Hard-particle-fluid equation of state and phase transition employing nearest-neighbor correlations

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An approach for determining the free energy of classical fluids developed in a recent paper [U. F. Edgal, J. Chem. Phys. **94**, 8179 (1991)] is employed here in an approximate form for the hard-sphere fluid. The nature of the hard-particle potential readily allows an accurate investigation of the equation of state essentially over the entire density regime. Although a direct prediction of a first-order-type phase transition is not made, the present approach is, however, able to provide results which agree well with computer-simulation data both in the low-density branch of the equation of state and also in the high-density branch. A van der Waals–like loop is also reproduced in the supposed phase-transition region. The equation of state of the hard-sphere fluid is formulated in terms of a (highly) nonlinear differential equation with a single unknown parameter. The approximate nature of the present scheme is then seen to be due to the approximate formulation provided for the unknown parameter.

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I. INTRODUCTION

We present an investigation of the hard-sphere fluid employing nearest-neighbor probability density functions [1,2] (NNPDF's) which describe nearest-neighbor correlations in fluid systems. In scaled particle theory [1], NNPDF's employing the first nearest neighbor is used to develop a theory of fluids, while more recently, generalizations involving more distant neighbors [2] have also been used to provide a theory of fluids. Developments indicate that the use of NNPDF's may be expected to allow for an "efficient" investigation of fluid or material systems (at all densities and temperatures). The investigation of hard-particle fluids employing NNPDF's is therefore of considerable importance as the hard-particle fluid is usually considered a good first-order model [3] in the investigation of most other realistic fluid systems. Interestingly enough, we find that the nature of the hard-sphere potential, i.e.,

$$\Phi(r)=\begin{cases}\infty & \text{for } r<2r_0\\ 0 & \text{for } r>2r_0\end{cases}$$

($2r_0$ being the hard-sphere radius of closest approach), allows for an exact analytic approach (avoiding extensive simulation computations) if the first-nearest-neighbor probability density function [2] $g_1(r_1)$ may be known analytically. However, since higher-order NNPDF's (which may be known exactly only from an elaborate scheme [2]) are required to obtain $g_1(r_1)$ exactly, a formulation for $g_1(r_1)$ is therefore provided which involves a single unknown parameter which is readily chosen adequately (although approximately) leading to accurate results for the equation of state of the hard-sphere system for all physically allowable densities. Scaled particle theory provides a different approximate approach for finding $g_1(r_1)$. (See also the article by Reiss [4] for a brief review.) Our formulation yields a nonlinear differential equation governing the compressibility factor which we integrate by the Runge-Kutta method. We assume the partition function $\tilde{Z}(N,V)$ may be written in terms of the "reduced volume" [2] $\tilde{V}$ as $(\Omega\tilde{V})^N/N!$. The quantity Ω is assumed to have the dimension of (volume)$^{-1}$ making the partion function dimensionless. The configurational contribution to the partition function $[Z(N,V)]$ is obtained by setting Ω to unity. $\tilde{V}$ may be expressed in one of two interesting ways, $\tilde{V}=(V-\epsilon NkV_0)$ or $\tilde{V}=\tilde{\epsilon}V$, of which we employ the former for the most part in this paper (the later expression was employed in Ref. [2]). V is the volume of the system containing N identical hard spheres each with a hard-core volume V_0. In the "closest-packed" state, the average volume per particle (the Wigner-Seitz or Voronoi cell) for N large enough is kV_0, where in one, two, and three dimensions, k is, respectively [5], 1, $(2/\pi)\sqrt{3}$, and $(3/\pi)\sqrt{2}$. Clearly, the maximum allowable density ρ $(=N/V)$ is reached when the packing fraction $\eta(=\rho V_0)$ is equal to $1/k(=\eta_{\max})$. The parameter ϵ is a dimensionless quantity which is expected to approach unity (while $\tilde{\epsilon}$ approaches zero) as η tends to $\eta_{\max}$ since $Z(N,V)\sim 0$ in the high-density limit. On the other hand, $\tilde{\epsilon}$ clearly approaches unity as $\eta\rightarrow 0$, while it is not so clear what ϵ may approach. (However, see the developments in Sec. II.)

In Sec. II the scheme employing NNPDF's and the governing nonlinear differential equations for ϵ and the compressibility factor are developed. The differential equations are then solved in the low-density limit yielding results which agree with well known results. In Sec. III, we present results for the equation of state at all densities (including possible phase-transition behavior) obtained from numerically integrating the above nonlinear differential equations. Our results agree quite well with computer simulation results both in the low- and high-density branches of the equation of state. This we consid-

er significant, as it has so far been difficult to provide an adequate theory of realistic fluid systems at high densities. Also, our method is able to reproduce a van der Waals–like loop in the region of the supposed phase transition. This therefore indicates that a full scale use of NNPDF's as detailed in Ref. [2] may be expected to provide accurate numerical results including a direct prediction of a first-order phase transition in the hard-sphere system which our present approximate approach has so far been unable to provide. Nevertheless, our results are also able to allow for reasonable assessment of certain methods of investigation and long-standing notions concerning the hard-particle system in the neighborhood of a phase transition.

II. SCHEME EMPLOYING NNPDF's AND APPROXIMATE SOLUTIONS FOR ϵ, ϕ

The scheme for determining ϵ (as discussed in an earlier paper [2]) is first presented in this section for the case of the hard-sphere fluid. We begin by employing the equation [2]

$$\tilde{Z}(N,V)=\int_0^V \tilde{Z}(N-1,V_1)P\Omega\, dV_1 \ . \tag{1}$$

Ω is the volume in internal coordinate space, which in our present situation may be set at unity. P is given as [2]

$$P=\int \cdots \int g_{1,\ldots,n}^{\mathbf{x}_1'}(\mathbf{x}_1,\ldots,\mathbf{x}_n) \times \exp[-\beta E_2(\mathbf{x}'_1,\mathbf{x}_1,\ldots,\mathbf{x}_n)]d\mathbf{x}_1\cdots d\mathbf{x}_n . \tag{2}$$

$g_1^{\mathbf{x}_1'}(\mathbf{x}_1,\ldots,\mathbf{x}_n)$ is the general point process [2] n-nearest-neighbor probability density function of the origin (said to be situated at $\mathbf{x}_1'$) assumed on the boundary of volume V_1 (V_1 may vary from 0 to V). It is assumed the boundary of V_1 is locally flat "almost everywhere" "almost always." Observe that in the present problem, we may employ P in place of its average $\langle P \rangle$ (see Ref. [2] for a detailed explanation). $E_2(\mathbf{x}_1',\mathbf{x}_1,\ldots,\mathbf{x}_n)$ is the contribution to the energy of the hard-particle system for the given configuration $\mathbf{x}_1,\ldots,\mathbf{x}_n$ of the n-nearest neighbors when a particle is introduced at the origin $\mathbf{x}_1'$. Since the system presently under consideration is sufficiently simple, we find E_2 is independent of $\mathbf{x}_1'$. In fact, the simplicity of the system (owing to the nature of its interaction potential) allows that knowledge of the distance of the origin to its nearest neighbor is sufficient to determine [2] E_2. Hence only the first-nearest-neighbor NNPDF (i.e., the $n=1$ case) need be considered in Eq. (2). In that case, Eq. (2) may be written exactly as

$$P=\int g_1^{\mathbf{x}_1'}(\mathbf{x}_1)e^{-\beta E_2(\mathbf{x}_1)}d\mathbf{x}_1 \ , \tag{3}$$

where

$$E_2(\mathbf{x}_1)=\begin{cases}0 & \text{for } r_1>2b_0\\ \infty & \text{for } r_1<2b_0\end{cases} .$$

r_1 is the radial part of $\mathbf{x}_1$ and b_0 is the radius of a hard-particle sphere. If the NNPDF ($n=1$ case) is known exactly, then ϵ and hence the equation of state of the hard-sphere fluid can be calculated exactly. $g_1^{\mathbf{x}_1'}(\mathbf{x}_1)$ is usually known exactly only through some extensive numerical calculations [2]. In the present paper however, an approximate scheme is employed to determine $g_1^{\mathbf{x}_1'}(\mathbf{x}_1)$; herein lies the approximate nature of the approach in this paper which is clearly a variation of that given elsewhere [2]. This scheme can be expected to be useful as we may envisage that physical arguments may readily be available for adequately approximating $g_{1,\ldots,n}^{\mathbf{x}_1'}(\mathbf{x}_1,\ldots,\mathbf{x}_n)$ especially when n is small (i.e., $n=1$, say). For systems with "softer" potentials, n needs to be at least ~ 10, indicating why the hard-particle fluid probably constitutes the simplest of known realistic fluid systems that can be investigated.

