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Equation of state for a fluid of hard convex bodies in any number of dimensions

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An equation of state is proposed for an isotropic fluid of hard convex bodies in any number of dimensions. In general, only knowledge of the first three virial coefficients is required. In three dimensions an approximation can be used that involves a single nonsphericity parameter. The result appears to be very accurate as far as it can be tested against available computer simulations.

I. INTRODUCTION

Hard nonspherical bodies are among the simplest models of molecular fluids.[1,2] Even more importantly, they play the role of reference systems in perturbation theories of molecular fluids,[3–9] similar to that of hard spheres in perturbation theories of simple fluids.[10–13] Much attention has therefore been given to finding accurate analytical equations of state for various hard nonspherical bodies,[6,14–17] and to testing them against computer-simulation data. A number of methods have been used, mostly based on known results for hard spheres, including extended scaled-particle theory,[14] modifications of the Carnahan-Starling equation for hard spheres,[16] knowledge of virial coefficients,[15,16] perturbation theory,[6] and excluded-volume theory.[17] However, all analytical equations proposed to date are limited to small or medium nonsphericity or are applicable only to specific models. There remains a need for an analytical equation of state of universal form for different models, and accurate even for medium and large nonsphericity.

In this paper we present an analytical equation of state for hard convex bodies. It has a universal form for different models and is very accurate, at least up to the limit of available computer-simulation data. The physical basis for its derivation is the same as that used to generalize the equation of state of hard spheres for any number of dimensions,[18] namely the lack of correlation between the motions of a body in different directions.

II. DERIVATION

The physical assumption underlying the present equation of state makes its generalization to d dimensions quite simple, so we will keep the dimensionality arbitrary for now. The equation of state for hard convex bodies for any number of dimensions can be written as

$$\frac{p}{\rho kT}=1+b\rho G , \tag{1}$$

where p is the pressure, ρ is the number density, kT has the usual meaning, b is the second virial coefficient, and G is the average contact pair distribution function for the hard convex bodies.[19] We can introduce a shape factor f in terms of the van der Waals covolume b_0 of hard spheres of the same volume,

$$b=b_0 f , \tag{2}$$

$$b_0=2^{d-2}v_0 , \tag{3}$$

where v_0 is the volume of one particle. it is always possible to calculate b, and hence f, analytically,[20] since it is a straightforward (although perhaps complicated) geometry problem.

For hard (hyper) spheres ($f=1$), G is the pair distribution function at contact, $g(\sigma^+)$, for which we have previously found a very accurate expression,[18]

$$g(\sigma^+)=\frac{F(\eta)}{(1-\eta)^d} , \tag{4}$$

where η is the packing fraction,

$$\eta=v_0\rho=b\rho/(2^{d-1}f) , \tag{5}$$

and $F(\eta)$ is some weak function of η. This form was deduced by considering the nature of the singularity near closest possible packing ($\eta=1$). For hard spheres it was sufficient to take $F(\eta)$ as a linear function of density,

$$F(\eta)=1-\gamma_1\eta , \tag{6}$$

in which the constant γ_1 was chosen to reproduce the correct third virial coefficient B_3,

$$\gamma_1=d-2^{d-1}(B_3/b^2) . \tag{7}$$

If we now assume that the motions of a nonspherical particle in different directions are uncorrelated, the same arguments apply as for hard spheres, and the most divergent contribution to G near $\eta=1$ is again found to be $(1-\eta)^{-d}$. The same overall form should thus hold for G as for $g(\sigma^+)$, namely Eq. (4), but a linear form for $F(\eta)$ may no longer be adequate for nonspherical bodies. We have found that a quadratic form works well for all the cases examined, so that a good approximation is

$$G=\frac{1-\gamma_1\eta+\gamma_2\eta^2}{(1-\eta)^d} . \tag{8}$$

The constants γ_1 and γ_2 are chosen to reproduce the correct third and fourth virial coefficients, B_3 and B_4, of the hard convex bodies,

$$\gamma_1=d-2^{d-1}(B_3/b^2)f , \tag{9}$$

$$\gamma_2=\tfrac{1}{2}d(d-1)-2^{d-1}d(B_3/b^2)f+2^{2(d-1)}(B_4/b^3)f^2 \ . \tag{10}$$

Although analytical expressions for B_3 and B_4 are not known in general, it is always possible to calculate values of B_3 and B_4 by numerical methods in particular cases. A number of such values are summarized for $d=3$ in Table III of Ref. 20. Once these values are known, Eq. (8) for G gives a prediction of the entire equation of state.

