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Percus–Yevick Virial Relation and Scaled Particle Theory

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The conditional probability of finding a cavity $G(r)$ devoid of molecular centers of hard sphere fluid is modified by making use of the discontinuity at $r = a/2$ (a is the diameter of a molecule). The new equation of state thus obtained is bounded by the Percus–Yevick compressibility and virial pressure equations of state, which may be the upper and lower bounds to the results of machine calculation.

KEY WORDS: Scaled particle theory; hard sphere fluids.

1. INTRODUCTION

The simplest version of the Percus–Yevick (PY) theory yields two approximate expressions[2] for the pressure p of a classical fluid of hard spheres (HS) of diameter a and number density ρ, the PY "compressibility" relation (PYC)

$$\beta pc/\rho = (1 + \eta + \eta^2)/(1 - \eta)^3 \tag{1}$$

and the PY "virial" relation (PYV)

$$\beta pv/\rho = (1 + 2\eta + 3\eta^2)/(1 - \eta)^2 \tag{2}$$

where $\beta = 1/kt$ and $\eta = \pi a^3 \rho/6$. Utilizing some very meager information about the geometry of the HS fluid (which will be summarized below), Reiss *et al.*[1] showed that the original formulation of the scaled particle

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theory (SP) led naturally to (1). Indeed, (1) was first derived from this SP theory. The mathematical shortcomings of (1) and (2) are quite evident. Besides their historical importance (1) and (2) are still of some interest because molecular dynamics studies[3] suggest that they are possibly an upper and a lower bound, respectively, on $\beta p/\rho$ of HS, although to date this has not been rigorously demonstrated. The similarity in the form of (1) and (2) suggests that they contain essentially the same amount (or lack thereof) of geometric information about the HS. We will show that a minor mathematical modification of the original formulation of SP theory, utilizing only the geometrical information contained in Ref. 1 (actually not all the available information) leads one to a sequence of approximate expressions for $\beta p/\rho$ of HS which contains as strict upper and lower bounds (1) and (2) respectively.

2. SCALED PARTICLE THEORY AND A MODIFICATION

In the SP theory of Ref. 1 attention is focused on a cavity of radius r (a spherical volume devoid of HS centers) in the HS fluid of density ρ. The reversible work necessary to increase the radius of the cavity, producing a volume change $dv = 4\pi r^2\,dr$ and a surface area change $ds = 8\pi r\,dr$, can be shown to be given by

$$dW(r, \rho) = p\,dv + \sigma(r, \rho)\,ds = \beta^{-1}\rho G(r)\,dv \tag{3}$$

with p the HS pressure, $\sigma(r)$ the HS surface tension against a cavity of radius r, and $G(r)\,dv$ the conditional probability of finding a HS center in the volume element dv adjacent to a cavity of radius r. Thus

$$G(r) = (p\beta/\rho) + [2\sigma(r)\beta/\rho r] \tag{4}$$

The central significance of the function $G(r)$ for the computation of the pressure lies in the fact that a cavity of radius $r = a$ behaves like a fixed HS so that[1]

$$G(a) = g(a) \tag{5}$$

$g(a)$ is the contact value of the radial distribution function of the HS fluid, thus providing a means, via the virial theorem for HS $[p\beta/\rho = 1 + \frac{2}{3}\pi\rho a^3 g(a)]$, for finding p once $G(a)$ is known. Since thermodynamic considerations suggest that as $r \to \infty$, $\sigma(r) \to \sigma_0$, the HS surface tension against a rigid flat wall, one can combine these facts into the single formula[1]

$$p\beta/\rho = G(\infty) = 1 + \tfrac{2}{3}\pi a^3 \rho G(a) \tag{6}$$

Since a cavity of radius $r < a/2$ can accommodate at most one HS center, while for $a/2 \leqslant r \leqslant a/\sqrt{3}$ at most two HS centers can be accommodated, etc., Reiss *et al.*[1] showed that