In the low-density limit, we expect the NNPDF for $n=1$ to tend to that for the "Poisson fluid" [2], i.e.,

$$\lim_{\rho\to 0} g_1(r_1)\to 2\pi r_1^2\rho e^{-(2/3)\pi\rho r_1^3} . \tag{4}$$

(The superscript $\mathbf{x}_1'$ has been dropped.) This is a "bell"-shaped function with "long lower tail." We expect the following properties for $g_1(r_1)$ at other densities on obvious physical grounds: (i) The basic bell-shape (with long lower tail) structure should be generally retained for $g_1(r_1)$ at virtually all densities, (ii) the "spread" of $g_1(r_1)$ (indicative of the variance of r_1 for the most part) should decrease as ρ increases; and (iii) the mean $\langle r_1 \rangle$ [which approximately corresponds to the peak of $g_1(r_1)$] should approach that for the Poisson fluid as $\rho\to 0$ (i.e., $\eta\to 0$); while for $\eta\to\eta_{\max}$, the mean should decrease towards zero. To satisfy the first and second conditions, we may simply employ the basic form of (4). To satisfy the third condition, an effective density $\tilde{\rho}$ (or $\tilde{\eta}$) must be employed such that $\tilde{\rho}\to\rho$ as $\eta\to 0$ (allowing $\langle r_1 \rangle$ coincide with that of the Poisson fluid) while for $\eta\to\eta_{\max}$, we require $\tilde{\rho}\to\infty$ (allowing $\langle r_1 \rangle$ to tend to zero). Several relations may be chosen between $\tilde{\rho}$ and ρ of which we employ the simple form

$$\tilde{\rho}=\rho(1-\eta/\eta_{\max})^{-m(\eta)} ,$$

where $m(\eta)$ is some positive function of η. If $m(\eta)$ varies slowly (as will be obvious in later developments) in a broad range of the η regime, the above form can be considered quite appropriate. The formulation for the ($n=1$ case) NNPDF is therefore given for all densities as

$$g_1(r_1)=2\pi r_1^2\tilde{\rho}e^{-(2/3)\pi\tilde{\rho}r_1^3} . \tag{5}$$

Hence we may write

$$P=\int_{2b_0}^{\infty} g_1(r_1)dr_1=\int_{2b_0}^{\infty} dr_1 2\pi r_1^2\tilde{\rho}e^{-(2/3)\pi\rho r_1^3} =\exp[-4\eta(1-\eta k)^{-m(\eta)}] . \tag{6}$$

At low densities, all but the upper tail of $g_1(r_1)$ contributes to the above integral; while at high densities, only the lower tail contributes. Hence we may expect that the rate of decrease of P (i.e., $|dP/d\eta|$) should generally increase from a small value at low densities, reach

a maximum somewhere at mid-density (η_b say), and become small again at high densities. Clearly, an estimate of η_b is obtained by determining the density where the location of the maximum of $g_1(r_1)$ [i.e., $r_1(\max)$ say] is equal to $2b_0$. We may readily show that [6] $r_1(\max)=(1/\pi\tilde{\rho})^{1/3}$. Hence η_b is then obtained from the equation

$$(1-\eta_b/\eta_{\max})^{-m(\eta_b)}=1/6\eta_b \ .$$

η_b is expected to be $\ll\eta_{\max}$, so the left-hand side of the above equation may be approximated as unity. η_b is then readily estimated as ~ 0.167 (in approximate conformity with the initial assumption). This result indicates that only in a very small region of the η domain (i.e., $0\lesssim\eta\lesssim 0.167$) do we have to bother about adequately formulating most portions (i.e., the upper tail and middle portions) of $g_1(r_1)$ to yield proper behavior for P. However, since at such low densities $\tilde{\rho}$ is substantially insensitive to variations in m, a similar insensitivity is also expected of $g_1(r_1)$ (and hence of P as well). In which case, it is sufficient to fix m at some (average) value in the very-low-density regime ($\eta\lesssim\eta_b$) to provide adequate behavior for P.

For densities reasonably greater than η_b, the form of most portions of $g_1(r_1)$ become irrelevant and only the lower tail region need be adequately approximated. Hence our original formulation of $g_1(r_1)$, in which it was claimed that $\langle r_1\rangle$ [which is usually close to $r_1(\max)$] tends to zero as $\eta\to\eta_{\max}$, was actually to provide a proper formulation for the lower tail of $g_1(r_1)$ which produces the right effect on P. (In fact, a consideration of the nature of the general point process [2] shows that $\langle r_1\rangle$, although monotonically decreasing with increasing η, does not necessarily tend to zero in the $\eta_{\max}$ limit.) From the above, it is clear that the nature of the decrease of P (as density increases) may be said to be partly due to a monotonic decrease of $\langle r_1\rangle$ [or $r_1(\max)$] and partly due to a monotonic decrease in the "spread" of $g_1(r_1)$. In our formulation, while the second effect may be said to be reasonable [as the spread in $g_1(r_1)$ tends to the right limit of zero in the $\eta_{\max}$ limit], the first effect is definitely "harsh" (as $\langle r_1\rangle$ is made to tend to zero rather than a nonzero value in the $\eta_{\max}$ limit). Hence we may expect that we need to decrease m as we increase η, in order to nullify the above effect, thus providing an appropriate behavior for P. In the region of the (supposed) phase transition, $\langle r_1\rangle$ will still definitely decrease monotonically with density as the average volume per particle must always decrease with density. However, owing to strong density fluctuations, the spread in $g_1(r_1)$ will be larger than what may be expected for the spread outside (but generally within the neighborhood of) the phase transition region [thus resulting in a $g_1(r_1)$ which is relatively less sharply peaked within the region of phase transition]. This effect has a tendency to either reduce the rate at which the area under the tail of $g_1(r_1)$ decreases (leading to decrease in the rate at which P decreases) or in fact increase the area under the tail (thereby increasing P) as η increases. These effects clearly result in a rapid decrease to much smaller m values implying that large gradients in $m(\eta)$ occur in the phase transition region. As we go into the high-density region within the phase transition, however, we may expect that the effect of the broadening of $g_1(r_1)$ should begin to decrease considerably [especially because the spread of $g_1(r_1)$ should begin to decrease substantially] thereby causing the rate of decrease of the area under the tail of $g_1(r_1)$ to "recover." Hence $m(\eta)$ is expected to stop dropping quickly (and in fact may possibly briefly increase). In conclusion therefore, we may expect that while $m(\eta)$ may drop with sharp gradients (in some nonobvious fashion) in the low-density region of the phase transition, it should also generally decrease with η but with much "milder" slopes outside the phase-transition region (low- and high-density portions), as well as in the high-density region within the phase-transition regime.