The physical assumption of uncorrelated motions in different directions must break down if the nonspherical molecules become rotationally ordered, which should occur for large nonsphericities at high densities. Thus we do not expect the above result for G to describe liquid-crystal formation or other phase changes, any more than the Carnahan-Starling equation of state for hard spheres describes freezing. However, we do expect it to be accurate over the isotropic fluid range, including gas, liquid, and perhaps metastable liquid.

III. COMPARISONS ($d=3$)

Although the foregoing results apply to any dimensionality, data for comparison are available only in three dimensions. These data consist of some computer-simulation results for prolate and oblate spherocylinders and ellipsoids,[21] and some proposed analytical expressions for G.[16]

In three dimensions a hard convex body can be characterized by three geometric quantities: volume v_0, surface area S, and an integrated mean radius of curvature R.[20] The second virial coefficient is characterized by a single dimensionless combination of these quantities,

$$\alpha \equiv RS/3v_0 \ . \tag{11}$$

This nonsphericity parameter is unity for spheres. In terms of α the second virial coefficient and the shape factor are

$$\frac{b}{v_0}=1+3\alpha \ , \tag{12}$$

$$f=\tfrac{1}{4}(1+3\alpha) \ . \tag{13}$$

Figures 1–4 show comparisons of the available computer simulations for G with the present Eq. (8), for prolate and oblate spherocylinders and ellipsoids. The comparisons are most conveniently given as G^{-1} versus $b\rho$ for different values of α. The agreement of Eq. (8) with the numerical simulations is excellent in all cases.

Also shown in Figs. 1–4 are the results for what is probably the best previous expression for G, obtained by Boublik as an extension of the Carnahan-Starling equation for hard spheres,[16]

$$G=\frac{1}{1-\eta}+\frac{3\alpha(1+\alpha)\eta}{(1+3\alpha)(1-\eta)^2}+\frac{\alpha^2\eta^2(7-2\eta)}{3(1+3\alpha)(1-\eta)^3} \ . \tag{14}$$

This equation is accurate for small values of α, but clearly becomes less accurate as α increases.

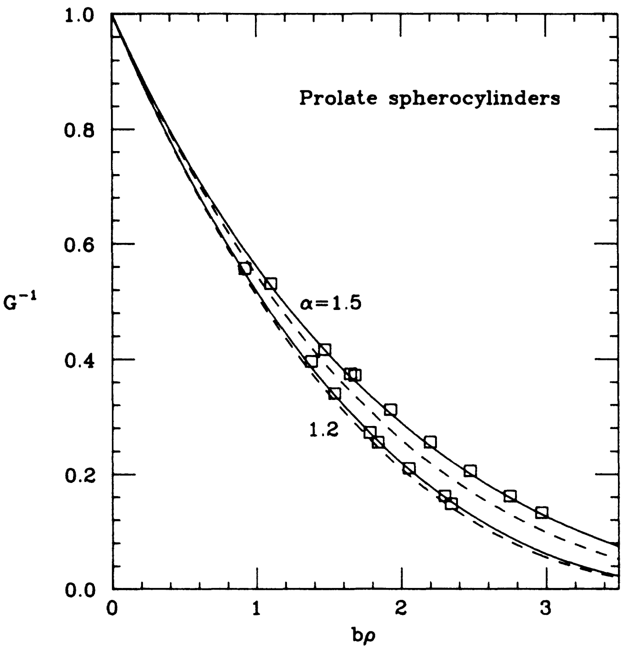

FIG. 1. Reciprocal of the average contact pair distribution function G as a function of density for prolate spherocylinders ($d=3$). The solid curves are the present Eq. (8) and the dashed curves are Eq. (14). The points are computer simulations. The values of α correspond to ratios of total length to diameter of 2 and 3.

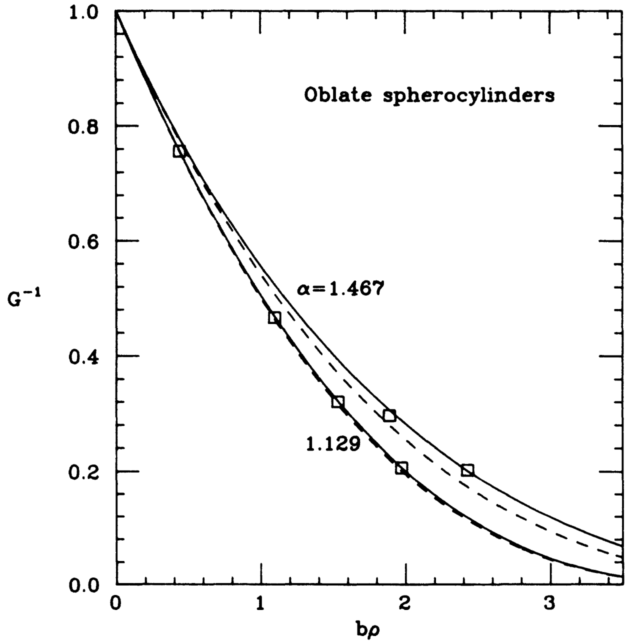

FIG. 2. Same as Fig. 1, for oblate spherocylinders. The values of α correspond to ratios of maximum-to-minimum dimensions of 2 and 3.5.

