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EQUILIBRIUM STATISTICAL MECHANICS OF HARD PARTICLE FLUIDS

by

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ABSTRACT
The governing equation for the ϵ-parameter which features in the density function in classical phase space is solved in low and high density regimes for the special case of the hard particle system. The results obtained for the equation of state are shown to compare favourably with those in the literature. The new solutions also suggest a re-examination of the nature of critical behaviour in the presence of hard-core interaction close to "Bernal" density.

1. INTRODUCTION

The density function in canonical phase space may be written as $\rho(p,q)$, where q represents a point in canonical coordinate subspace and p represents a point in canonical momentum subspace. In the canonical ensemble,

$$\rho(p,q) = \exp(-\beta H_N)/(\int \exp(-\beta H_N)dpdq) \quad (1)$$

where $\beta = 1/kT$, k is Boltzmann's constant, T is temperature, and H_N is the classical Hamiltonian. It is usually easy to integrate over the momentum subspace. On doing this, the resulting density function may be written as $\rho(q)$. The following functional form is proposed for $\rho(q)$ for a hard particle fluid of N particles in volume V:

$$\rho(q) = \left\{ \left[a(V - \epsilon NKV_o)\right]^N/N! \right\}^{-1} \quad (2)$$

where a is some fixed constant with the dimension V^{-1}, which thus allows $\rho(q)$ to be dimensionless. Eq (2) is valid when no two or more hard cores of particles overlap, otherwise $\rho(q)$ is zero. The particles are point-like, hence ϵ is a dimensionless quantity which is independent of location in phase space and depends only on N and V. Because $\rho(q)$ does not depend on location in coordinate subspace, this implies that all allowed particle configurations are equally probable. V_o is the volume of the hard core of each particle and KV_o is the average volume of space per particle at "closest parking" of identical hard particles. (This paper is restricted to a consideration of identical hard spheres.) Eq (2) shows that the solution for the ϵ function gives the complete statistical thermodynamics of the problem. Introducing Boltzmann's factor (see eq (1)), allows the extension of eq (2) to systems with soft core interactions.

2. RESULTS AND DISCUSSION

Ref [1] gives details of the derivation of the differential equation which governs ϵ in the hard particle case. A similar differential equation can be derived for the soft core interaction case. The differential equation, accurate at all allowed densities, in the hard core case, is

$$1 + \eta^2 K d\epsilon/d\eta = \exp - \{\eta(1 - \epsilon\eta K)^{-1}[4 - \epsilon K + K\eta(4\eta - 1)d\epsilon/d\eta]\} \quad (3)$$

where $\eta \equiv \tau V_o$ is the packing fraction, and τ is the number density N/V. This is a nonlinear equation, for which analytic solutions at arbitrary densities would be difficult to find. At extreme ends of the density regime however, simple closed form solutions are possible. One observes in eq (3) that $\epsilon = 4/K$ is a trivial solution. To obtain nontrivial solutions, we expand eq (3) as a power series in η. To allow for systematic successive approximations, the power series will be developed on one side of the equation, that is,

$$(1 + \eta^2 K d\epsilon/d\eta)\exp(-\epsilon\eta K - \eta^2(\epsilon^2 K^2 - 4\epsilon K + K d\epsilon/d\eta) + \dots) = \exp(-4\eta).$$

This allows the rewriting of eq (3) in series form as

$$1 - \epsilon\eta K + \eta^2(4\epsilon K - \tfrac{1}{2}\epsilon^2 K^2) + \dots = \exp(-4\eta) \quad (4)$$

At low densities, one may keep terms of order η on the left hand side of eq (4), yielding

$$\epsilon = (1 - \exp(-4\eta))/\eta K \quad (5)$$

In the "very low" density limit, we find that we obtain the trivial solution. Eq (5) leads to the result

$$\rho(q) = ((aV\exp(-4\eta))^N/N!)^{-1} \quad (6)$$

The partition function obtained using eq (6) agrees with results in the literature (see ref [2]). To obtain results which are valid at high densities, we need to keep more terms in eq (4). As this leads to nonlinear differential equations which are difficult to solve, some other means of solving eq (3) must be sought. Note that the maximum value η may have is $\eta_{max} = 1/K$. Also, because the volume in configuration space is expected to tend to zero at maximum density, we may expect $\epsilon \longrightarrow 1$ for $\eta \longrightarrow \eta_{max}$. If, for instance, the quantity in square brackets in eq (3) is nonzero in the high density limit, we find, instead, that $d\epsilon/d\eta \longrightarrow -K$. Inverting eq (3), we find

$$\epsilon = [\ln(1 + \eta^2 K d\epsilon/d\eta) + 4\eta + \eta^2 K(4\eta - 1)d\epsilon/d\eta][\eta K(1 + \ln(1 + \eta^2 K d\epsilon/d\eta))]^{-1} \quad (7)$$

