate walls. The only condition we impose on \mathcal{D} is that it extends to infinity in at least one direction. Typically \mathcal{D} can be the outside of a sphere or the half-space of the electrode problem.

The particles interact by means of a two body force of the form

$$F_{\alpha_1 \alpha_2}^s(x_1 - x_2) + e_{\alpha_1} e_{\alpha_2} F(x_1 - x_2) \quad (14)$$

where $F_{\alpha_1 \alpha_2}^s(x)$ is short range and $F(x)$ is the Coulomb force,

$$F(x) \sim \frac{x}{|x|^v}, \quad |x| \rightarrow \infty. \quad (15)$$

The thermodynamic equilibrium state of the system at a temperature T is assumed to be described by means of correlation functions $\rho_{\alpha_1}(x_1)$,

$\rho_{\alpha_1 \alpha_2}(x_1, x_2) \dots$, which have their usual meaning, $\rho_{\alpha_1}(x_1)$ being the density of species α_1 at x_1 , etc. We shall write these as $\rho(q_1)$, $\rho(q_1, q_2)$, $\rho(Q)$, using the abbreviated notation $q_1 = (\alpha_1, x_1)$, $Q = (q_1, \dots, q_n)$. These functions are assumed to satisfy the stationary BBGKY equation

$$kT \nabla_1 \rho(q_1, Q) = [e_{\alpha_1} E(x_1) + \sum_{j=2}^n F(q_1 - q_j)] \rho(q_1, Q) + \int \rho dq F(q_1 - q) [\rho(q_1, q, Q) - \rho(q_1, Q) \rho(q)]. \quad (16)$$

Here $E(x)$ is the electric field due to all the charges, i.e. all the system's and all the external charges, $F(q_1 - q_2) = e_{\alpha_1} e_{\alpha_2} F(x_1 - x_2)$.

Eq. (16) together with certain clustering assumptions on the "truncated" correlation functions imply the absence of non-translation in-variant Gibbs states, Gruber and Martin (1981) as well as certain sum rules.

Electrostatic sum rules

Define the excess charge density at x in presence of charges $Q = (q_1, \dots, q_n)$ as,

$$C(x|Q) = \sum_{\alpha} e_{\alpha} \left[\frac{\rho(q, Q)}{\rho(Q)} + \sum_{j=1}^n \delta_{\alpha \alpha_j} \delta(x - x_j) - \rho(q) \right] \quad (17)$$

and consider the following relations.

0-sum rule: neutrality

$$\int C(x|Q) dx = 0. \quad (18)$$

More explicitly,

$$\left(\sum_j^n e_{\alpha_j} \right) \rho(Q) + \int dx \sum_{\alpha} e_{\alpha} [\rho(q_{\alpha}, Q) - \rho(q_{\alpha}) \rho(Q)] = 0. \quad (19)$$

1-sum rule: absence of dipolar moment

$$\int x C(x|Q) dx = 0,$$

or

$$\left(\sum_j^n e_{\alpha_j} x_j \right) \rho(Q) + \int dx \sum_{\alpha} e_{\alpha} x_{\alpha} [\rho(q_{\alpha}, Q) - \rho(q_{\alpha}) \rho(Q)] = 0. \quad (20)$$

2-sum rule: isotropy

$$\int x^r x^s C(x|Q) dx = \delta_{rs} \frac{1}{v} \int |x|^2 C(x|Q) dx. \quad (21)$$

Proposition.

Let the truncated correlation functions, i.e. $\rho(q_1, q_2) - \rho(q_1)\rho(q_2)$, etc. decay faster than $|x|^{-(\nu+\ell)}$ for $|x| \rightarrow \infty$. If this holds with $\ell = 0, 1, 2$ then the 0, 1, 2 sum rules follow respectively, except in one dimensional Coulomb systems.

Validity of Clustering Assumption

B. Jancovici (1981) has found that for the semi-infinite Jellium system in two dimensions, at the special temperature $\beta e^2 = 2$, the truncated pair correlation decays, in the direction parallel to the wall, only as r^{-2} . In all other directions it decays like a Gaussian. Our clustering conditions are therefore not satisfied. He finds that the $\ell = 0$ sum rule is satisfied but not the $\ell = 1, 2$. It is not clear just how general this slow decay may be but it certainly argues for caution in assuming exponential screening, a la Debye, even at high temperatures, c.f. Blum et al. (1981).

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