Equations of state for classical hard-core systems

Moorad Alexanian*
Department of Physics and Astronomy, Southern Illinois University at Carbondale, Carbondale, Illinois 62901
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A method, based on the first few virial coefficients, is used to generate the pressure P of a classical d-dimensional hard-core system at arbitrary density ρ—the method is exact for $d=1$. The equation of state reproduces all the virial coefficients used on expanding P/k_BT about $\rho=0$. Also, $P/\rho_c k_B T \rightarrow R/(1-\rho/\rho_c)$ as $\rho \rightarrow \rho_c$ and $\partial(P/k_BT)/\partial\rho > 0$ for $0 \leqq \rho < \rho_c$. As the order of the approximation increases, the position ρ_c of the simple pole approaches the density ρ_0 of closest packing and the residue R increases beyond the value of the spatial dimensionality d of the system. The equation of state is in rather good agreement with the molecular-dynamics results especially for the case of hard disks as expected.

I. INTRODUCTION

The purely repulsive hard-core potential plays an important role in equilibrium statistical mechanics. A hard-core potential is the simplest characterization of the impenetrability of atoms and molecules in real gases. In addition, when supplemented by an attractive interaction, the hard-core potential becomes a useful reference system with which to treat perturbatively the weak attractive part of the potential. Nonetheless, despite the simplicity of this system there exists no exact result for the equation of state at moderate or high density. However, at low density, recourse is made of the virial expansion for the pressure P with exactly determined first few virial coefficients.

The interest in the hard-sphere fluid was stimulated certainly by Kirkwood's conjecture that this system would show a fluid-solid transition at a density below the maximum density attainable at close packing. The Kirkwood transition was found[1] in computer experiments. Needless to say, a theoretical description of the Kirkwood transition still remains a challenging problem. Attempts at theoretical studies, via Padé[2,3] and other[4] approximants, have led to considerable controversies as to the occurrence and nature of singular points in the virial series.[5]

Some years ago, a method[6] to overcome the convergence difficulties of the quantum-mechanical Born series was employed[7] to improve the convergence of the virial expansion. The method leads to a first-order nonlinear differential equation for the pressure P of the form

$$\frac{d\eta_n(b)}{db} = \sum_{k=2}^{n} C_k(b)[\eta_n(b)]^k \tag{1.1}$$

with boundary condition $\eta_n(0)=\rho$, where $\eta \equiv P/k_BT$ and b is the second virial coefficient B_2 and so

$$b \equiv B_2 = \frac{\pi^{d/2}\sigma^d}{d\Gamma(d/2)} \tag{1.2}$$

for a d-dimensional system of particles with hard-core potential—hard lines of length σ, hard disks or spheres with diameter σ. [For the hard-sphere fluid, the independent variable used in Ref. 7 in the differential Eq. (1.1) was the soft-sphere variable $f=e^{-\epsilon/k_BT}-1$ with b fixed. The differential equation was integrated to $f=-1$ to give the hard-sphere equation of state. The present analysis with (1.1) deals directly with hard-core systems, viz. $f=-1$, and considers a variable σ.] The one-dimensional system of hard rods is obtained[7] exactly already in the lowest approximation, viz. $C_2=1$ and $C_k(\sigma)\equiv 0$ for $k=3,4,\ldots$. However, for the hard-sphere gas, the successive approximations to the equation of state developed[7] a sort of instability, an apparent bifurcation, at a rather low value of the density which worsened with succeeding approximations. Nonetheless, the approximation scheme gives rise[7] to a non-negative pressure which is a monotonic nonincreasing function of the specific volume ρ^{-1}—thermodynamic stability condition. In addition, a series expansion for the pressure P in terms of the density ρ reproduces[7] the virial coefficients introduced to generate the given approximation. These good features of the approximation scheme, together with the availability of more virial coefficients, suggest a closer analysis of the method in order to find a way to stabilize the solution of the nonlinear differential equation in the higher density range. The latter can be accomplished, while preserving the above-mentioned features, by requiring the pressure in our approximation scheme to possibly develop a simple (first-order) pole as a function of the density ρ. Note that the position of the simple pole as well as the corresponding residue are determined entirely by the first few virial coefficients. Note also that when searching for poles, one may be excluding from consideration the possibility of finding a singularity of the virial series associated with the amorphous close-packed state—random close packing. Such singularity may be of the branch-point type rather than a simple pole.[8] Therefore, we expect[8] the simple pole to represent the crystalline close-packed state at infinite pressure or zero temperature—ordered close packing of hard spheres (disks) at $\rho_0=\sqrt{2}/\sigma^3$ ($\rho_0=2/\sqrt{3}\sigma^2$). Regarding the residue at the simple pole, there is no prediction of its value other than the value d given by the free-volume approximation result[9] at high density.