From Eq. (1), we easily arrive at the equation

$$\frac{\partial Z(N,V)}{\partial V}=Z(N-1,V)e^{\tilde{P}(\eta)} \ , \tag{7}$$

where $P=e^{\tilde{P}(\eta)}$ and hence $\tilde{P}(\eta)=-4\eta(1-\eta k)^{-m(\eta)}$. We may write

$$\epsilon(N-1,V)=\epsilon(N,V)-\frac{\partial\epsilon(N,V)}{\partial N}=\epsilon-\frac{1}{V}\frac{d\epsilon}{d\rho} \ . \tag{8}$$

(It is assumed ϵ may be written as a function of only the single variable ρ.) Writing P',H as pressure and Helmholtz free energy respectively, we have from $P'=-(\partial H/\partial V)_T$ (T is temperature) the hard-sphere fluid equation of state:

$$\phi=(1-\epsilon\eta k)^{-1}\left[1+\eta^2 k\frac{d\epsilon}{d\eta}\right] \ . \tag{9}$$

ϕ is the compressibility factor $P'/\rho KT$ (where K is the Boltzmann constant). Employing the expression of Eq. (8) in Eq. (7) yields the differential equation governing ϵ as

$$\left[1+\eta^2 k\frac{d\epsilon}{d\eta}\right]=e^{\tilde{P}(\eta)}\exp\left[-1+(1-\epsilon\eta k)^{-1}\left[1+\eta^2 k\frac{d\epsilon}{d\eta}\right]\right] \ . \tag{10}$$

This is a "differential algebraic equation" [7] whose solutions are usually found either by approximate techniques or at best by numerical means, owing to extreme nonlinearities. $\tilde{P}(\eta)$ is some function of η which may be formulated approximately by formulating the $m(\eta)$ function approximately. ϵ and $m(\eta)$ may be presumed analytic functions of η in the low-density limit. Hence we may write in the low-density limit, $\epsilon=\sum_{m=0}^{\infty}a_m\eta^m$, $m(\eta)=\sum_{n=0}^{\infty}b_n\eta^n$, and employing these in (10) yields

$$\left[1-\eta k\sum_{m=0}^{\infty}a_m\eta^m\right]\ln\left[1+\eta^2 k\sum_{m=1}^{\infty}ma_m\eta^{m-1}\right]$$
$$=\eta^2 k\sum_{m=1}^{\infty}ma_m\eta^{m-1}+\eta k\sum_{m=0}^{\infty}a_m\eta^m$$
$$-\left[1-\eta k\sum_{m=0}^{\infty}a_m\eta^m\right]4\eta(1-\eta k)^{-\sum_{n=0}^{\infty}b_n\eta^n}. \quad (11)$$

Keeping up to terms of order η easily yields the result $a_0=4/k$, which agrees with the low-density result given in Ref. [2] (after employing the approximation $e^{-4\eta}\approx 1-4\eta$. Note also that the ϵ variable of Ref. [2] actually has the same meaning as the variable $\tilde{\epsilon}$ in this paper.) Using this result in (9) is also seen to yield the well known van der Waals [3] equation of state for hard-particle fluids. If next we keep say up to terms of order η^3 in (11) and equate coefficients, we obtain the first three coefficients in the expansion for ϵ and hence we may write

$$\epsilon=4/k+(4b_0-16/k)\eta$$
$$+(4b_1+2kb_0+2kb_0^2-48b_0+128/k)\eta^2+\cdots .$$

We may then deduce the equation of state

$$\phi=1+4\eta+(8kb_0-16)\eta^2$$
$$+(256-96b_0k+12b_1k+6k^2b_0^2+6k^2b_0)\eta^3+\cdots . \quad (12)$$

The first two coefficients in the above expansion agree with the exact virial coefficients [3], implying our scheme is actually reasonable at least in the very-low density regime. However, the third, fourth, etc. coefficients are expressed in terms of yet unknown parameters b_0, b_1, etc. [associated with the variable $m(\eta)$]. Employing known exact results for the third and fourth virial coefficients (which are respectively 10 and 18.365) [3], we get $b_0=2.407$ and $b_1=-0.9468$. In which case, we may write

$$m(\eta)=2.407-0.9468\eta+\cdots . \quad (13)$$

The above expression indicates $m(\eta)$ decreases (reasonably slowly) with η, confirming our earlier conjecture. Since the virial series is usually expected to be valid only in the low-density regime (before the phase transition), the series of (13) (even when extensively developed by retaining higher-order virial terms) may therefore be said to be only a low-density series. Also, we find that the series of (12) shows that the behavior of $m(\eta)$ has little effect on the equation of state in the very-low-density regime (a statement in line with this fact was earlier made). In which case, we may expect that only in the large-η region of the low-density regime (which is a reasonably small region near the phase transition) may the variation of $m(\eta)$ become of considerable effect. Since $m(\eta)$ is not so rapidly varying outside phase transition, we therefore expect that some fixed (average) value for m is sufficient to accurately reproduce the equation of state throughout the entire low-density regime (agreeing with a similar remark earlier made for the very-low-density regime $\eta\lesssim\eta_b$). This (average) value should obviously be smaller than the leading term (i.e., 2.407) in the series of (13). Similarly, we may also expect that a suitable average for $m(\eta)$ (which should be smaller than that used in the low-density regime) may be employed in the high-density region (beyond the phase transition) as this region is known to be of rather small width.

Next, we attempt to formulate a differential equation for ϕ. From (9), we have

$$\phi(1-\epsilon\eta k)=\left[1+\eta^2 k\frac{d\epsilon}{d\eta}\right].$$

Using this in (10) yields

$$\phi(1-\epsilon\eta k)=\exp\{\phi-1+\tilde{P}(\eta)\}. \quad (14)$$

Hence we obtain

$$\epsilon=\frac{1}{\eta k}-\frac{1}{\eta k\phi}\exp[\phi-4\eta(1-\eta k)^{-m(\eta)}-1]. \quad (15)$$

We can invert (10) expressing ϵ in terms of $d\epsilon/d\eta$, i.e.,

$$\epsilon=\frac{\ln\left[1+\eta^2 k\frac{d\epsilon}{d\eta}\right]+4\eta(1-\eta k)^{-m(\eta)}-\eta^2 k\frac{d\epsilon}{d\eta}}{\eta k\left[\ln\left[1+\eta^2 k\frac{d\epsilon}{d\eta}\right]+1+4\eta(1-\eta k)^{-m(\eta)}\right]}. \quad (16)$$

From (16), we have

$$1-\epsilon\eta k=\frac{1+\eta^2 k\frac{d\epsilon}{d\eta}}{\ln\left[1+\eta^2 k\frac{d\epsilon}{d\eta}\right]+1+4\eta(1-\eta k)^{-m(\eta)}}.$$

Hence, using (9) yields

$$\phi=\ln\left[1+\eta^2 k\frac{d\epsilon}{d\eta}\right]+4\eta(1-\eta k)^{-m(\eta)}+1. \quad (17)$$

We then obtain

$$\frac{d\epsilon}{d\eta}=\frac{1}{\eta^2 k}[\exp(\phi-1-4\eta(1-\eta k)^{-m(\eta)})-1]. \quad (18)$$

But from (15), we have

$$\frac{d\epsilon}{d\eta}=-\frac{1}{\eta^2 k}+\left\{\frac{1}{\eta^2 k\phi}+\frac{1}{\eta k\phi^2}\frac{d\phi}{d\eta}-\frac{1}{\eta k\phi}\left[\frac{d\phi}{d\eta}-4(1-\eta k)^{-m(\eta)}\right.\right.$$
$$\left.\left.-4\eta\left\{km(\eta)(1-\eta k)^{-1-m(\eta)}-(1-\eta k)^{-m(\eta)}\frac{dm(\eta)}{d\eta}\ln(1-\eta k)\right\}\right]\right\}$$
$$\times\exp[\phi-4\eta(1-\eta k)^{-m(\eta)}-1]\ . \tag{19}$$

Equating (18) and (19) then finally yields

$$\frac{d\phi}{d\eta}=-\frac{\phi\left[\phi-1-4\eta(1-\eta k)^{-m}-4\eta^2\left\{mk(1-\eta k)^{-m-1}-(1-\eta k)^{-m}\frac{dm}{d\eta}\ln(1-\eta k)\right\}\right]}{\eta(\phi-1)}\ . \tag{20}$$

The above equation is an *exact* reformulation of the equation of state of the hard-particle system in terms of the parameter $m(\eta)$. The fact that $m(\eta)$ can only be approximated provides the reason why our present scheme is actually an approximate scheme. Equation (20) is an ordinary first-order (nonlinear) differential equation (in standard form) for which standard methods [7] are available for solving it. It is usual [7] to guarantee the analyticity of the dependent variable such as ϕ in Eq. (20) by showing that the right-hand side of the equation is an analytic function of the two variables η,ϕ; however, in our present treatment, we expect we may presume that ϕ is analytic at least at low densities. Hence writing ϕ as $\sum_{n=0}^{\infty}c_n\eta^n$, we easily employ (20) to obtain (after a very lengthy algebraic manipulation)

$$c_0c_1\eta-c_1\eta+c_1^2\eta^2+2c_0c_2\eta^2-2c_2\eta^2+3c_1c_2\eta^3-3c_0c_3\eta^3+3c_3\eta^3+\cdots$$
$$=-c_0^2+c_0-2c_0c_1\eta+c_1\eta+4c_0\eta-2c_0c_2\eta^2+c_2\eta^2-c_1^2\eta^2+4c_1\eta^2+8b_0c_0k\eta^2-2c_0c_3\eta^3+c_3\eta^3$$
$$-2c_1c_2\eta^3+4c_2\eta^3+8b_0c_1k\eta^3+12b_1c_0k\eta^3+6c_0k^2b_0^2\eta^3+6c_0b_0k^2\eta^3+\cdots\ .$$