$$G(r) = 1/(1 - \tfrac{4}{3}\pi r^3 \rho), \qquad r \leqslant a/2 \tag{7}$$

and

$$G\left(\frac{a}{2}\right) = \frac{1}{1-\eta} \tag{8}$$

$$G'\left(\frac{a}{2}\right) = \frac{\pi a^2 \rho}{1-\eta} \tag{9}$$

$$G''\left(\frac{a}{2}\right) = \frac{4\pi a\rho}{(1-\eta)^2} + \frac{2\pi^2 a^4 \rho}{(1-\eta)^3} + \Delta_G \tag{10}$$

with $\Delta_G \equiv -[8\pi a\rho/(1-\eta)]G(a)$; Δ_G is the discontinuous part of $\partial^2 G/\partial r^2$ evaluated at $r = a/2$. Even more geometric information as it affects this function $G(r)$ is contained in Ref. 1 but will not be used here.

Using essentially the "smoothness" of the function $G(r)$ in the annular region $a/2 \leqslant r \leqslant a$, the basic approximation of Reiss *et al.*[1] was to replace in that region and for $r > a$ the exact function by the analytic quadratic polynomial in a/r

$$G_a(r) = \frac{\beta p}{\rho} + \frac{2\sigma_0\beta}{\rho r}\left(1 + \frac{\delta a}{2r}\right) = P + \Sigma\cdot\left(\frac{a}{r}\right) + \Delta\cdot\left(\frac{a}{r}\right)^2 \tag{11}$$

with $P(\eta) = \beta p/\rho$, $\Sigma(\eta) = 2\beta\sigma_0/\rho a$, and $\Delta(\eta) = \beta\sigma_0\delta/\rho a$. The detailed arguments supporting (11) need not be repeated here. The coefficients of (11) are evaluated by substituting (11) into (6), (8), and (9), and solving the resulting system of three homogeneous equations for P, Σ, and Δ. The resulting equation for P as a function of the reduced density η is (1).

In deriving (1), no use was made of the jump condition in the second derivative of $G(r)$, Eq. (10). Eventually, a serious program of modification of this theory for $G(r)$ must take systematic account of the discontinuities in the successively higher derivatives of $G(r)$ at $r = a/2$, $a/\sqrt{3}$, etc. This is not our purpose here. Rather, our modification will simply consist in augmenting (11) by a term which enables us to make use of the first jump condition on the higher derivatives of $G(r)$, namely (10). We thus replace (11) by

$$G_1(r) = G_a(r) + G_{1d}(r)$$

$$G_{1d}(r) = T(\eta)\left[E\left(r - \frac{a}{2}\right)\left(\frac{2r}{a} - 1\right)^2\right]\left(\frac{a}{r}\right)^n, \qquad n \geqslant 2 \tag{12}$$

where $G_a(r)$ is given by (11) and $G_{1d}(r)$ is the contribution to the approximate $G(r)$, $G_1(r)$, arising from the discontinuity in the second derivative of $G(r)$ at $r = a/2$, with $E(r - a/2)$ the Heaviside function of the indicated argument. The factor in the square bracket in $G_{1d}(r)$ ensures the proper behavior at $r = a/2$. The remaining factor must be a "smooth" function of η and r/a which vanishes sufficiently rapidly as $r \to \infty$ so that $G_{1d}(r)$ is bounded. The choice made in (12) is mathematically perhaps the simplest in form which is consistent with Ref. 1 and would certainly not be made if we were interested in optimal curve fitting. We shall return to this point later. The form given in (12) with $n = 3$ would be consistent with the curvature expansion of the Gibbs–Tolman–König surface tension formula. This is not an argument which supports (12) since that formula is an approximation whose statistical geometric basis is incompletely understood.