II. MODIFIED IMPROVED SOLUTION

The virial expansion of the pressure for a d-dimensional system of particles with purely repulsive hard-core interaction is of the form

$$\eta \equiv P/k_B T = B_1\rho + B_2\rho^2 + B_3\rho^3 + \cdots \tag{2.1}$$

with $B_n = A_n b^{n-1}$, where A_n are pure numbers with $A_1 = A_2 = 1$ and the second virial coefficient b is given by (1.2). The function η is analytic[10] in some neighborhood of $\rho = 0$. [In fact, the radius of convergence of the virial expansion is at least[10] $V_0/V = 0.039\,905$ for hard disks, where $V_0 = N\sigma^2\sqrt{3}/2$ and $V_0/V = 0.024\,437$ for hard spheres, where $V_0 = N\sigma^3/\sqrt{2}$.] On differentiating (2.1) with respect to b,

$$\frac{d\eta}{db} = B_2\rho^2/b + 2B_3\rho^3/b + 3B_4\rho^4/b + \cdots \tag{2.2}$$

and eliminating ρ with the aid of (2.1), one obtains

$$\frac{d\eta}{db} = C_2\eta^2 + C_3\eta^3 + \cdots$$

$$\equiv \eta^2 f(b\eta) , \tag{2.3}$$

where

$$C_2 = B_2/b = 1 ,$$
$$C_3 = 2B_3/B_2 - 2B_2 , \tag{2.4}$$
$$C_4 = 2B_4/B_2 - 8B_3 + 5B_2^2 ,$$

and so on. (See Appendix A for the implicit expressions of the coefficients C_2 to C_8.) Note that $f(z)$ in (2.3) is analytic at $z = 0$. However, the radius of convergence of the series (2.3), which is determined by the radius of convergence of the virial expansion (2.1), is unknown. Note also that the form of the nonlinear differential equation (2.3) is a direct consequence of the scaling form for the equation of state (2.1), viz. $b\eta = h(b\rho)$, where $h(x) = A_1 x + A_2 x^2 + A_3 x^3 + \cdots$.

The solution of the differential equation (2.3) with boundary condition $\eta = \rho$ for $b = 0$ is

$$\ln(b\eta) - \int_0^{b\eta} \frac{f(x)dx}{1 + xf(x)} = \ln(b\rho) . \tag{2.5}$$

Note that the integral in (2.5) has singularities at the zeros of $1 + xf(x)$ and also at the point of infinity. On differentiating (2.5) with respect to ρ for fixed b one obtains

$$\frac{d\eta}{d\rho} = (\eta/\rho)[1 + b\eta f(b\eta)] \equiv (\eta/\rho) g(b\eta) . \tag{2.6}$$

The boundary condition for the differential equation (2.6) is $\eta = \eta_0$ for $\rho = \rho_0$ with $\eta_0/\rho_0 \to 1$ as $\rho_0 \to 0$.

If $\eta^2 f(b\eta)$ is defined and continuous in an open set $D \subset R^2$, then the solution of (2.3) is defined and is both continuous and differentiable in the open interval $I \subset R$—with $(b,\eta) \in D$ for $b \in I$. Also, the initial-value problem with $\eta = \rho$ for $b = 0$ gives rise to a unique solution in D. Accordingly,[7] $d\eta/d\rho > 0$ and so by (2.6), $g(z) > 0$ in the open interval I. The possibility $d\eta/d\rho = 0$ is associated with the existence of singular solutions of the differential equation (2.3). For instance, if $1 + x_0 f(x_0) = 0$, then $b\eta = x_0$ is a singular solution of both (2.3) and (2.6). Of course, the possibility $d\eta/d\rho < 0$ can also arise if $f(z)$ in (2.3) is singular.