By equating coefficients we readily see we obtain the result of Eq. (12). In the high-density regime, we expect $\phi\gg1$. Hence we may approximate Eq. (20) as

$$\frac{d\phi}{d\eta}\sim-\left[\frac{1}{\eta}\right]\phi+\left[\frac{1}{\eta}+4(1-\eta k)^{-m}\right.$$
$$+4\eta\left\{mk(1-\eta k)^{-m-1}\right.$$
$$-(1-\eta k)^{-m}\frac{dm}{d\eta}$$
$$\left.\left.\times\ln(1-\eta k)\right\}\right]\ . \tag{21}$$

This equation is a linear differential equation whose solution is readily obtained by exact methods [7]. Alternatively, we find from inspection of Eq. (17) that since the logarithmic function is generally not a strongly varying function, we may immediately deduce the high-density asymptotic solution for ϕ as

$$\phi\sim4\eta(1-\eta k)^{-m(\eta)}\ . \tag{22}$$

Since both $m(\eta)$ and $\ln(1-\eta k)$ are (relatively) not strongly varying functions, we find that both sides of (21) behave asymptotically as $4\eta km(\eta)(1-\eta k)^{-1-m(\eta)}$ [employing the solution of (22)], hence verifying the adequacy of (22). Also, using standard methods [7], the solution to (21) is obtained as

$$\phi=\exp\left[\int g(\eta)d\eta\right]\left[c+\int\exp\left[-\int g(\eta)d\eta\right]f(\eta)d\eta\right]\ , \tag{23}$$

where c is a constant of integration, $g(\eta)=-1/\eta$, and

$$f(\eta)=\frac{1}{\eta}+4(1-\eta k)^{-m}$$
$$+4\eta\left\{mk(1-\eta k)^{-m-1}\right.$$
$$\left.-(1-\eta k)^{-m}\frac{dm}{d\eta}\ln(1-\eta k)\right\}\ .$$

For ease of evaluating (23), we may further approximate the original differential equation [i.e., Eq. (21)] and hence write the valid approximation

$$f(\eta)\approx\frac{1}{\eta}+\frac{4}{\eta k}(1-\eta k)^{-m'}+\frac{4}{\eta k^2}\frac{d}{d\eta}(1-\eta k)^{-m}$$

(where m' is some constant [say, $m(\eta_{\max})$], which is arbitrarily close to $m(\eta)$ everywhere in the neighborhood of $\eta_{\max}$, provided the neighborhood may be chosen sufficiently small. Clearly, this choice for m' is possible because $m(\eta)$ is assumed to be generally a slowly varying function). Observe that even though the difference between this expression and the previous expression for $f(\eta)$ may increase as $\eta\to\eta_{\max}$, their ratio nevertheless tends to unity in likeness to Stirling's approximation. Hence a good estimate of Eq. (23) becomes

$$\phi(\eta)=\frac{1}{\eta}\left[c+\int\left\{1+\frac{4}{k}(1-\eta k)^{-m'}+\frac{4}{k^2}\frac{d}{d\eta}(1-\eta k)^{-m}\right\}d\eta\right]$$
$$=\begin{cases}\left[\frac{c}{\eta}+1\right]-\frac{4}{\eta k^2(-m'+1)}(1-\eta k)^{-m'+1}+\frac{4}{\eta k^2}(1-\eta k)^{-m(\eta)} & (m'\neq 1)\\ \left[\frac{c}{\eta}+1\right]-\frac{4}{\eta k^2}\ln(1-\eta k)+\frac{4}{\eta k^2}(1-\eta k)^{-m(\eta)} & (m'=1)\,.\end{cases} \tag{24}$$

Since m' is "close" to $m(\eta)$, the last terms of the rightmost expressions above certainly dominate sufficiently close to $\eta_{\max}$. [It is assumed that $m(\eta)>1$.] It therefore becomes clear that the asymptotic expression as given by (22) is actually valid since $4\eta\to 4/\eta k^2$ in the limit.

III. NUMERICAL COMPUTATIONS FOR THE EQUATION OF STATE AND THE PHASE TRANSITION

In this section, we determine the equation of state of the hard-sphere system for all physically allowable densities (η) by numerically integrating the governing equations of Sec II. The (conjectured) phase-transition region is also investigated. Clearly, we may first solve completely for either ϵ or ϕ before solving for the other. Alternatively, we may also solve for both ϵ and ϕ simultaneously by, for instance, making some initial choice of $\epsilon(\eta)$ (for all η) and then using this (along with $d\epsilon/d\eta$ which is easily deduced) in (9) to compute $\phi(\eta)$. This is then employed in (15) to compute a new $\epsilon(\eta)$. [It is assumed that $m(\eta)$ is known.] A new function is then derived for $\phi(\eta)$ again employing (9). After some iterations, we may expect that both ϵ and ϕ may be obtained accurately (simultaneously). Unfortunately, however, our experience is that the errors in the initial choice for ϵ soon lead to significant error in ϵ which makes $[1+\eta^2 k(d\epsilon/d\eta)]$ and hence ϕ negative at several η values; thereafter, ϵ and hence ϕ do not seem to be able to "recover" in further iterations. A similar difficulty was also encountered when Eqs. (15) and (17) were solved iteratively as above. In this case, the logarithmic function in (17) could not be computed (at several η values) after a few iterations due to "unavoidable" numerical errors causing its argument to be negative.

On the other hand, we may attempt to solve for ϵ completely first, employing Eq. (16) in an iteration process [by making an initial choice for $d\epsilon/d\eta$ and then using (16) to compute ϵ and hence $d\epsilon/d\eta$, etc.]; however, for similar reasons as above, the logarithm function in (16) soon becomes impossible to compute. The above difficulties seem to us to arise from the fact that the extreme nonlinearities in the governing equations are so "sensitive" that the initial incompatibility of the "inexact" functional form for $\tilde{P}(\eta)$ [or $m(\eta)$] and the initial choice for ϕ or ϵ leads to further errors from which we never recover. It is our speculation therefore, that a possible solution to this difficulty may be found by progressively varying $\tilde{P}(\eta)$ [or $m(\eta)$] in a way compatible with ϵ or ϕ such that the functional form for $\tilde{P}(\eta)$ tends (in the limit) to the desired form. In the present work, our approach to averting the above difficulty is by solving completely for ϕ first [employing Eq. (20)] before deducing $\epsilon(\eta)$. It is our belief that this method is probably the only computationally viable way (under the circumstance).