An iterative scheme for solving eq (7) is now proposed. As a first guess for $d\epsilon/d\eta$, we choose $-K$, and this ensures that the resulting expression for ϵ is accurate near η_{max}. On the first iteration, we therefore obtain the expression

$$\epsilon = [\ln(1 - \eta^2 K^2) + 4\eta + \eta^2 K^2 - 4\eta^3 K^2][\eta K(1 + \ln(1 - \eta^2 K^2))]^{-1} \quad (8)$$

Eq (8) is then used to determine a new expression for $d\epsilon/d\eta$ and this, in turn, is substituted in eq (7) to find a new expression for ϵ. If this process is repeated several times, accuracy of ϵ from the highest density up to some value of mid-density may be hoped for. The equation of state is derived from the expression

$$P = -(\partial F/\partial V)_T$$

where P is pressure and F is Helmholtz free energy. From eq (2), we deduce that the equation of state is

$$\phi = (1 - \epsilon\eta K)^{-1}(1 + \eta^2 K d\epsilon/d\eta) \qquad (9)$$

where $\phi = P/\tau kT$. At low densities, eq (5) may be substituted into eq (9) to obtain the result

$$\phi = 1 + 4\eta \qquad (10)$$

This is a two-term series which reproduces the first two terms of the virial expansion for the hard sphere fluid [3]. Figure 1 shows that eq (10) is an approximation which compares well with low density computer simulation results, up to a packing fraction of about 0.2. In the van der Waal approximation, we have

$$\phi = (1 - 4\eta)^{-1} = 1 + 4\eta + 16\eta^2 + 64\eta^3 + \ldots$$

Although the first two coefficients in the expansion agree exactly with eq (10), higher order terms allow the equation to deteriorate more rapidly than eq (10). Figure 1 shows that the van-der-Waal (VdW) curve compares well with computer simulation (CS) results, only up to a packing fraction of about 0.15. In figure 1, curve (B) is from an approximate equation of state (see ref 1), and (C) is from a high-density linearization of eq (7).

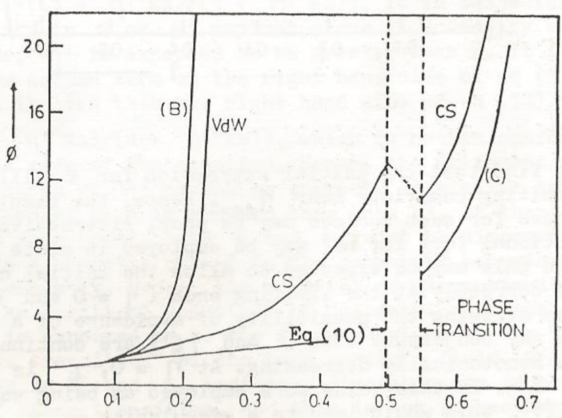

Figure 1

In eq (7), if our initial choice for $d\epsilon/d\eta$ is ϵ' in the iteration scheme introduced earlier, and if ϵ' is taken as some constant (independent of η) in the range from $-K(1 - 1/e)$ to $-\infty$, eq (7) will become singular at

$$\eta = ((1 - 1/e)/(K|\epsilon'|))^{\frac{1}{2}},$$

which is a point within the relevant η region, implying an undesirable initial expression for ϵ. (Note that the "pole" of eq (7) at the above η value is not cancelled by a "zero"). Hence, the initial choice $\epsilon' = -K$, was not entirely appropriate, as it leads to a singularity in ϵ at