For the nth-order improved solution,[7] the function $f(z)$ in (2.3) is a polynomial of degree n and so the possibility arises that $g(z_0) = 0$ for some $0 < z_0 < \infty$. [Recall that $g(0) = 1$ since $f(0) = C_2 = 1$.] Let $x_0 > 0$ be the closest zero to the origin. Therefore, since

$$\left.\frac{d^k\eta}{d\rho^k}\right|_{b\eta = x_0} = 0 \quad \text{for } k = 1,2,\ldots ,$$

we have that $\eta \to x_0/b$ monotonically as $\rho \to \infty$. (Actually the physical region for a hard-core system is $0 \le \rho \le \rho_0$, where ρ_0 is the maximum density at close packing.) Note that $\eta = x_0/b$ is a singular solution of the differential equations (2.3) and (2.6) since $g(x_0) = 1 + x_0 f(x_0) = 0$. However, if $g(z) > 0$ for $z > 0$, then the nth approximation diverges and so

$$\eta = \rho_c R(1 - \rho/\rho_c)^{1/(1-n)} \quad \text{as } \rho \to \rho_c , \tag{2.7}$$

where

$$\rho_c R = [(n-1)bK_n]^{1/(1-n)} \tag{2.8}$$

for $n = 2,3,\ldots$. In obtaining (2.7), use is made of the scaling form $b\eta = h(b\rho)$ and $d\eta/db = \eta^2 f(b\eta) \cong K_n \eta^n$ as $\eta \to \infty$ for the nth approximation as given by (2.3). The value of ρ_c, with $0 < \rho_c < \infty$, is given by

$$\ln(b\rho_c) = \int_1^\infty \frac{dx}{x[1 + xf(x)]} - \int_0^1 \frac{f(x)dx}{[1 + xf(x)]} \tag{2.9}$$

with the aid of (2.5) for our case when $1 + xf(x) > 0$. It so happens that the coefficients $C_2, C_3, \ldots, C_8$ for both hard disks and hard spheres alternate in sign and so the even approximations of (2.3) diverge while the odd approximations of (2.3) approach a finite constant as $\rho \to \infty$. (This behavior was already evident in Ref. 7 for both the two-dimensional lattice gas of hard squares and the system of hard spheres.)

Now the divergence of the pressure at the density of closest packing is that of a simple pole or stronger.[8] Therefore, result (2.7) suggests summing the series in (2.3) in such a fashion that $f(b\eta) \to \text{const} \ne 0$ as $b\eta \to \infty$. [If $f(b\eta) \to \infty$ as $b\eta \to \infty$, then divergences weaker than simple poles would ensue. However, if $f(b\eta) \to (b\eta)^\epsilon$ as $b\eta \to \infty$ with $-1 < \epsilon < 0$, then divergences stronger than simple poles would follow.] We only consider expressions for $f(b\eta)$ which are rational functions of $b\eta$. Therefore, $f(b\eta) \to \text{const} > 0$ as $b\eta \to \infty$ gives rise to a solution of (2.3) with a simple pole, in the finite ρ plane.

III. NUMERICAL RESULTS

The nonlinear differential equation (B2) for hard disks and hard spheres were solved numerically for the successive approximations with the constants $A, B, \ldots, F$ given by Eq. (B3) to (B5) and (B6) to (B8), respectively. All the approximations for the pressure P have a simple pole at some finite density $\rho = \rho_c$ given by (2.9) and the residue (2.8) becomes, for $n = 2$,

TABLE I. Values of critical density $\rho_c \equiv N/V_c$ and residue R for hard disks and hard spheres for different approximations (see Appendix B); $P/\rho_c k_B T \rightarrow R(1-V_c/V)^{-1}$ as $V \rightarrow V_c$.