Equation (20) may be written in standard form as

$$\frac{d\phi}{d\eta}=f(\eta,\phi)\,. \tag{25}$$

Clearly, the right-hand side of this equation is singular at the points $(\eta=0,\phi\neq 1)$, $(\eta\neq 0,\phi=1)$, $(\eta=\eta_{\max})$ in the η-ϕ plane. Hence, even though both sides of (25) may be said to be analytic at a point such as $(\eta=0,\phi=1)$ (as is clear from the analysis of Sec. II), we have found that techniques requiring use of Taylor-series expansion of "f" to integrate (25) (such as the Runge-Kutta method which is employed in this paper) may be expected to yield unreliable results in general close to both ends of the η regime. This is because we expect several terms of a Taylor-series expansion to be required to appropriately approximate $f(\eta,\phi)$ close to the point $\eta=0$ (which is close to points of singularity). We therefore transform to new variables in an attempt to obtain a right-hand side of (25) which is free of singularities in essential regions of the relevant η domain. We begin by employing the new variable x defined as $x=\ln\eta$, and this leads to

$$\frac{d\phi}{dx}=\frac{-\phi\left[(\phi-1)-4e^x(1-ke^x)^{-m}\left[1+\frac{mke^x}{1-ke^x}-\frac{dm}{dx}\ln(1-ke^x)\right]\right]}{(\phi-1)}\,. \tag{26}$$

We observe the $\eta=0$ point is mapped to $x=-\infty$ while $\eta=\eta_{\max}$ is mapped to $x=x_{\max}=-0.30046$. Hence we may never begin integration from $\eta=0$. However, it may be noted that we may go sufficiently close to $\eta=0$ without needing to make $|x|$ unmanageably large (as for instance, for $\eta=0.001$, x is only $-6.907\,76$). Also we find that taking equal "steps" in the x domain (during integration) allows us to move more slowly near $\eta=0$ (than

in the higher-density regions). Hence we find "good" computational accuracy may usually be guaranteed for arbitrary closeness to $\eta=0$ since the above transformation allows us to take smaller step sizes in the η domain as we approach the $\eta=0$ point (in the limit $\eta\to 0$, the step size tends to zero). This development is clearly related to the fact that the finite Taylor-series expansion (used to develop the Rung-Kutta scheme for the numerical integration) is valid within a region which gets smaller as the point about which the Taylor series is developed approaches a singularity. In which case, we may expect that computational accuracy may be ascertained for situations where for instance the right-hand side of (26) may be transformed into a function whose Taylor-series expansion has a nonvanishing radius of convergence which at the worst may decrease to zero as we approach the $\eta=0$ point.

We further employ the transformation involving the variable u where $u=(\phi-1)^2$. It is assumed $\phi\geq 1$, hence $u\geq 0$. Now, we have

$$\frac{1}{2}\frac{du}{dx}=(\phi-1)\frac{d\phi}{dx}\ ,$$

in which case we may write

$$\frac{du}{dx}=2(\sqrt{u}+1)\left[-\sqrt{u}+4e^{x}(1-ke^{x})^{-m}\left[1+\frac{mke^{x}}{1-ke^{x}}-\frac{dm}{dx}\ln(1-ke^{x})\right]\right]\quad [u(-\infty)=0]\ . \tag{27}$$

The right-hand side has no singularity except at $x=x_{\max}$, where we expect $\phi,u\to\infty$. Hence (27) is readily integrated adequately starting from arbitrarily close to $\eta=0$. A practical condition that may be used to integrate (27) is $u(x_i)=0$ for x_i sufficiently negative. [Alternatively, we may note that the expansion $\phi\approx 1+4e^{x}$ is adequate at sufficiently low densities and hence we may write $u(x_i)=16e^{2x_i}$, which is, however, close to zero for x_i sufficiently negative.]

In Sec. II, we conjectured the existence of two distinct branches of the ϕ vs η curve (one in the low-density regime before a supposed phase transition region and the other at high densities beyond the phase transition) with distinct (roughly) constant m values. In Fig. 1, we present plots of ϕ vs η for various constant m values obtained by integrating Eq. (27) employing the Runge-Kutta method in fourth order. The results of computation are found essentially not to change as we increased the number of Runge-Kutta steps from 100 to 1000 (and above). A comparison with computer simulation results from the literature [8] (also presented in Fig. 1) clearly shows that constant m values are reasonably adequate to characterize the low-density branch and at least the low-density end of the high-density branch of the equation of state. For the low-density branch, good "global" agreement between computer simulation results and our computations is obtained for $m\approx 1.84$ [which is less than the leading term in the series expansion developed for $m(\eta)$ in Sec. II], while for the low-density end of the high-density branch, we require $m\approx 1.14$ to obtain good agreement. A careful observation shows that in the low-density end of a given branch, our values for ϕ are slightly smaller than those of computer simulation, while at the high-density end, our values for ϕ become slightly larger. This therefore shows that the $m(\eta)$ function used for either branch of the equation of state must monotonically decrease with η (with a "gentle" slope) in conformity with our earlier speculations. In particular, we note that unlike the low-density regime (before the phase transition), $\phi(\eta)$ is sensitive to the behavior of $m(\eta)$ almost everywhere in the high-density regime (beyond the phase transition). Also, we may expect that the high-density region beyond phase transition is of considerably greater width than the region at low densities where $m(\eta)$ may be said to be of substantial influence on $\phi(\eta)$. Hence (unlike in the low-density branch of the equation of state), the use of some constant average value for "m" in determining the high-density branch of the equation of state can only be very crude. In which case, it may therefore be worthwhile attempting to calculate $m(\eta)$ more accurately at high densities. At this stage, it is necessary to point out that, owing to the nature of our present investigation [in which a rigorous formulation of $m(\eta)$ is absent], we content ourselves only with some average global comparison of our results with computer simulation results. For further comparison with other results involving a variety of analytical methods, the reader may refer to developments in Ref. [8]. Note also that computations very close to $\eta_{\max}$ had to be avoided as they involved such problems as "large numbers," "inability to compute sensitive functions a $\ln(1-\epsilon\eta k)$ (due to unavoidable nu-

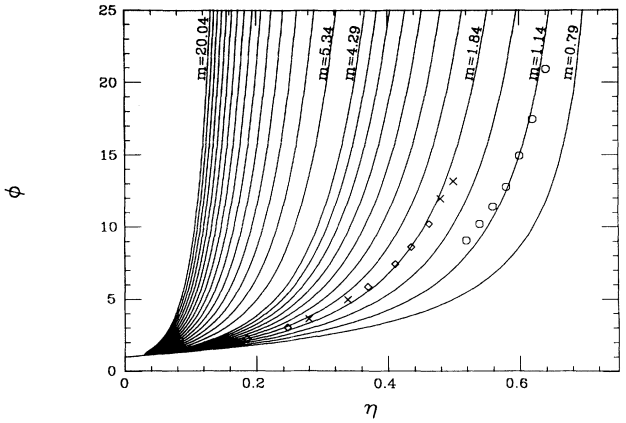

FIG. 1. ϕ vs η for different constant m values in the hard-particle system (m is varied from 0.79 to 4.29 in increments of 0.35 and from 5.34 to 20.04 in increments of 1.05); ◇, computer simulation data from Erpenbeck and Wood [8(a)]; ×, low-density branch computer simulation data from Ref. [8(b)]; ○, high-density branch computer simulation data from Ref. [8(b)].

merical errors which resulted in negative argument)," etc. Consequently, our largest density of consideration was usually only slightly larger than 0.735.

In the mid-density region (occurring within the density regime over which the low- and high-density branches of the equation of state are usually said to be invalid), earlier methods (both analytic and computer simulation) have sometimes been unable to yield results totally devoid of ambiguities. In fact, difficulties often exist in ascertaining [9] whether or not computer simulations adequately sample phase space in the high-density regime (including the mid-densities). Hence such a region (especially at mid-densities) is usually seen necessarily as one of metastability [9]. In some cases, however, the mid-density region is treated as one of an equilibrium first-order phase transition (as was originally conceived [8,10]) involving fixed temperature, pressure, and chemical potential (between different phases). Modern analytic theories (such as the density-functional theory [11]) which employ this point of view have provided some progress, as they yield results which approximately agree with those of computer simulation methods (in which the metastability problem is cleverly avoided [10]).

