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A UNIFIED TREATMENT OF THE EQUATION OF STATE OF HARD LINEAR BODIES

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Abstract

An unified treatment of the equation of state of convex (spherocylinders) and non-convex (dumbells) hard bodies is presented. Comparison of our results with simulation shows very good agreement for diatomics and excellent for triatomics.

Introduction

Most of the equations of state proposed for the Hard Interaction Site Models (HISM) exploit the idea of its similarity to Hard Convex Bodies (HCB). In fact, the limit for infinite atoms of a HISM molecule with constant separation between the outermost atoms is just a spherocylinder. Then, a consistent equation of state of HISM molecules should give - in the limit of ∞ sites - the equation of state of the spherocylinders. This requirement fails in the case of Boublik and Nezbeda equation (1), which produces the closest agreement with simulation results (2,3) of dumbells because the limit of this equation is the Boublik HCB equation which is a relatively poor equation of spherocylinders (4). Thus, it seems that BN equation for HISM systems is based on an approximate functional dependence on density of the compressibility factor. Errors must be cancelled by a fortunate choice of the anisotropic factor α. However, the BN definition of α seems to be obvious and very accurate. We may wonder where the failure lies

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in the definition of α. We think that the answer is in the use of a geometrically suitable but physically inadequate relation for the volume of the hard fused spheres. If we are concerned about pressure effects, the volume of a hard body denotes the inaccesible region to any other molecule because of the infinity of the intermolecular potential function. That volume is not affected by the presence of internal holes into the hard body and for hard convex molecules is just the geometrical volume. But if the molecules are not convex, there are points outside the surface which cannot be reached by a second molecule for any relative orientation. These points act as "external holes" of the particle and they define an effective volume for hard non-convex bodies (figure 1). Indeed, the pressure of a system of hard non-convex bodies and that of its corresponding effective bodies is exactly coincident, so we propose to use the effective body so far pressure effects are involved. It is worthwhile to note that the effective HISM system is closer to a HCB than is the actual one.

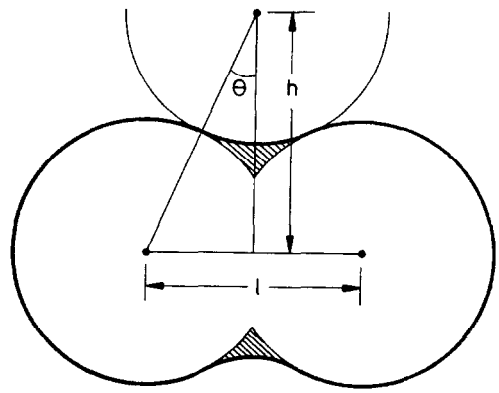

Figure 1.- Solid line showing the effective volume as defined in the text

In this paper we investigate the validity of the HCB equations for the effective HISM systems. As far as we are aware, Nezbeda HCB equation (5) gives the best agreement with the simulation data for spherocylinders. This relation, together with a recently proposed expression for α, will define our equation of state. It covers a wide range of systems from hard spheres to linear HISM molecules with n sites which in the limit of $n \to \infty$ converts in the spherocylinder case.

Equation of state of linear hard bodies

Our aim is to apply the most accurate HCB equation to the effective body. In particular, Nezbeda equation (5) has the form

$$\frac{\beta p}{\rho} = \frac{1+(3\alpha-2)y+(\alpha^2+\alpha-1)y^2-\alpha(5\alpha-4)y^3}{(1-y)^3} \qquad |1|$$

Now, both the shape factor, α, and the packing fraction, y, must be evaluated. Recently, it has been shown (6) that the relation

$$\alpha = \frac{1}{3\pi} \frac{(\partial V/\partial\sigma)\ (\partial^2 V/\partial\sigma^2)}{V} \qquad |2|$$

predicts the exact α for spherocylinders and reduces to the BN prescription for dumbells. We only need to know the volume of the effective body. A general expression is easily derived for the effective n-sites linear body. We first consider the volume between two consecutive sites separated by a distance ℓ

$$V_{ss} = (\pi\sigma^3/6)\ (3\ell-\ell^3/2-3h\theta) \qquad |3|$$

with $h=(1-\ell^2/4)^{1/2}$ and $\theta=\sin^{-1}(\ell/2)$ all the distances being reduced with the diameter σ. Then, for a molecule made-up of n-sites