	Disks		Spheres	
B_n considered	V_0/V_c	R	V_0/V_c	R
B_2	0.551	1.00	0.338	1.00
$B_2, \ldots, B_4$	0.799	1.56	0.589	1.65
$B_2, \ldots, B_6$	0.894	2.15	0.726	2.45
$B_2, \ldots, B_8$	0.926	2.48	0.815	3.34

$$R = (Kb\rho_c)^{-1} , \tag{3.1}$$

where $K=1$, A/B, C/D, or E/F for the different approximations—which include knowledge of the virial coefficients up to and including B_2, B_4, B_6, and B_8. Table I contains the position of the simple pole and its corresponding residue for both hard disks and hard spheres for the different approximations. Note that for both cases, the value of the residue increases beyond the spatial dimensionality d of the hard-core system—the free-volume approximation result.[9] Also, the position ρ_c of the simple pole seems to be approaching the close-packed configuration ρ_0, viz. $\rho_0 = 2/\sigma^2\sqrt{3}$ for hard disks and $\rho_0 = \sqrt{2}/\sigma^3$ for hard spheres.

The singularity at the density of closest packing is[8] of the form $P/\rho_0 k_B T \rightarrow U(1-\rho/\rho_0)^{-\lambda}$ with $\lambda \geq 1$ and $U > 0$ as $\rho \rightarrow \rho_0$. Therefore, if the virial expansion gives rise to this singularity, then the virial coefficients $B_n \rho_0^{n-1} \rightarrow U n^{\lambda-1}/\Gamma(\lambda)$ as $n \rightarrow \infty$—this quantity approaches either a constant, when $\lambda = 1$, or infinity, when $\lambda > 1$. Note, however, that a singularity at the density of random close packing may be[8] of the form $P/\rho_{\rm RCP} k_B T \rightarrow W(1-\rho/\rho_{\rm RCP})^{-\mu}$ with $\mu < 1$ and $W > 0$ as $\rho \rightarrow \rho_{\rm RCP} < \rho_0$. Hence, if this singularity follows from the virial expansion, then the virial coefficients $B_n \rho_0^{n-1} \rightarrow [W n^{\mu-1}/\Gamma(\mu)](\rho_0/\rho_{\rm RCP})^{n-1} \rightarrow \infty$ as $n \rightarrow \infty$ since $\rho_{\rm RCP} < \rho_0$. The values of $B_n \rho_0^{n-1}$ as a function of $1/n$ for hard disks and hard spheres may be fitted[4] by a straight line for $n \leq 7$. However, this in no way warrants the conclusion[4] that the first singularity of the virial expansion for the pressure occurs at the density of closest packing with $\lambda = 1$. It may be that $B_n \rho_0^{n-1} \rightarrow \infty$ as $n \rightarrow \infty$ in which case two possibilities arise regarding the divergence of the virial series: Either (i) a singularity at closest packing with $\lambda > 1$, or (ii) a singularity at random close packing. The latter case can be distinguished from the former by considering $(\rho_{\rm RCP})^{n-1} B_n \rightarrow W n^{\mu-1}/\Gamma(\mu) \rightarrow 0$ as $n \rightarrow \infty$ for appropriate values of $\rho_{\rm RCP} < \rho_0$ and $0 < \mu < 1$ in order to ensure the correct asymptotic behavior.

It should be remembered that the only known analytic property of the virial expansion is analyticity at $\rho = 0$. Hence, no one knows the nature or location of the first singularity of the virial series. In the present work, we have built in the possibility that the first singularity be a simple pole and up to the approximation worked out the possibility is realized and the results predict both the position and the residue of the simple pole. Clearly, we have not searched for the random close-packing configuration since such a search would entail[8] a weaker singularity.

In Figs. 1 and 2, the solutions of the differential equation (B2) are plotted together with the molecular-dynamics data.[11,12] One expects the two-dimensional hard-core system to be more accurately given than that for the three-dimensional system since our approximation scheme is exact to lowest order for $d=1$. This is borne out in our numerical results as given in Figs. 1 and 2. The agreement with molecular-dynamics data may be improved by varying B_6, B_7, and B_8 within the quoted errors.[12–14] Note, however, that our highest approximation requires knowledge of all these three virial coefficients and that the approximate value for B_8 is estimat-