In the present paper, we do not work within the general limitations of computer simulation methods so that we may always assume existence of equilibrium for which the partition function (as given in Sec. I) is well defined for all physically allowable densities. We begin investigation of the mid-density range by first attempting to compute the possible chemical potential everywhere in the η-ϕ plane. Employing the expression for $Z(N,V)$ in terms of ϵ, and noting from first principles that:

$$\frac{d}{dN}[\ln(N!)]=\ln[(N+1)!]-\ln[N!]\sim\ln N \quad \text{for } N\gg 1 ,$$

we easily obtain the chemical potential as

$$\mu = Ag(\eta,\phi)+B , \tag{28}$$

where A,B are constants dependent on temperature and $g(\eta,\phi)=\phi+\ln\{\eta(1-\epsilon\eta k)^{-1}\}$. We evaluate ϕ for given constant m at 10 000 equispaced points in the x domain (corresponding to logarithmically distributed points in the η domain varying from $\eta\sim 0.01$ to $\eta_{\max}$). This is repeated for various constant m values ranging from 0.5 to 10 in steps of 0.05, allowing us to fill the η-ϕ plane with possible curves that may serve as branches of the equation of state. By proper tabulation, we are then able (by simple interpolation) to determine for a given pressure (P') the different η and μ values corresponding to different constant m values. With these data, it is then easy to search (given the P' value) for the η value at which a given μ value occurs. Clearly, some interpolation scheme is necessary here. Also we may expect our computations (including interpolations) to be highly accurate as about 200 equation of state curves (each computed using "double precision" calculations at 10 000 points as mentioned above) are involved. By the above, we are then able to accurately plot several equi- (chemical) potential curves in the η-ϕ plane, the intent being to discover if in one or a few distinct regions of the P'-V plane, we may find equipotential curves having slope dP'/dV close to zero. This way, many more acceptable solutions for our equation of state may be constructed (employing notions of the first-order phase transition) by linking different equation of state curves (with different constant m values) through the neighborhood of the above described regions of "near-zero slope." On doing this (cf. Fig. 2), we find that over a broad region of the P'-V plane, the equipotential curves intersect very many equation of state curves (for a broad range of m values) over a "small" pressure range. This is definitely a near-zero slope behavior for the equipotential curves over a broad region of the P'-V plane. Hence even though the above procedure may not allow us to identify one or a few local regions as locations of possible phase transition, the above observation nevertheless provides some validation of a possible phase transition in the hard-sphere system.

We note as in Sec. II that $m(\eta)$ (although a very difficult function to determine at a phase transition) may nevertheless be reasonably approximated as a linearly decreasing function in the low-density portion of phase transition, while in the high-density portion (beginning from $\eta=\eta_{\mathrm{TH}}$ say), it may be taken as a constant (m_{HD}). The introduction of a nonvanishing slope for $m(\eta)$ at the phase transition obviously results in a slightly modified solution for $\phi(\eta)$, $\epsilon(\eta)$, and μ in the high-density regime [see, for instance, Eq. (27)]. Hence there exists some promise of observing the features of a phase transition. Clearly, each η point (referred to as η_{TL}) on the low-density branch of the equation of state may serve as possible candidates for the density at the onset of the phase transition. Also, various η_{TH}, m_{LD}, and m_{HD} values are possible. (m_{LD} is taken as the constant m value used for the low-density branch of the equation of state.) Interestingly enough, we find that suitable combinations of $\eta_{\mathrm{TL}},\eta_{\mathrm{TH}},m_{\mathrm{LD}},m_{\mathrm{HD}}$ values exist which allow us to have a van der Waals–like loop in the equation of state. This is particularly encouraging as it provides a valid (though approximate) means by which we may once more attempt to locate a phase-transition region. We impose certain

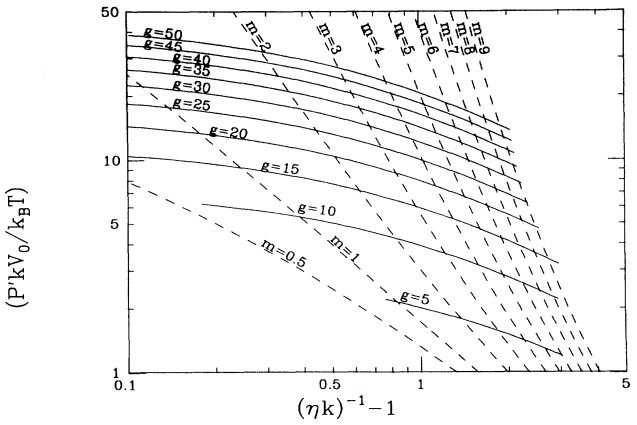

FIG. 2. Equi- (chemical) potential lines (solid lines) in the pressure-volume plane. Equations of state for different m values are shown as dashed lines; chemical potentials are computed as the g function of Eq. (28).

conditions consistent with behavior at a phase transition of the first-order type. We, however, first note that in our experience, no combination(s) of the parameters $\eta_{TL}, \eta_{TH}, m_{LD}, m_{HD}$ may be found which allows pressure to remain constant over an appreciable density range; implying a linear drop in $m(\eta)$ is actually a crude, though reasonable approximation for the behavior at a phase transition. The parameters are therefore chosen to allow a van der Waals–like loop to fully develop. Since a legitimate systematic approach may readily be developed for the formulation of $m(\eta)$ at low densities (see Sec. II), we concentrate our effort in trying to formulate $m(\eta)$ beyond the low-density branch. Hence we fix m_{LD} preferably at the value corresponding to that of computer simulation results. Various m_{HD} values are then arbitrarily chosen. For each m_{HD} value, we chose various possible η_{TL} values. For a given m_{HD}, η_{TL} combination, η_{TH} is then adjusted until the average pressure $\langle P' \rangle$, which occurs over the density range from η_{TL} to $(\eta_{TL}+\Delta\eta)$, is equal to the pressure P'_T obtained at η_{TL}. ($\langle P' \rangle$ is simply computed by employing several pressure values at equally spaced intervals in the η domain.) The point $\eta=\eta_{TL}+\Delta\eta$ (where $\Delta\eta>0$) is the density at which the pressure is also equal to P'_T. Clearly, by the "Maxwell equal area construction" [3], $\Delta\eta$ is the width of the possible phase transition region [which begins from $\eta=\eta_{TL}$ where $m(\eta)$ begins to drop. Clearly, we expect $\Delta\eta > \eta_{TH}-\eta_{TL}$]. Additionally, it is also required that the chemical potential at $\eta=\eta_{TL}+\Delta\eta$ be equal to that at $\eta=\eta_{TL}$, and interestingly enough, this was usually found to be the case. Note that in all of the above, the requirement of equality is usually said to be reasonably satisfied when it is to within at least one decimal place or so. In Table I, we display several m_{HD} values and their associated values for η_{TL}, $(\eta_{TH}-\eta_{TL})$, $\Delta\eta$, $P'_T, \langle P' \rangle$, $\mu(\eta=\eta_{TL})$, and $\mu(\eta=\eta_{TL}+\Delta\eta)$. Interpolation had to be done in a number of cases. The pressure was computed as $\eta k\phi$. Also the chemical potential was computed using the $g(\eta,\phi)$ function of Eq. (28).

Table I shows that $\eta_{TL}\approx 0.498$ usually provides the largest region over which a phase transition may occur for a given m_{HD} value (elaborate data are provided for the $m_{HD}=1.14$ case). Hence it would therefore seem that the phase transition is somewhat "frustrated" at other η_{TL} values, implying we may have some criterion (though definitely not rigorous) for suggesting that the (low) density at onset of the phase transition may be taken as ~ 0.498. This is interesting as it agrees accurately with the earlier result [10]. Other obvious features which may help in fixing η_{TL} (including m_{HD}) more rigorously do not seem to exist. However, we may expect that future investigations may employ nonobvious features [as "degree of constancy of pressure" in the phase transition region, or the behavior of $\epsilon(\eta)$ and hence of $Z(N,V)$ beyond the phase transition etc.] in more rigorously determining values for η_{TL} and m_{HD}. Clearly of course,

TABLE I. Data for possible phase-transition behavior in the hard-sphere system ($m_{LD}=1.84$).