$$\eta = K^{-1}(1 - e^{-1})^{\frac{1}{2}},$$

as is seen in figure 2. For initial choices of ϵ' outside this

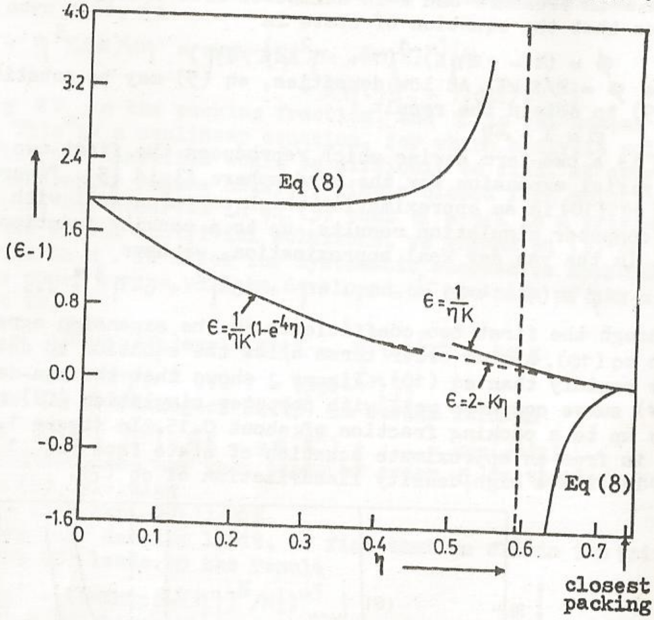

Figure 2

range, we find that the initial expression for ϵ will not have the proper limiting behaviour near η_{max}. Hence, the resulting iteration process for such choices may be poor. Alternatively, some initial functional form for ϵ' may be employed in place of a constant value, and this may be expected to allow the initial expression for ϵ behave correctly at the limiting ends ($\eta = 0$ and $\eta = \eta_{max}$), while also allowing the possibility of avoidance of a singularity in ϵ. We may conjecture that ϵ and $|\epsilon'|$ are continuous functions which are monotonically decreasing. At $\eta = 0$, ϵ' is correctly given as $-8/K$. If this value were employed as being valid for all η in eq (7), this would lead to a singularity at $\eta_s \approx 0.223$. If smaller values for $|\epsilon'|$ are employed, larger values will be obtained for η_s. (For example, it is already clear that for $\epsilon' = -K$, η_s is approximately 0.589). Hence, as η increases continuously from 0 to η_{max} (≈ 0.74), $|\epsilon'|$ should decrease continuously from $8/K$ to K, and the corresponding η_s values will increase from 0.223 to 0.589. Hence, the value of η under consideration and η_s must correspond somewhere, necessitating that ϵ be singular somewhere, which is unphysical. Hence, the initial conjecture concerning the functional form for ϵ and ϵ' must be false. More generally, we have that similar difficulties are also encountered if one conjectures that ϵ and ϵ' are continuous functions (not necessarily monotonic) satisfying the conditions that at $\eta = 0$, $\epsilon = 4/K$ and

$\epsilon' = -8/K$, while at $\eta = \eta_{max}$, $\epsilon = 1$ and $\epsilon' = -K$. Therefore, it is necessary that discontinuities in ϵ and/or ϵ' must be allowed if ϵ must always be finite. If ϵ is taken as discontinuous at some point, then eq (7) shows that a discontinuity in ϵ' is also necessary. We may ask whether it is possible to have a discontinuity in ϵ' if ϵ is continuous. If ϵ' has values a and b at some value $\eta = \eta'$, then the assumption that ϵ is continuous at η' would imply that eq (7) yields the following:

$$\epsilon\eta' K(1 + \ln(1 + \eta' Ka)) = \ln(1 + \eta'^2 Ka) + 4\eta' + \eta'^2 K(4\eta' - 1)a$$

$$\epsilon\eta' K(1 + \ln(1 + \eta' Kb)) = \ln(1 + \eta'^2 Kb) + 4\eta' + \eta'^2 K(4\eta' - 1)b$$

These then lead to

$$\epsilon\eta' K\ln((1 + \eta'^2 Ka)/(1 + \eta'^2 Kb)) = \ln((1 + \eta'^2 Ka)/(1 + \eta'^2 Kb)) + \eta'^2 K(4\eta' - 1)(a - b) \qquad (11)$$

Clearly, the maximum value ϵ may assume for any given η is $1/\eta K$. Hence, we may assume $\epsilon\eta' K \leq 1$. Then, for a > b, the left hand side of eq (11) will be some positive quantity which is less than or equal to $\ln((1 + \eta'^2 Ka)/(1 + \eta'^2 Kb))$. It is conjectured that a discontinuity in ϵ or ϵ' may not occur at a density as low as $\eta = \frac{1}{4}$. Hence, η' is expected to be greater than $\frac{1}{4}$. It follows then that the second term on the right hand side of eq (11) is positive. This implies that the right hand side of eq (11) is greater than $\ln((1 + \eta'^2 Ka)/(1 + \eta'^2 Kb))$, which is not in conformity with the left hand side of the equation. Hence, the statement that ϵ may be continuous at η' cannot be correct. (A similar conclusion is also arrived at if a is assumed less than b). It therefore implies that at some point, both ϵ and ϵ' must be discontinuous. This suggests a dramatic change in the geometric behaviour of the hard sphere assembly. Hence, the point(s) of discontinuity may be referred to as "critical point(s)" of "geometrical phase transition", which is expected to be the fundamental basis for "thermodynamic phase transition" of the hard particle fluid. From eq (9), discontinuity in ϵ and ϵ' indicates discontinuity in pressure at the point of phase transition, and this is not in keeping with notions of first order phase transition usually conjectured for the hard particle fluid. One may therefore conclude that the phase transition in the hard sphere system must involve at least a discontinuous pressure change. It is the author's opinion that the results reported in this paper form the first fundamental theory which is able to predict phase transitions in a realistic three dimensional model for a fluid.