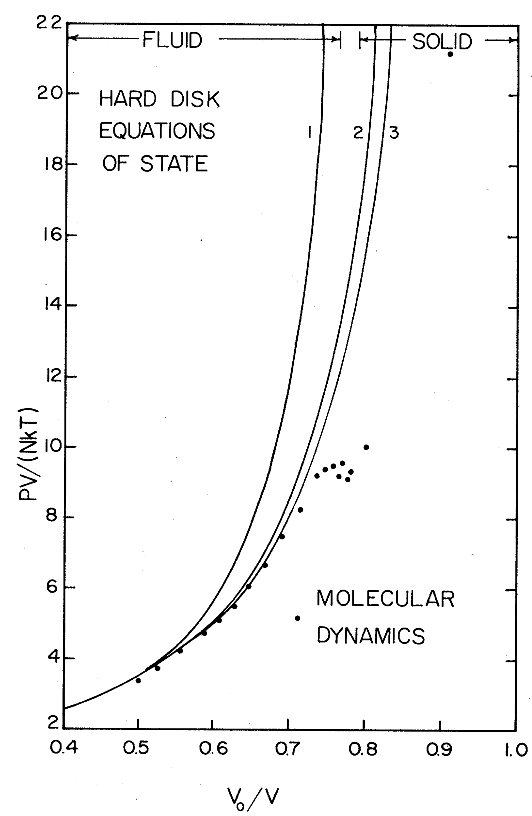

FIG. 1. Plot of PV/Nk_BT vs V_0/V for hard disks. V_0 is the volume at closest packing, $N\sigma^2\sqrt{3}/2$. The curves are (1) solution of (B2) with coefficients (B3), (2) solution of (B2) with coefficients (B4), and (3) solution of (B2) with coefficients (B5). Molecular-dynamics results of Hoover and Alder (Ref. 11) are indicated by dots.

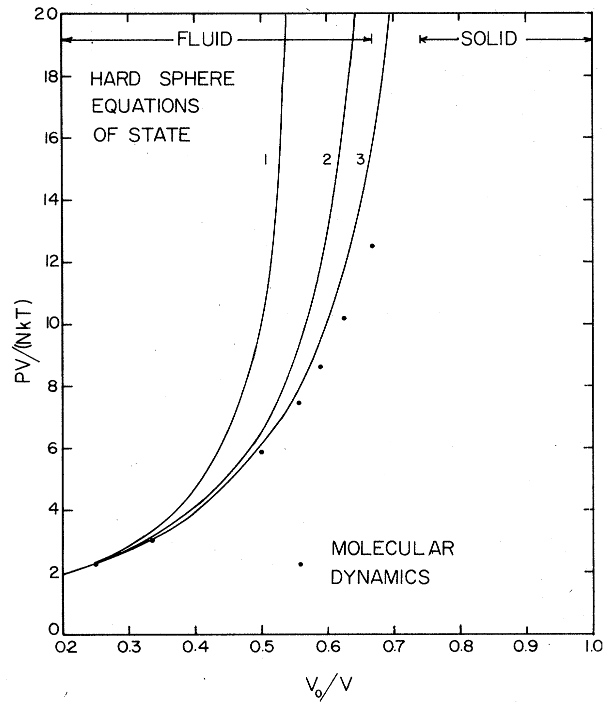

FIG. 2. Plot of PV/Nk_BT vs V_0/V for hard spheres. V_0 is the volume at closest packing, $N\sigma^3/\sqrt{2}$. The curves are (1) solution of (B2) with coefficients (B6), (2) solution of (B2) with coefficients (B7), and (3) solution of (B2) with coefficients (B8). Molecular-dynamics results of Erpenbeck and Wood (Ref. 12) are indicated by dots.

ed using several approximations. Now for hard disks,[13] $\delta(B_6/b^5)=\pm 0.000\,24$, $\delta(B_7/b^6)=\pm 0.0005$, and $\delta(B_8/b^7)=\pm 0.0004$. Therefore, the following values of the residue R and the position ρ_c/ρ_0 of the simple pole may be obtained: $R=2.23-2.93$ (probable value: 2.48) and $\rho_c/\rho_0=0.904-0.957$ (probable value: 0.926). Similarly, for hard spheres,[14] $\delta(B_6/b^5)=\pm 0.0004$, $\delta(B_7/b^6)=\pm 0.0006$, and $\delta(B_8/b^7)=\pm 0.0006$. Therefore, $R=3.11-3.98$ (probable value: 3.34) and $\rho_c/\rho_0=0.796-0.861$ (probable value: 0.815). It is interesting that for both hard disks and hard spheres, whenever R increases ρ_c/ρ_0 also increases.

