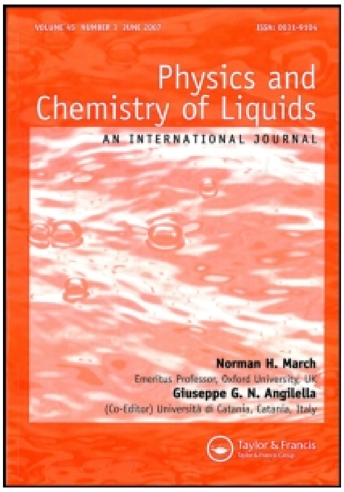

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Generalized boublick equation: an accurate expression for the equation of state of hard fused spheres

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Generalized Boublîk Equation: An Accurate Expression for the Equation of State of Hard Fused Spheres

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A simple expression to calculate the shape factor of hard bodies is proposed. Introducing this factor in the Boublîk equation of state, very good results are obtained for hard dumbells and more complicated systems of linear homonuclear hard fused spheres. Agreement with available Monte Carlo results are also satisfactory enough for heteronuclear molecules. Furthermore, the new expression is reduced to the classical shape factor for hard convex bodies and provides a common basis to manage to concave and convex hard bodies.

I INTRODUCTION

In the last years, a considerable interest has been devoted to the properties of systems composed of two or more hard fused spheres. Indeed, these systems can explain the main features of the diffraction pattern of molecular liquids.[1] Furthermore, this model has been used recently as a reference

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system in different treatments of perturbation theories[2-4] applying to homonuclear diatomic molecules. However, even for the simplest body composed of hard fused spheres: hard dumbell, proposed analytic equations for these systems show several defects: either the equations do not cover the complete range of reduced elongations and densities,[5] or are an extension in some artificial way of equations for hard convex bodies,[6] whose properties are well-known, or the coefficients have no clear physical meaning.[7] In this paper we propose in section II a simple formula which is a generalization of the accurate Boublîk formulae[8-9] for spherocylinders. Application to homonuclear and heteronuclear hard spheres is presented in section III and compared with the available Monte Carlo results. Finally, we will discuss an interesting suggestion for hard bodies proposed by Nezbeda *et al.*[10] in the light of the new formula.

II THEORETICAL

The point of departure is the well known Boublîk equation for hard-convex bodies:

$$z = \frac{1}{1-y} + \frac{3\alpha y}{(1-y)^2} + \frac{3\alpha^2 y^2 + \beta y^3}{(1-y)^3} \tag{1}$$

where $y = \rho V$ is the reduced density and $\alpha = RS/3V$. V, S and R mean, respectively, volume, surface, and $(4\pi)^{-1}$ times mean curvature of convex body. Besides

$$\beta = -\alpha^2 \tag{2}$$

$$\beta = -\alpha(6\alpha - 5) \tag{3}$$

for the different variants of Boublîk formula.[8-9]

It is easy to verify the parameter α can be written as:

$$\alpha = \frac{1}{3\pi} \frac{(\partial V/\partial \sigma) \cdot (\partial^2 V/\partial \sigma^2)}{V} \tag{4}$$

for spherocylinders and spheres of diameter equal to σ. However, we can see that, for example, there is a discontinuity in the second derivative for hard dumbells at $\sigma = L$, being L the separation between the centers, since:

$$V = \frac{\pi\sigma^3}{6}\left[1 + \frac{3}{2}\frac{L}{\sigma} - \frac{1}{2}\left(\frac{L}{\sigma}\right)^3\right] \qquad L < \sigma \tag{5a}$$

$$V = \frac{\pi\sigma^3}{3} \qquad L > \sigma \tag{5b}$$

On the other hand, we can think about the formula (5) as the volume of a scaled particle growing from two isolated points, separated at a distance L, to a hard dumbell of diameter σ. If we think that formula (1) can be derived in a way related to scaled-particle-theory (SPT),[11] we may conclude that prescription (4) is the right way to calculate α for hard dumbells and also for more complicated systems of hard fused spheres. We postulate further that equation (5a) is applied even for $\sigma = L$, i.e. $L^* = L/\sigma = 1$, for taking $(\partial^2 V/\partial\sigma^2)$ in the prescription (4).