$$V_n = (n-1)V_{ss}+\pi\sigma^3/6 = (\pi\sigma^3/6)\ |1+3L-L^3/2(n-1)^2-3(n-1)h\theta| \qquad |4|$$

where $L=(n-1)\ell$ is the distance between the outermost atoms. Taking successive derivatives with respect to σ in |4| we get

$$\frac{\partial V}{\partial\sigma} = \frac{\pi\sigma^2}{2} \left|1+5L/2-3(n-1)h\theta-\frac{L^2\theta}{4(n-1)h}\right| \qquad |5|$$

$$\frac{\partial^2 V}{\partial\sigma^2} = \pi\sigma \left|1+2L-3(n-1)h\theta-\frac{3L^2\theta}{8(n-1)h}+\frac{L^3}{16(n-1)^2h^2}+\frac{L^4\theta}{32(n-1)^3h^3}\right| \qquad |6|$$

If $n\to\infty$ then $h\to1$ and $\theta\to L/2(n-1)$ and |2| transforms to the exact expression for spherocylinders. Thus, it fulfills the condition mentioned in the introduction: we only need one equation of state to describe the behavior of HISM and HCB systems.

In table I appear the results obtained from equations |1|-|6| for diatomics. Comparison with Monte Carlo data shows that the equation predicts very fair values for the compressibility factor. Departures, which can reach up to 1.5 percent, indicate that pressure is slightly underestimated. BN results are also displayed in table I. They still

remain the most accurate values for dumbells with L=0.6 in spite of the lack of theoretical basis. Nevertheless, BN equation predicts too low values at moderately high densities for L=1. It has been shown elsewhere that BN choice of α for diatomics is equivalent to that of eq. 2. It is interesting to note that the same is almost right for the effective dumbells when BN definition is extended as

$$\alpha = (R\ S)_{SC} / V_{eff} \qquad |7|$$

i.e., an auxiliary spherocylinder (SC) is used not only to evaluate R, the mean curvature, but also S, the surface. This definition is consistent with the original one since the surface of a diatomic is just the same than that of its auxiliar spherocylinder. Computed values from |7| are almost coincident with those produced by |2| when the same expression is used for the compressibility factor, namely, eq. 1. Thus, equivalence between both the definitions is kept for the effective volume

Table I.- Compressibility factor for diatomics

$\rho\sigma^3$	MC		This work		BN
	Ref.2	Ref.3	Eq. 2	Eq. 7	
L=0.6					
0.1116	1.64	1.64	1.63	1.63	1.63
0.2000	2.49	2.46	2.47	2.47	2.47
0.2232	2.79	2.76	2.77	2.77	2.77
0.3000	4.12	4.04	4.07	4.07	4.07
0.3348	4.94	4.86	4.88	4.88	4.89
0.4000	7.06	6.96	6.95	6.95	6.99
0.4464	9.21	9.14	9.07	9.06	9.15
0.5000	12.72	12.7	12.53	12.53	12.70
L=1					
0.1	1.81	1.80	1.82	1.82	1.80
0.2	3.36	3.36	3.37	3.35	3.33
0.3	6.39	6.39	6.36	6.32	6.31
0.35	8.92	8.88	8.85	8.79	8.82
0.4	12.60	12.8	12.60	12.40	12.49
0.45	18.10	17.9	17.94	17.83	18.02

Results for triatomics are displayed in table II together with simulation data (7,8). Now, our values are much closer to the MC results than those obtained from BN which clearly fail in this case. This could be expected because the effective triatomic is very close to a spherocylinder and it is well known that the BN equation gives too high values, specially for the higher axis ratio (4). Again, equations |7| and |2| give essentially the same results (differences are now less than 0.005).

Table II.- Compressibility factor for linear triatomics

$\rho\sigma^3$	MC	Eq. 2	Eq. 7	BN
L=0.897	(Ref.7)			
0.3977	12.84	12.95	12.95	13.54
L=0.9118	(Ref.8)			
0.3919	12.85	12.74	12.74	13.33
0.4127	14.88	15.03	15.04	15.82
0.4284	16.82	17.10	17.10	18.08

Finally, we would like to point out that similar arguments could also be applied to non-linear molecules. Since no simulation has been reported for non-linear molecules, we are not able to confirm this point. However, Nezbeda (9) used and alike line of reasoning to justify second virial coefficients of triatomic molecules with different shapes. So we believe that steric factors must play a more important role in the properties of general hard non-convex bodies.

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