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APPENDIX A: COEFFICIENT C_j

In this appendix we obtain the coefficients C_j of the differential equation (2.3) in terms of the virial coefficients B_j of the virial expansion (2.1). An implicit expression is obtained by substituting (2.1) into (2.3) and equating equal powers of ρ to those of result (2.2). [An explicit expression follows directly by inverting (2.1) and substituting the series of ρ in terms of η into (2.2).] After an elementary but lengthy computation one obtains

$$B_2/b=C_2\ , \tag{A1}$$

$$2B_3/b=2B_2C_2+C_3\ , \tag{A2}$$

$$3B_4/b=(B_2^2+2B_3)C_2+3B_2C_3+C_4\ , \tag{A3}$$

$$4B_5/b=(2B_4+2B_2B_3)C_2+(3B_2^2+3B_3)C_3+4B_2C_4+C_5\ , \tag{A4}$$

$$5B_6/b=(B_3^2+2B_5+2B_2B_4)C_2+(3B_4+6B_2B_3+B_2^3)C_3+(6B_2^2+4B_3)C_4+5B_2C_5+C_6\ , \tag{A5}$$

$$\begin{aligned}6B_7/b=&(2B_6+2B_2B_5+2B_3B_4)C_2+(3B_3^2+3B_5+6B_2B_4+3B_2^2B_3)C_3+(4B_2^3+4B_4+12B_2B_3)C_4\\&+(10B_2^2+5B_3)C_5+6B_2C_6+C_7\ ,\end{aligned} \tag{A6}$$

$$\begin{aligned}7B_8/b=&(B_4^2+2B_7+2B_2B_6+2B_3B_5)C_2+(3B_6+6B_2B_5+6B_3B_4+3B_2B_3^2+3B_2^2B_4)C_3\\&+(B_2^4+12B_2^2B_3+6B_3^2+4B_5+12B_2B_4)C_4+(5B_4+20B_2B_3+10B_2^3)C_5+(15B_2^2+6B_3)C_6+7B_2C_7+C_8\ .\end{aligned} \tag{A7}$$

1. Hard disks

The numerical values of the coefficient C_j for hard disks of diameter σ are based on the following values for the virial coefficients:[13]

$$\begin{aligned}&B_2\equiv b=(\pi/2)\sigma^2\ ,\\&B_3/b^2=\tfrac{4}{3}-\sqrt{3}/\pi=0.782\,004\,4\ ,\\&B_4/b^3=2-9\sqrt{3}/2\pi+10/\pi^2=0.532\,231\,8\ ,\\&B_5/b^4=0.333\,556\,1\ ,\\&B_6/b^5=0.198\,93\ ,\\&B_7/b^6=0.1148\ ,\\&B_8/b^7=0.0653\ .\end{aligned} \tag{A8}$$

The virial coefficients B_5 to B_7 are obtained by Monte Carlo integration while the coefficient B_8 is estimated. On substituting (A8) in (A1) to (A7),

$$\begin{aligned}&C_2=1\ ,\\&C_3/b=-0.436\,000\ ,\\&C_4/b^2=0.340\,690\ ,\\&C_5/b^3=-0.326\,124\ ,\\&C_6/b^4=0.350\,167\ ,\\&C_7/b^5=-0.406\,639\ ,\\&C_8/b^6=0.504\,649\ .\end{aligned} \tag{A9}$$

Note that $|C_j/b^{j-2}|$ increase in value as j increases beginning with $j=5$.

2. Hard spheres

The numerical values of the coefficients C_j for hard spheres of diameter σ are determined with the aid of the following[14] virial coefficients:

$$\begin{aligned}
&B_2 \equiv b=(2\pi/3)\sigma^3 , \\
&B_3/b^2=\tfrac{5}{8}=0.625\,000 , \\
&B_4/b^3=-\tfrac{89}{280}+219\sqrt{2}/2240\pi \\
&\qquad +(4131/2240\pi)\cos^{-1}(1/\sqrt{3}) \\
&\qquad =0.286\,950 , \\
&B_5/b^4=0.110\,252 , \\
&B_6/b^5=0.0389 , \\
&B_7/b^6=0.0137 , \\
&B_8/b^7=0.0045 .
\end{aligned} \tag{A10}$$