III APPLICATION TO HARD FUSED SPHERES

a Hard dumbell systems

In this case, with the prescription (4):

$$\alpha = \frac{(L^* + 1)(L^*/2 + 1)}{1 + 3L^*/2 - L^{*3}/2} \tag{6}$$

This result has the same form as the previous one written down by Boublîk and Nezbeda.[6] But, an important difference remains: the circumscribed spherocylinder must be used in Ref. 6 in order to obtain the mean curvature. This choice of a second model is arbitrary.[12] No second model is used in our formulation framework.

Second and third reduced virial coefficients are given by:

$$B_2^* = \frac{(1 + 3\alpha)}{4}$$

$$B_3^* = \frac{(1 + 6\alpha + 3\alpha^2)}{16} \tag{7}$$

In Table I, the results are compared for B_2^* and B_3^* computed from formulae (6)–(7) and Tildesley and Streett results[7] with recent results of simulation. Prior data were compared in Ref. 6. Tildesley and Streett results are slightly better for B_2^* and this is not strange because they fit their values of coefficients to B_2^*, but our results are in general very good for B_2^* and B_3^*. This agreement is very important because Barboy and Gelbart[13] have shown that an expansion in $y/(1 - y)$ converges very quickly and three terms give very good results. In fact, formula (1) might be seen as a Barboy–Gelbart expansion with a final term approximating the sum of terms higher than the third one.

In Table II, a few selected results are given which are obtained from Eqs. (4) and (1). As Boublîk and Nezbeda[6] have pointed out, closure (2) is

TABLE I

Values for the second and third virial coefficient of hard dumbells. Experimental values are taken from Ref. (7), except the marked one with asterisk which come from (5)

L^*	B_2^*			B_3^*		
	This work	Ref. (7)	exp.	This work	Ref. (7)	exp.
0.2	1.014	1.021	1.014	0.637	0.658	0.639
0.4	1.054	1.055	1.053	0.697	0.706	0.684
0.6	1.120	1.115	1.119	0.750	0.784	0.757
0.8	1.222	1.214	1.216	0.864	0.908	0.878
1.0	1.375	1.364	1.357*	1.047	1.092	1.058
			1.361			

TABLE II

Values for the compressibility factor from Eq. (4). The rest id. as Table I.

L^*	ρd^3	z(Eq. 2)	z(Eq. 3)	z_{exp}
0.2	0.2	1.56	1.56	1.56 ± 0.03
	0.5	3.31	3.30	3.36 ± 0.07
	0.9	10.98	10.91	11.17 ± 0.22
0.6	0.4	2.77	2.75	2.78 ± 0.06
				2.76 ± 0.02 (*)
	0.8	9.15	8.80	9.23 ± 0.18
				9.14 ± 0.06 (*)
1.0	0.2	1.80	1.80	1.79 ± 0.04
	0.5	4.57	4.40	4.62 ± 0.09
	0.9	18.02	15.37	18.06 ± 0.36

excellent for this type of systems. The agreement with Eq. (3), which is slightly better than (2) for spherocylinders (9), is less satisfactory and fails at high densities and elongations.

b Three and more homonuclear hard fused spheres

Perhaps, the most interesting point of Eq. (4) is the easy extension to more complicated systems than hard dumbells. For a system composed of three homonuclear hard spheres of diameter σ and centers equally spaced to a distance L, Eq. (4) produces:

$$\alpha = \frac{(1 + L^*)(1 + 2L^*)}{1 + 3L^* - L^{*3}} \tag{8}$$

In our knowledge, the only available simulations for these systems are those of Streett and Tildesley[13] for $\rho\sigma^3 = 0.897$, and $L^* = 0.4485$. The results are shown in the second line of Table IV and will be discussed below.

For a general case, namely, N hard fused spheres of radius σ and whose outermost centers are separated to a distance λ, the result is:

$$\alpha = \frac{[(1 + L^*)(L^* + 2)]}{[2 + 3L^* - L^{*3}/(N - 1)^2]} \tag{9}$$

where

$$L^* = \frac{\lambda}{\sigma} \tag{10}$$

Now, when N goes to infinity, the value of α for a spherocylinder is recovered.

c Heteronuclear hard fused systems

Having account of additivity of volumes and linearity of derivatives, the most intuitive way to generalize Eq. (4) seems to be :

$$\alpha = \frac{1}{3\pi} \frac{(\sum_i \partial V_i/\partial\sigma_i)(\sum_i \partial^2 V_i/\partial\sigma_i^2)}{\sum_i V_i} \tag{11}$$

where V_i means the volume of each spherical part of diameter σ_i, and the sums are extended to all the spherical zones forming the molecule.