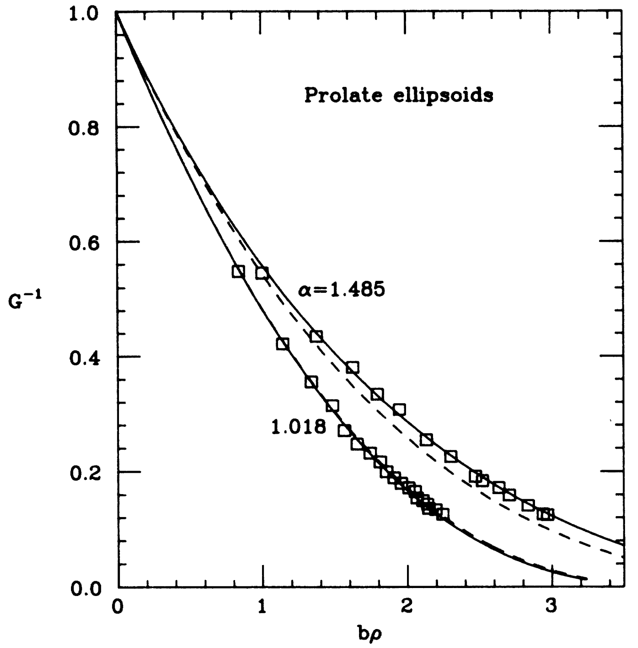

FIG. 3. Same as Fig. 1, for prolate ellipsoids. The values of α correspond to ratios of major-to-minor axes of 1.25 and 3.

IV. VIRIAL COEFFICIENTS ($d=3$)

It is inconvenient that general expressions for B_3 and B_4 are not available, since they are needed to determine the coefficients γ_1 and γ_2 in G. We therefore note here some approximations for B_3 and B_4 in three dimensions that give good results for G.

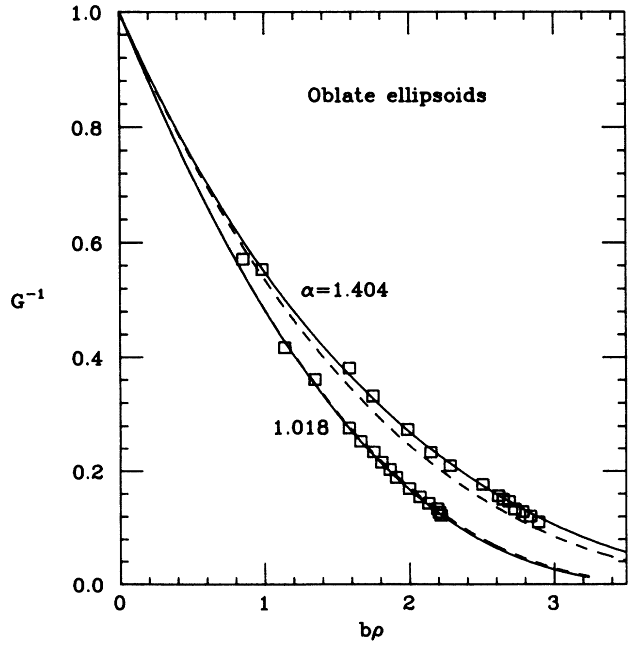

FIG. 4. Same as Fig. 1, for oblate ellipsoids. The values of α correspond to ratios of major-to-minor axes of 1.25 and 2.75.

The single nonsphericity parameter α is not sufficient to characterize B_3. An additional nonsphericity parameter is needed, which is taken to be $\tau \equiv 4\pi R^2/S$ ($\tau=1$ for spheres). Kihara and Miyoshi[22] have obtained upper and lower bounds for B_3, which can be expressed as

$$\frac{B_3}{v_0^2} = 1 + 6\alpha + 3\alpha^2\phi(\tau) \ , \tag{15}$$

$$1/\tau \le \phi(\tau) \le \tau^2 \ . \tag{16}$$

We can obtain a reasonable approximation for B_3 by taking $\tau=1$ as for spheres,

$$\frac{B_3}{v_0^2} \approx 1 + 6\alpha + 3\alpha^2 \ . \tag{17}$$

This is the same result that would be extracted from Boublik's Eq. (14) for G.