m_{HD}	η_{TL}	$\eta_{TH}-\eta_{TL}$	$\Delta\eta$	P'_T	$\langle P' \rangle$	$\mu(\eta=\eta_{TL})$	$\mu(\eta=\eta_{TL}+\Delta\eta)$
	0.4011	0.0480	0.0512	3.662	3.663	8.737	8.782
1.40	0.4985	0.0557	0.0581	9.722	9.724	18.579	18.622
	0.6017	0.0506	0.0508	38.779	38.778	56.730	56.363
	0.4011	0.0605	0.0646	3.662	3.664	8.737	8.758
1.30	0.4985	0.0697	0.0728	9.722	9.725	18.579	18.537
	0.6017	0.0627	0.0637	38.779	38.774	56.730	56.400
	0.4011	0.0765	0.0830	3.662	3.665	8.737	8.773
1.18	0.4985	0.0873	0.0935	9.722	9.722	18.579	18.750
	0.6017	0.0771	0.0789	38.779	38.775	56.730	56.477
	0.3511	0.0710	0.0782	2.336	2.337	6.131	6.172
	0.4011	0.0820	0.0893	3.662	3.665	8.737	8.769
	0.4508	0.0900	0.0969	5.893	5.898	12.609	12.628
1.14	0.4888	0.0930	0.0993	8.750	8.745	17.115	17.134
	0.4985	0.0934	0.0993	9.722	9.724	18.579	18.599
	0.5083	0.0931	0.0991	10.886	10.887	20.256	20.307
	0.5494	0.0917	0.0947	17.923	17.919	30.157	30.365
	0.6017	0.0818	0.0834	38.779	38.733	56.730	56.951
	0.4011	0.0880	0.0958	3.662	3.668	8.737	8.749
1.10	0.4985	0.0996	0.1071	9.722	9.725	18.579	18.749
	0.6017	0.0867	0.0878	38.779	38.774	56.730	56.696
	0.4011	0.1025	0.1138	3.662	3.661	8.737	8.762
1.00	0.4985	0.1155	0.1251	9.722	9.725	18.579	18.781
	0.6017	0.0987	0.0991	38.779	38.771	56.730	56.594

an ultimate resolution of the behavior of $m(\eta)$ everywhere may be expected only through the use of the much more extensive simulation procedure involving nearest-neighbor correlations as suggested in an earlier paper [2].

The "free-volume" theory [8,10,12], which along with its extensions, are largely phenomenological (as the extent of their validity may not be readily assessed even for η slightly removed from $\eta_{\max}$), may, however, be expected to be "exact" at the limit of $\eta_{\max}$. Interestingly enough, the theory predicts the asymptotic expression

$$\phi(\eta)\sim 3(1-\eta k)^{-1}\ , \tag{29}$$

which agrees exactly in form with our asymptotic expression of Eq. (22). Recent methods [13] relate thermodynamic properties to geometrical features of the hard-particle system. Close to $\eta_{\max}$, where essential parameters that characterize the geometrical features are easily formulated, this is found to lead to the same asymptotic equation of state as (29). The free-volume theory is actually also a theory which focuses on geometry in the hard-sphere system, and its relationship with similar theories is made clear in the articles by Speedy [14] using ensemble theory. (See also Ref. [4], where Reiss gives a review, including a discussion of the similarity in the statistical geometric approaches to both porous or composite media and fluids.) Equation (29) suggests we may assume $m\rightarrow 1$ as an exact solution at the $\eta=\eta_{\max}$ limit. Clearly also, the factor of 4η in Eq. (22) tends to 2.9619 in the $\eta_{\max}$ limit, agreeing quite accurately with the prefactor in (29). Hence, up to this point, the following may be considered significant achievements made by our theory in the high-density regime. First, we have been able to reproduce the van der Waals loop usually considered an expected result for a valid "first-order" model (or theory) of phase transitions. Second, we have also been able to determine a limiting value for m as $\eta\rightarrow\eta_{\max}$. Finally, the density at onset of phase transition (low-density side) has been identified (though nonrigourously).

In Fig. 3 we present a plot of pressure ($P'kV_0/k_BT$) vs volume ($1/\eta k-1$) employing $m_{\rm LD}=1.84$, $\eta_{\rm TL}=0.498$, and the $m_{\rm HD}$ value corresponding with literature data (see Fig. 1); i.e., $m_{\rm HD}=1.14$. Note here that $m(\eta)$ is made to drop linearly from 1.14 at the phase transition edge (high density side, i.e., $\eta=0.5978$) to 1.0 at $\eta=\eta_{\max}(\approx 0.7405)$ corresponding to a gentle slope as was expected. Comparison with computer simulation data over a broad pressure range is facilitated by use of a full log plot which simply shows very good agreement practically everywhere. (We note, however, that the phase transition region width of ~ 0.045 usually quoted in the literature [8] is about half of ours.) The van der Waals–like loop is not shown in this case. In Fig. 4, we also show for this case, a plot of $m(\eta)$ vs η. Since our theory was unable to predict an $m_{\rm HD}$ of 1.14, we present additional data in Fig. 3 for the case $m_{\rm HD}=1$ (which our theory may be said to approximately predict). The van der Waals loop is shown in this case.

From Eq. (6), we have that

$$\frac{dP}{d\eta}=-\left[4(1-\eta k)^{-m}+4\eta mk(1-\eta k)^{-(m+1)}-4\eta(1-\eta k)^{-m}\frac{dm}{d\eta}\ln(1-\eta k)\right]\times\exp[-4\eta(1-\eta k)^{-m}]\ . \tag{30}$$

Hence $dP/d\eta=0$ when the condition $\eta(dm/d\eta)\ln(1-\eta k)=1+\eta mk(1-\eta k)^{-1}$ is satisfied. In the region $\eta_{\rm TL}<\eta<\eta_{\rm TH}$, $dm/d\eta=(m_{\rm HD}-m_{\rm LD})/(n_{\rm TH}-\eta_{\rm TL})$. Hence for the case involving $m_{\rm LD}=1.84$, $\eta_{\rm TL}=0.498$, and $m_{\rm HD}=1.14$, we have that $dm/d\eta=-7.4946$. We find in this case therefore that at η slightly less than 0.498, $dP/d\eta=-2.6645\times10^{-5}$, while for η slightly larger than 0.498, $dP/d\eta=-3.4130\times10^{-6}$. This is a sudden large decrease in $|dP/d\eta|$ as we enter into phase transition (in conformity with the discussion in Sec. II). We observe also from Eq. (30) that as η increases from 0.498, $dP/d\eta$ remains negative, until at $\eta\approx 0.5315$, $dP/d\eta$ changes sign, becoming positive. This implies, by the discussion of Sec. II, that the fluctuation and hence the broadening in the NNPDF $g_1(r_1)$ begins to get so enormous that $P(\eta)$ actually starts

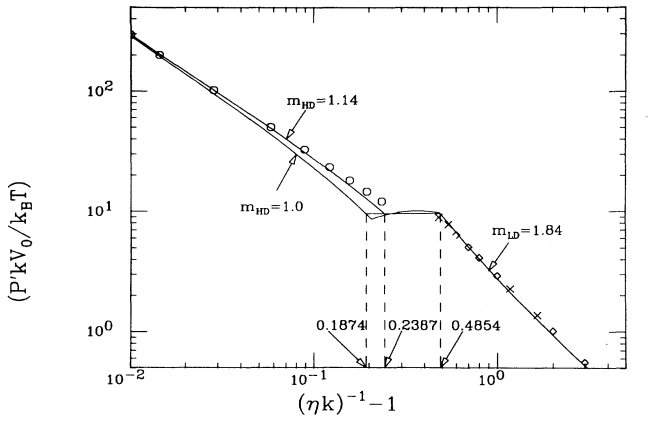

FIG. 3. Equation of state of the hard-particle system using $m_{\rm LD}=1.84$. Computer simulation data are shown with symbols (the plot symbols are the same as in Fig. 1).

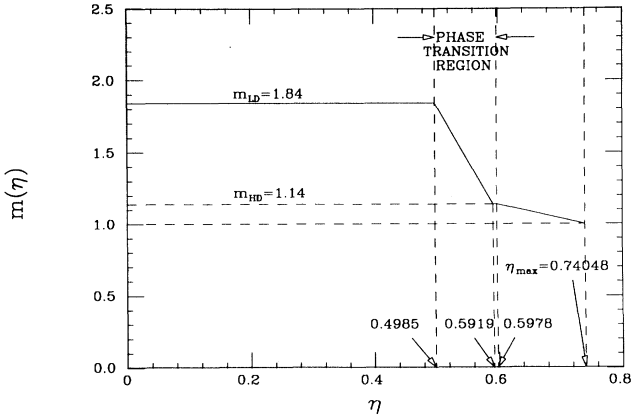

FIG. 4. $m(\eta)$ vs η ($m_{\rm LD}=1.84$, $m_{\rm HD}=1.14$).

to increase even though $r_1(\max)$ [the location of the peak of $g_1(r_1)$] moves to smaller r values as η increases. At $\eta=\eta_{TH}=0.5919$, $dP/d\eta$ changes sign once more, becoming negative, implying that the effect of the motion of $r_1(\max)$ to smaller r_1 values begins to dominate the spread in $g_1(r_1)$ (in agreement with what was earlier envisaged).