The simplest case to be considered is two spheres of diameter σ, and $\gamma\sigma$, whose centers are separated a distance L. Then, formula (11) produces:

$$\alpha = \frac{(1 + \gamma^2 + 2L_1^* + 2\gamma L_2^*)(1 + \gamma + L_1^* + L_2^*)}{2[(1 + \gamma^3) + 3(L_1^* + \gamma^2 L_2^*) - 4(L_1^{*3} + L_2^{*3})]} \tag{12}$$

where $L_i^* = 2L_i/\sigma$ and L_1 and L_2 are the distances in which the intersecting plane of the two spheres divides the distance L.

Results are shown in Table III and compared with simulation data from Jolly *et al.*[14] Agreement is, in general, good enough within the experimental error of 5 % but worse for molecules with a great ratio L_2/L_1. Agreement is better for virial coefficients than for equation of state. This fact suggests Boublîk equation is not so accurate in this case but closure (2) seems again to be more adequate. In any case, formula (11) provides more accurate results than any other formula applied to heteronuclear molecules with the exception, in some cases, of zeroth-order term in Perram–Morriss perturbation theory.

TABLE III

Virial coefficients and equation of state for heteronuclear hard dumbells. Experimental results from Ref. (14).

σ	L^*	B_2^* calc.	B_2^* exp.	B_3^*/B_2^{*2} calc.	B_3^*/B_2^{*2} exp.	ρd^3	Z(Eq. 2)	Z(Eq. 3)	Z_{exp}	L_2^*/L_1^*
1.5	0.75	1.062	1.080	0.610	0.615	0.4	2.64	2.64	2.75 2.58[a]	3.50
						0.7	6.18	6.09	6.45	
1.5	1.0	1.157	1.162	0.590	0.598	0.4	2.84	2.82	2.93	1.91
						0.7	6.93	6.68	7.13	
1.8	0.9	1.032	1.063	0.617	0.615	0.4	2.58	2.58	2.68	5.48
						0.7	5.95	5.91	6.34	
1.2	0.6	1.086	1.087	0.605	0.609	0.4	2.69	2.68	2.78	1.88
						0.7	6.36	6.24	6.51	

[a] Non-cubic box.

Extension to linear molecules x-y-x with $\sigma_y = \gamma\sigma_x$ is also very easy and results are summarized in Table IV in comparison with available MC results.[12] Calculated values from Eq. (2) are within the experimental error of 5 % and are much better than for Eq. (3) except in the case $\gamma = 1$.

TABLE IV

Virial coefficients and compressibility factors for three hard fused spheres ($L^* = 0.4485, \rho^* = 0.897$). Experimental results from Ref. (12).

γ	α	$B_{2_{calc.}}$	$B_{2_{exp}}$	Z(Eq. 2)	Z(Eq. 3)	$Z_{exp.}$
5/6	1.3157	1.213	1.210	14.48	13.22	14.84
1	1.2184	1.164	1.153	13.54	12.62	12.84
7/6	1.1378	1.103	1.114	12.43	11.89	12.88

IV FINAL DISCUSSION AND CONCLUSIONS

An interesting suggestion was proposed by Nezbeda *et al.*[10] This suggestion is that for hard spheres (*HS*), hard dumbells (*HD*) and hard spherocylinders (*SC*) at the same density and equal elongation L for the dumbell and the spherocylinder:

$$z_{HS} \leq z_{HD} \leq z_{SC}$$

We consider here only the second inequality, (the first is proved enough), in relation to formula (4). According to this, values for αV and $\alpha^2 V^2$ are the same for both bodies since for the SC:

$$\alpha_{SC} = \frac{(1 + L^*)(1 + L^*/2)}{(1 + 3L^*/2)} \tag{13}$$

Nevertheless, the values for $(1 - y)^{-n}$, $n = 1, 2, 3$, are greater for spherocylinders because of its greater volume, and the closure term that would be greater for dumbells at some densities is much smaller than the other terms for all the densities with physical meaning.

Therefore, Eq. (4) does not only provide a basis for general equations of hard bodies—fused spheres and convex bodies—but also it holds an interesting conjecture useful for testing simulation experiments, indirectly.

The simple form of the expression proposed in this paper, with good results in every case, suggests that application to more complicated systems could be instructive. In fact, very good results are obtained when it is applied to mixtures of hard dumbells[15] and to the relatively simple nonlinear molecule of propane.[16]

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