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A Corresponding-States Principle for the Equation of State of Hard-Convex-Body Fluids

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A theoretically based corresponding-states principle is developed for the equation of state of hard-convex-body fluids. For all the fluids considered, the excess compressibility factor, reduced by means of a parameter which can be determined analytically, lies on a single curve whose analytical expression can be obtained from the equation of state of the hard-sphere fluid.

KEY WORDS: equation of state; corresponding states; hard-convex-body fluids; hard spheres.

1. INTRODUCTION

As is well-known, the corresponding-states principle establishes that, for similar substances, the equation of state can be put in the form

$$p_r = f(T_r, V_r) \tag{1}$$

where subindex r indicates a reduced quantity and f is a common function for all these substances. Generally the reducing quantities are the critical constants, so that $p_r = p/p_c$, $T_r = T/T_c$, and $V_r = V/V_c$. Although a simple analytical expression for the function f has not been derived, experimental evidence has shown that the principle is obeyed by many substances, for which the plots of reduced thermodynamic quantities lie on a single curve.

However, many other substances deviate markedly from this principle. Apart from quantum effects in certain substances and the polarity of the molecules in others, the reason for this deviation is the considerable departure of many molecules from spherical shape. Thus, several attempts have

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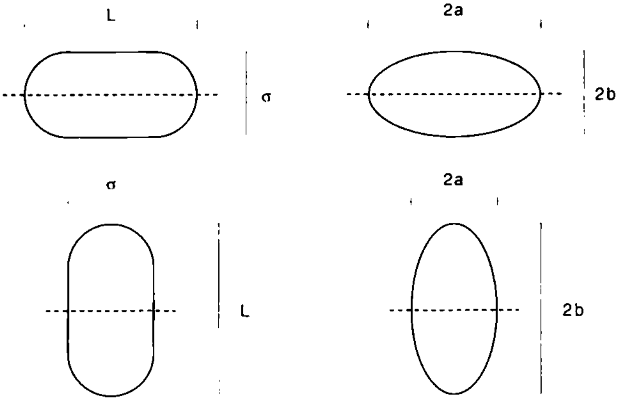

Fig. 1. Several of the geometrical shapes considered. Tridimensional bodies are obtained from the rotation of these planar figures aroud the axis denoted by dashed lines. Left: Prolate (top) and oblate (bottom) spherocylinders. Right: Prolate (top) and oblate (bottom) ellipsoids of revolution. The parameters characterizing the geometry of the molecules are $\gamma = L/\sigma$ for spherocylinders, and $\kappa = a/b$ for ellipsoids of revolution. For hard—Gaussian—overlap molecules the shape is not well defined, but they behave rather similarly to ellipsoids of revolution and are characterized also by the aspect ratio κ.

been made to extend the corresponding-states principle by including one additional parameter that accounts for the effect of the nonsphericity of the molecules. Particularly fruitful has been the acentric factor ω, defined by [1, 2]

$$\omega = -\log p_r - 1.000 \tag{2}$$

where p_r is the reduced vapor pressure at $T_r = 0.7$. Then the extended corresponding-states principle is expressed in the form

$$p_r = f(T_r, V_r, \omega) \tag{3}$$

In this papar, we derive a corresponding-states principle for hard-convex-body (HCB) fluids (see Fig. 1) in terms of a theoretically determined parameter defining the shape of the molecules.

2. THEORETICAL BASIS

The virial theorem for a one-component HCB fluid can be expressed as [3]

$$Z^{\mathrm{HCB}} = 1 + \tfrac{1}{3}\rho(S + 4\pi R^2)\,\sigma^{\mathrm{av}} g^{\mathrm{av}}(0) \tag{4}$$

where $Z^{\mathrm{HCB}} = pV/NkT$ is the compressibility factor; $g^{\mathrm{av}}(0)$ is the pair correlation function at contact, averaged over all orientations of the pair of molecules 1 and 2; and $\sigma^{\mathrm{av}} = \langle \mathbf{r}_{12} \nu \rangle$, with $\mathbf{r}_{12}$ the position vector from a reference point in molecule 1 to another in molecule 2 and ν the unit vector normal to the surface at the contact point. S is the surface of the molecule and R its mean radius of curvature.