In the very high density regime, we may look for a simple linear expression, such that $d\epsilon/d\eta = -K$ and $\epsilon \longrightarrow 1$ at η_{max}. Such a linear function is easily obtained as $\epsilon = 2 - K\eta$. This function is close to the $\epsilon = 1/\eta K$ curve (which gives the maximum possible value for ϵ at any η value) in the high density regime, as is evident from the plot in figure 3. Employing the linear expression for $\in$, we obtain the equation of state, which is accurate at high densities, as

$$\phi = (1 + \eta K)/(1 - \eta K) \tag{12}$$

In figure 4, a plot of PV_{cp}/NkT against $(V/V_{cp} - 1)$ is given, where V_{cp} is the closest packed volume NKV_o. The curve corresponding to eq (12) is marked "A". This curve however indicates a slightly lower pressure than that predicted by computer simulation.

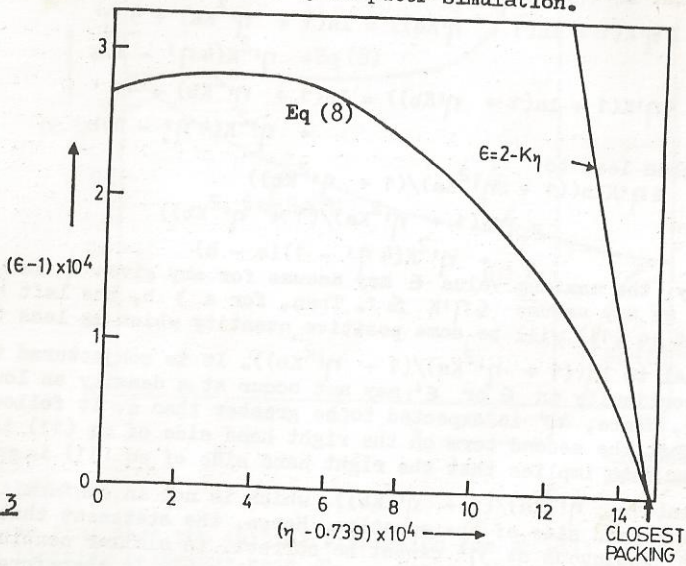

Figure 3

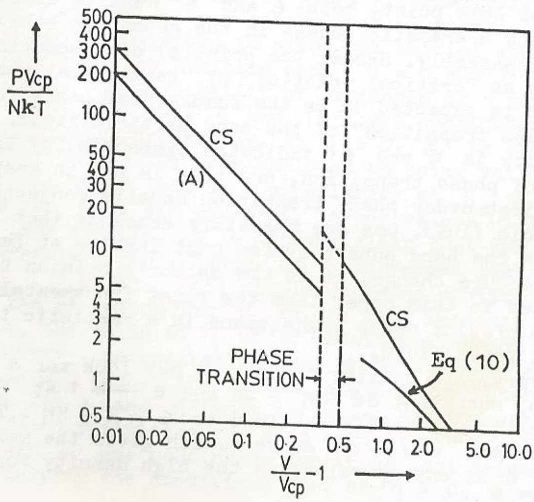

Figure 4

Finally, in view of the results reported here, it will be useful to re-evaluate the notion of a possible singularity in pressure at "Bernal density", a conjecture widely seen in the literature, and which is somewhat supported by results of computer experiments (see ref [3]). From inspection of eq (9), we have that a singularity in pressure at some density $\hat{\eta} < \eta_{max}$, would require that either $d\epsilon/d\eta$ be singular at $\hat{\eta}$ or $\epsilon\hat{\eta}K$ be equal to unity. The latter condition requires that the partition function Z_N be zero at $\hat{\eta} < \eta_{max}$. As this is unrealistic (since Z_N, which is simply a measure of the size of space of the allowed set of configurations, may not be expected to be zero at any allowed density other than $\eta = \eta_{max}$), we are only left with the possibility $d\epsilon/d\eta \longrightarrow \infty$ at $\hat{\eta}$. We already had that ϵ is discontinuous at one or more points in the region $\eta < \eta_{max}$. Therefore, it is possible that for finite N and V, regions around such points of discontinuity may constitute regions of sharp gradients in ϵ, allowing the possibility of large pressures in the neighbourhoods of such points for "small" finite systems. Hence, this may explain observations of computer experiments; and in the thermodynamic limit, such point(s) of discontinuity in ϵ may well be interpreted as isolated point(s) of infinite pressure, contradicting the idea of a gradual approach to infinite pressure as is usually suggested in the literature.

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