To evaluate $P(\eta)$, $\Sigma(\eta)$, $\Delta(\eta)$, and $T(\eta)$ of (12) we substitute (12) into (6) and (8)–(10) to obtain

$$
\begin{gathered}
(4\eta - 1)P + 4\eta\Sigma + 4\eta\Delta + 4\eta T = -1 \\
P + 2\Sigma + 4\Delta = (1-\eta)^{-1}, \qquad -2\Sigma - 8\Delta = 3\eta/(1-\eta) \\
3(1-\eta)^{-1}P + 4\Sigma + 24\Delta + 32T = 6/(1-\eta)^2 + 18\eta^2/(1-\eta)^3
\end{gathered}
\tag{13}
$$

respectively. [$G(a)$ in (10) was eliminated using (6).] Solving the homogeneous system of equations yields the desired coefficients. Setting $\zeta = 2^{-n+1}$, one has

$$P(\eta) = [1 + 5\zeta\eta + 8\zeta\eta^2 + (-1 + 5\zeta)\eta^3]/D \tag{14}$$

$$\Sigma(\eta) = -(3\eta/2)[1 + 5\zeta\eta - (1 - 4\zeta)\eta^2]/D \tag{15}$$

$$\Delta(\eta) = [3\eta^2 + (9\zeta - 3)\eta^3]/4D \tag{16}$$

$$T(\eta) = -3\eta^2\zeta(2 + \eta)/4D \tag{17}$$

where $D \equiv (1-\eta)^2[1 + (-2 + 5\zeta)\eta + (1 - 2\zeta)\eta^2]$. Equations (12) and (14)–(17) constitute the simplest version of this modification of the SP theory. For $n = 2$ ($\zeta = 1/2$), (14) reduces to (2), while for $n \to \infty$ ($\zeta = 0$), (14) leads to the original SP theory result (1).

3. PROPERTIES OF THE MODIFIED SP THEORY

Since the virial theorem (6) is employed in determining the η-dependent coefficients in $G_1(r)$, one does not expect it to exactly satisfy the thermodynamic "compressibility pressure relation" derived in Ref. 1,

$$P - 1 = \rho \int_0^a dr\, G(r, \rho) 4\pi r^2 - \frac{1}{\rho} \int_0^\rho \rho'\, d\rho' \int_0^a dr\, G(r, \rho') 4\pi r^2 \tag{18}$$

The only analytic, approximate $G(r, \rho)$ which satisfies (18) is $G_a(r, \rho)$.

If $P(\eta)$ and $G_1(r)$ are expanded as formal power series in η for all $\zeta \leqslant 1/2$, we find that (18) is satisfied only by the constant and linear term of the expansion of $G_1(r)$ and up to and including the quadratic term of $P(\eta)$ given by (14). By direct substitution of the η expansions of (12) and (14) in (18) one finds that there is a unique value of $\zeta = \hat{\zeta} = 2^{-n+1}$ for which the quadratic term in the $G_1(r)$ expansion and up to the cubic term of the $P(\eta)$ expansion fulfill (18). This value of $n = \hat{n}$ satisfies

$$[8 - 5\hat{n} + \hat{n}^2 - 1/2\hat{\zeta}]/[(5 - \hat{n})(4 - \hat{n})(3 - \hat{n})] = 2/9 \tag{19}$$

A straightforward numerical solution yields

$$\hat{n} \cong 3.69 \tag{20}$$

These facts suggest that at least for sufficiently small values of η, $G_1(r)$ may be a potential candidate which, as we shall see, provides improved values of the lower-order virial coefficients.

The behavior of $G_1(r)$ and its coefficients [like that of $G_a(r)$] for values of η approaching unity is unsatisfactory. Clearly the divergence of $G_1(r)$, etc. as $\eta \to 1$ is not in accord with the facts of geometry. There is *no* improvement in the behavior of $G_1(r)$ over $G_a(r)$ in that regard. We have no rigorous result to compare the behavior of $G_1(r)$ for intermediate values of η. We can do a little better if we examine the behavior of the reduced pressure $P(\eta)$ as a function of η.