The coefficients B_5 to B_7 are obtained by Monte Carlo integration whereas B_8 is estimated. On substituting (A10) into (A1) to (A7), one obtains

$$\begin{aligned}
&C_2=1 , \\
&C_3/b=-0.7500 , \\
&C_4/b^2=0.860\,850 , \\
&C_5/b^3=-1.170\,05 , \\
&C_6/b^4=1.750\,84 , \\
&C_7/b^5=-2.785\,99 , \\
&C_8/b^6=4.621\,14 .
\end{aligned} \tag{A11}$$

Note again the increase of $|C_j/b^{j-2}|$ with increasing j beginning with $j=3$. The behavior is much more acute than that for hard disks given by (A9).

APPENDIX B: NONLINEAR DIFFERENTIAL EQUATIONS

Let us obtain the modified improved solution of (2.3) by replacing the polynomial

$$f(b\eta)=1+C_3\eta+C_4\eta^2+\cdots+C_{n+2}\eta^n \tag{B1}$$

for $n=0,2,4,6$ associated with the nth-order improved solution by a rational function of the form

$$\begin{aligned}
\frac{d\eta}{db}&=\eta^2 f(b\eta) \\
&=\eta^2\frac{1+Ab\eta+C(b\eta)^2+E(b\eta)^3}{1+Bb\eta+D(b\eta)^2+F(b\eta)^3} ,
\end{aligned} \tag{B2}$$

where the pure numbers $A,B,..,F$ are determined by the coefficients $C_3,\ldots,C_8$ on expanding (B2) about $b\eta=0$ and comparing the coefficients of the series with those of (B1). Note that this modification is such that the solution of the nonlinear differential equation (B2) preserves all the good features of the improved scheme,[7] viz. all the virial coefficients used in the approximation are reproduced on expanding the solution for P as given by (B2) about $\rho=0$ and $\partial P/\partial\rho\geq 0$.

The singularities of (B2) are poles and/or algebraic branch points whose location depends on the density ρ. Note that by requiring $f(b\eta)\to\text{const}\neq 0$ as $b\eta\to\infty$, we ensure that the solution of (B2) becomes infinite for finite values of ρ and that the singularity may be a simple pole. It is interesting that the sequence of quantities A and B; A, B, C, and D; and A, B, C, D, E, and F associated with the successive approximations generated by (B2) for the equation of state for both hard disks and hard spheres are all positive. Consequently, the solution of (B2) with boundary condition $\eta=\rho$ for $b=0$ diverges with a simple pole for finite b or equivalently, by (2.6), for finite ρ.

1. Hard disks

With the aid of (A9) one gets the sequence of approximations (B2) for $f(b\eta)$ with

$$\begin{aligned}
&A=0.345\,399 , \\
&B=0.781\,399 ,
\end{aligned} \tag{B3}$$

$$\begin{aligned}
&A=1.155\,30 , \\
&B=1.591\,30 , \\
&C=0.142\,333 , \\
&D=0.495\,451 ,
\end{aligned} \tag{B4}$$

$$\begin{aligned}
&A=2.387\,87 , \\
&B=2.823\,87 , \\
&C=1.382\,76 , \\
&D=2.273\,27 , \\
&E=0.112\,033 , \\
&F=0.467\,241 .
\end{aligned} \tag{B5}$$

2. Hard spheres

For the present case, the coefficients in (B2) for the successive approximations are given, with the aid of (A11), by

$$A = 0.397\,800\,,\quad B = 1.147\,80\,, \tag{B6}$$

$$A = 1.491\,37\,,\quad B = 2.241\,37\,,\quad C = 0.192\,401\,,\quad D = 1.012\,58 \tag{B7}$$

$$A = 2.467\,54\,,\quad B = 3.217\,54\,,\quad C = 1.392\,79\,,\quad D = 2.945\,10\,,\quad E = 0.086\,199\,1\,,\quad F = 0.695\,249\,. \tag{B8}$$

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*Permanent address: Centro de Investigación y de Estudios Avanzados, Apartado Postal 14-740, 07000 México, D.F., Mexico.

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