Only guesses by analogy are available for B_4, with the only firm requirement being that the hard-sphere result be reproduced, which is

$$\left[\frac{B_4}{v_0^3}\right]_{\mathrm{HS}} = \frac{2707}{70} + \frac{438\sqrt{2} - 4131\cos^{-1}(\frac{1}{3})}{70\pi} = 18.3648 \ . \tag{18}$$

We have found that the following expression for B_4 gives a good fit to the computer simulations of Figs. 1–4,

$$\frac{B_4}{v_0^3} \approx 1 + \left[\left[\frac{B_4}{v_0^3}\right]_{\mathrm{HS}} - 3\right]\alpha + 2\alpha^2 \ . \tag{19}$$

For comparison, the result from Boublik's Eq. (14) for G is

$$\frac{B_4}{v_0^3} \approx 1 + 9\alpha + \tfrac{25}{3}\alpha^2 \ . \tag{20}$$

These two formulas give comparable results only if α is close to unity.

The approximate values for γ_1 and γ_2 obtained from the above approximate expressions for B_3 and B_4 are

$$\gamma_1 \approx 3 - \frac{1+6\alpha+3\alpha^2}{1+3\alpha} \ , \tag{21}$$

$$\gamma_2 \approx 3 - \frac{1+[21-(B_4/v_0^3)_{\mathrm{HS}}]\alpha + 7\alpha^2}{1+3\alpha} \ . \tag{22}$$

Use of these values in the present Eq. (8) for G gives results that are indistinguishable from the solid curves in Figs. 1–4.

As a check, approximate values of the fifth virial coefficient B_5 can be extracted from the expressions for G, for comparison with available computer calculations (summarized in Table III of Ref. 20). The approximations of this section applied to Eq. (8) for G yield

$$\frac{B_5}{v_0^4} \approx 1 + 3\left[\left[\frac{B_4}{v_0^3}\right]_{\mathrm{HS}} - 8\right]\alpha - 3\alpha^2 \ , \tag{23}$$

and Boublik's Eq. (14) for G yields

TABLE I. Comparison of fifth virial coefficients ($d = 3$).

Dimension ratio[a]	α	Accurate[b]	Present Eq. (23)	Boublik Eq. (24)
		Prolate spherocylinders		
2	1.200	31.90	33.99	37.48
3	1.500	36.80	40.89	53.50
4	1.818	39.70	47.62	73.51
5	2.143	39.90	53.86	97.12
6	2.471	63.00	59.51	124.24
		Oblate spherocylinders		
2	1.129	32.38	32.28	34.09
2.5	1.234	35.79	34.80	39.16
3	1.348	39.02	37.46	45.04
4	1.589	43.90	42.84	58.79
		Prolate ellipsoids		
1.5	1.059	29.88	30.58	30.92
2.0	1.179	31.87	33.50	36.49
		Oblate ellipsoids		
1.5	1.059	29.51	30.58	30.92
2.0	1.179	33.18	33.50	36.49

[a] Ratio of maximum to minimum dimension.

[b] Reference 20.

$$\frac{B_5}{v_0^4} \approx 1 + 12\alpha + \tfrac{46}{3}\alpha^2 \; . \tag{24}$$

The results are compared in Table I. Equation (23) seems to be superior to Eq. (24) as α increases.

V. CONCLUSIONS

The present results give the equation of state for hard convex bodies in any number of dimensions, over the isotropic fluid range. The average contact pair distribution function G, which is the heart of the equation of state, has the very simple form of a quadratic in η divided by $(1-\eta)^d$.

Knowledge of the first three virial coefficients is required in general, but in three dimensions an approximation can be used that involves only the single nonsphericity parameter α. In particular, from Eqs. (21) and (22) for γ_1 and γ_2 we obtain

$$\frac{p}{\rho kT} \approx 1 + \frac{\eta}{(1-\eta)^3}\big((1+3\alpha) - (2+3\alpha-3\alpha^2)\eta + \{1 + [(B_4/v_0^3)_{\mathrm{HS}} - 12]\alpha - 7\alpha^2\}\eta^2\big) \; . \tag{25}$$

The accuracy appears to be very good, insofar as it can be checked against available three-dimensional computer simulations. Equation (25) should make an excellent reference equation for perturbation theories of real molecular fluids.

ACKNOWLEDGMENTS

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