First we note that that $P(\eta)$ given by (14) is nondecreasing with respect to n for fixed η, $0 \leqslant \eta \leqslant 1$, and with respect to η for fixed $n \geqslant 2$. Specifically,

$$\partial P/\partial \zeta \leqslant 0, \quad 0 \leqslant \eta \leqslant 1; \qquad \partial P/\partial \eta \geqslant 0, \quad \text{for all} \quad n \geqslant 2 \tag{21}$$

The virial expansion of $P(\eta)$ gives

$$P(\eta) = \sum_{j=1}^{\infty} B_j \eta^{j-1} \tag{22}$$

with

$$B_1 = 1, \qquad B_2 = 4, \qquad B_3 = 10, \tag{23}$$

which are all exact, and

$$\begin{aligned} B_4 &= 19 - 6\zeta \\ B_5 &= 31 - 33\zeta + 30\zeta^2 \\ B_6 &= 46 - 105\zeta + 213\zeta^2 - 150\zeta^3 \end{aligned} \tag{24}$$

Table I. Numerical Values of the Virial Coefficients of (22)

B_j	Exact or machine result	PY virial (2) $n = 2$	PY compressibility (1) $n = \infty$	$n = \hat{n}$
B_4	18.365	16	19	17.98
B_5	28.24	22	31	26.26
B_6	39.5	28	46	33.57

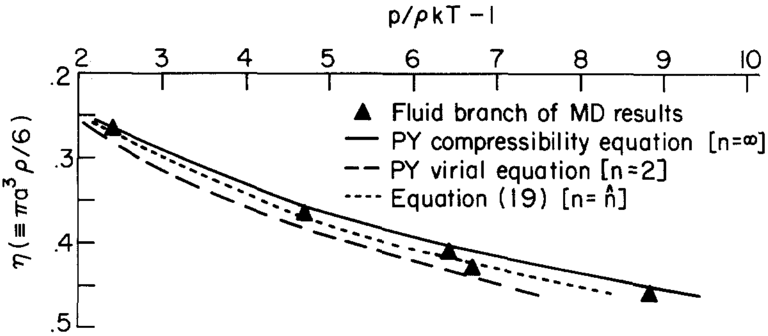

Fig. 1

Table I summarizes the numerical comparison in the lower virial coefficients with exact or machine results.[3]

We have compared $P(\eta)$ for $n = \hat{n}$ with the molecular dynamics (MD) computations of Alder and Wainwright[3] in Fig. 1. Below the phase transition as seen in the MD result (i.e., along the fluid branch) the agreement is satisfactory; above the density of this transition it is unsatisfactory.

The low-density expansion of the reduced surface tension $\Sigma(\eta)$ given by (15) gives

$$\Sigma(\eta) = -\tfrac{3}{2}\eta[1 + 4\eta + (9 - 4\zeta)\eta^2 + \cdots] \tag{25}$$

This can be compared with Bellemans'[4] two-term exact (virial) expansion

$$\Sigma(\eta)(\text{Bellemans}) = -\tfrac{3}{2}\eta(1 + 4.256\eta + \cdots) \tag{26}$$

We see there is no improvement over the original SP theory in the second term (in η^2) of this expansion. Nonetheless a nonvanishing ζ does reduce significantly the value of σ_0. For example, if we treat argon at 85°K as an effective HS fluid with $a = 3.4 \times 10^{-8}$ cm, we find $\sigma_0(\zeta = 0) = 16.4$ dyn/cm and $\sigma_0(\zeta = \hat{\zeta}) = 15.0$ dyn/cm, while the experimental value is 13.2 dyn/cm.

Figure 1 shows a plot of the reduced pressure versus the reduced density for (14) with $n = \hat{n}$. In the fluid range the agreement is excellent.

4. DISCUSSION

It should be noted that the $G_1(r, \rho)$ for $n = 2$ which yields (2) behaves for large r as a quadratic polynomial in $1/r$ like $G_a(r, \rho)$ which yields (1). The major point of this paper is that there is no new physical or geometric insight, beyond what is found in Ref. 1, which is necessary to provide one with (2). The weakness of these approximations is clearly evident from the fact that no improvement is forthcoming in the second virial coefficient of the surface tension σ_0. Use of other more complicated trial functions such as

$[(a/r)^n + (a/r)^m]$ or sums of exponentials, etc. instead of $(a/r)^n$ in (12) produces no significant improvement, except for slight shifts in the numerical values of the lower-order virial coefficients.

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