Finally, we make some remarks about the structure of the hard-sphere system in a global sense by investigating the volume in phase space [The NNPDF $g_1(r_1)$, on the other hand, was used to study the system structure at a microscopic scale.] To accomplish the global structure study, we investigate the function $\tilde{\epsilon}(\eta)$ defined as $\tilde{\epsilon}=1-\epsilon\eta k$. Employing our results for which $m_{HD}=1.14$, $\eta_{TL}=0.498$ (providing results which closely corresponds with literature results as shown in Fig. 3), we easily employ Eq. (15) to compute $\epsilon(\eta)$. In Fig. 5 we show the result for $\tilde{\epsilon}(\eta)$. We find that $\tilde{\epsilon}$ starts at unity and ends at zero (in agreement with earlier statements), while the magnitude of the slope of the $\tilde{\epsilon}$ function decreases rapidly and monotonically. This indicates that since we may write $Z(N,V)=(\tilde{\epsilon}V)^N/N!$ and assuming N fixed (to avoid a dimensionality problem, while V may vary as we vary η), the volume in phase space decreases very rapidly at low densities (as compared to the decrease rate at high densities). Hence the hard-particle system may be said to depart (in fundamental qualities) very quickly from the ideal gas model as we increase η from 0, perhaps explaining why most theories (which are usually of a perturbative nature) are rigorously applicable only in the very-low-density realm of the hard-particle fluid (and other realistic fluid models). Also, we find for $\eta\gtrsim 0.5$, the $\tilde{\epsilon}$ plot indicates the volume in phase space is relatively of approximately zero measure, strongly suggesting this region corresponds to the solid phase of the hard-sphere system.

Clearly, the probability of constructing allowable configurations of the entire system by randomly generating particle centers is $(\tilde{\epsilon}V)^N/V^N=\tilde{\epsilon}^N$. Hence such a random generation scheme will require extremely long run times (especially for large N) when $\eta\gtrsim 0.5$ (where $\tilde{\epsilon}\sim 0$).

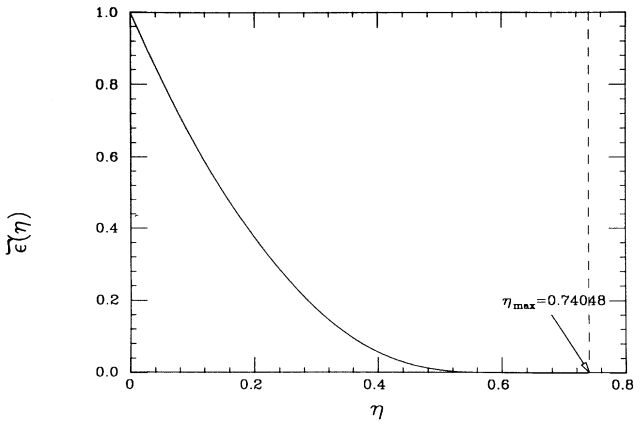

FIG. 5. $\tilde{\epsilon}(\eta)$ vs η ($m_{LD}=1.84$, $m_{HD}=1.14$).

In which case, we can see why it may be almost impossible for computer simulations (which may even be much more efficient than the simple random scheme described above) to adequately sample phase space by generating configurations for an entire system at high densities. An investigation of $\tilde{\epsilon}$ (or ϵ) in the supposed phase transition region shows that $\tilde{\epsilon}$ (or ϵ) changes only slightly in comparison with an approach in which the parameter m is held fixed at a variety of values (including $m=1.84$). This is not surprising as $\tilde{\epsilon}$ is a global parameter and so is expected to have some averaging effect (a microscopic investigation employing NNPDF's however, may be expected to show some dramatic change at phase transition). From Eq. (9) we find that if pressure may be infinite at some mid-density point $\tilde{\eta}(0<\tilde{\eta}<\eta_{max})$, then we require either $\tilde{\epsilon}$ or ϵ be discontinuous at $\eta=\tilde{\eta}$ or $\epsilon\tilde{\eta}k$ be equal to unity. But a discontinuity in $\tilde{\epsilon}$, or the condition $\epsilon\tilde{\eta}k=1$, implies, respectively, a discontinuous change in $Z(N,V)$ or a zero value at mid-density for $Z(N,V)$. Since $Z(N,V)$ is simply a measure of the size of space of the allowed set of configurations in the hard-particle system, a discontinuous change or mid-density zero for $Z(N,V)$ therefore seems unphysical. Hence it would therefore seem that against the background of the behavior of ϵ, the concept of an infinite pressure somewhere at mid-density (the Bernal density) [7], sometimes conjectured in the literature is untenable as an equilibrium phenomenon. By showing the temperature dependence explicitly in the equation of state [i.e., $P'=\rho k_B T\phi(\eta)$], we find also that the temperature variable may not provide any mechanism by which our above conclusion may be invalidated. Our arguments, therefore lends support to claims [7] that simulations at high densities ($\eta\gtrsim 0.5$) may usually have difficulty relaxing adequately to equilibrium.

IV. REMARKS AND CONCLUSIONS

It has always been the desire in the area of statistical mechanics to obtain an exactly soluble realistic three-dimensional problem. Although exact results [2] involving the one-dimensional liquid model, the two-dimensional Ising magnet, existence theorems, use of pseudolattices, etc. have in the past succeeded in clarifying various notions concerning real systems, this has not, however, usually been considered entirely satisfactory. This is more so especially as such expositions are often deduced from models involving lattices and interaction types usually considered to be too artificial. In recent times, the computer simulation method has come to be recognized as a major means by which accurate results may be obtained for realistic systems. However, difficulties are known to exist in assessing the adequacy of results sometimes provided by the method. For instance, in the computer simulation of the well-known hard-particle system (considered one of the most appropriate first order models for a variety of realistic fluid systems) it is usually not easily determined whether or not adequate relaxation to equilibrium is achieved, especially at high densities [7]. Analytic methods, on the other hand, employed for investigating the hard-particle system have

usually been rigorous only at low densities, while at higher densities, they have largely been of a phenomenological nature.

In the present paper, we have used the concept of nearest neighbor correlations [2] (in particular, the first-nearest-neighbor PDF) in investigating the hard-particle fluid. This has provided a theory of hard-particle fluids in terms of a single unknown parameter m, reminiscent of phenomenological theories such as the van der Waals model involving one or more unknown parameters. Our approach is in no way phenomenological, however, as our parameter m may generally be computed from fundamental considerations. In the low-density branch of the equation of state we noted that $m(\eta)$ may be rigorously formulated. At the phase transition and beyond, however, only an approximate means is available for formulating $m(\eta)$. Interestingly enough, the approximate means allows us to locate the density at onset of phase transition (in very good agreement with simulation data), thereby allowing us to carry out a reasonable investigation of the phase-transition region employing the approximate form for $m(\eta)$ at high densities beyond the phase transition. As a result, we have not only been able to reproduce a van der Waals–like loop at the phase transition (considered a valid first-order result at a first-order phase transition) but also we have been able to carry out an accurate analytic investigation of the hard-particle system in the "solid phase" (where hitherto it has been difficult to develop a rigorous theory) as evidenced by comparison with computer simulation data. In the low-density branch of the equation of state, our results are in excellent agreement with computer simulation results.

On the whole, the present paper may be said to provide a first-order theory of the hard-particle system valid at all densities. It may be envisaged that more accurate means may be developed in future investigations for approximating $m(\eta)$ at the phase transition and beyond. Clearly it will also be interesting if in future investigations the series for $m(\eta)$ as prescribed in this paper may be developed to much higher powers. This may be very beneficial as the series may converge much faster than the virial series (usually used to investigate fluids at low densities) considering that $m(\eta)$ is a slowly varying function, thereby providing essentially a complete theory for the low-density branch of the equation of state.

A global structure analysis indicates a rapid decrease of the volume in phase space even at low densities, thereby suggesting why rigorous analysis have so far been restricted to low densities and why computer experiments may have difficulty in appropriately simulating the hard-particle fluid at high densities. Also, the global structure study indicates that the concept of an infinite pressure at the "Bernal density" is unphysical.

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