For hard spheres of diameter σ, the virial theorem is expressed in the form

$$Z^{\mathrm{HS}} = 1 + \tfrac{2}{3}\pi\rho\sigma^3 g^{\mathrm{HS}}(0) \tag{5}$$

so that, for a given density ρ and provided that spheres have volume $v_{\mathrm{m}} = (\pi/6)\sigma^3$ equal to that of the HCB molecules, we can write

$$\frac{Z^{\mathrm{HCB}} - 1}{Z^{\mathrm{HS}} - 1} = \frac{(S + 4\pi R^2)\,\sigma^{\mathrm{av}} g^{\mathrm{av}}(0)}{12 v_{\mathrm{m}} g^{\mathrm{HS}}(0)} \tag{6}$$

or, in terms of the shape factor $\alpha = RS/3v_{\mathrm{m}}$,

$$\frac{Z^{\mathrm{HCB}} - 1}{Z^{\mathrm{HS}} - 1} = \frac{1}{2}\left(\alpha + \frac{4/3\pi R^3}{v_{\mathrm{m}}}\right)\frac{\sigma^{\mathrm{av}}}{2R}\,\frac{g^{\mathrm{av}}(0)}{g^{\mathrm{HS}}(0)} \tag{7}$$

We can obtain $g^{\mathrm{HS}}(0)$ from the very accurate Carnahan–Starling (CS) equation [4]

$$Z = \frac{pV}{NkT} = \frac{1 + y + y^2 - y^3}{(1 - y)^3} \tag{8}$$

where $y = \rho v_{\mathrm{m}}$ is the packing fraction for molecules of volume v_{m}. Then we have previously shown [5] that the relation

$$\frac{\sigma^{\mathrm{av}}}{2R}\,\frac{g^{\mathrm{av}}(0)}{g^{\mathrm{HS}}(0)} \approx 1 \tag{9}$$

holds for hard-oblate-spherocylinder fluids, for which there are data for both σ^{av} and $g^{\mathrm{av}}(0)$ [6], for values of the packing fraction equal to those of the hard-sphere fluid. Consequently, the ratio

$$\frac{Z^{\mathrm{HCB}} - 1}{Z^{\mathrm{HS}} - 1} \approx \frac{1}{2}\left(\alpha + \frac{4/3\pi R^3}{v_{\mathrm{m}}}\right) \tag{10}$$

must be a constant for a given fluid, since the right-hand side depends only on the shape of the molecule, not on density.

The same paper [5] showed that the constancy of the ratio $(Z^{\mathrm{HCB}}-1)/(Z^{\mathrm{HS}}-1)$, with the simulation data being used for Z^{HCB} and the CS Eq. (8) for Z^{HS}, also holds for other HCB fluids.

On the other hand, for a sphere, $4\pi R^3 = RS$ and $\sigma^{\mathrm{av}} = \sigma = 2R$, and for HCB with shapes not differing very much from sphericity, that is, for values of the shape factor α close to 1, we can approximate $(4/3)\,\pi R^3/v_{\mathrm{m}} \approx RS/3v_{\mathrm{m}} = \alpha$, and thus

$$\frac{1}{2}\left(\alpha + \frac{4/3\pi R^3}{v_{\mathrm{m}}}\right) \approx \alpha \tag{11}$$

Although the introduction of the approximation given by Eq. (9) into Eq. (7) results in a slight overestimation of the right-hand side of Eq. (7), when the approximation given by Eq. (11) is also introduced, it was shown [5] that the two approximations largely cancel. Thus, introducing Eq. (11) into Eq. (10), as a very good approach we can put

$$Z^{\mathrm{HCB}} \approx 1 + \alpha(Z^{\mathrm{HS}} - 1) \tag{12}$$

This equation formally resembles a number of equations of state proposed for molecular fluids [7–10]. Introducing the CS equation, Eq. (8), for Z^{HS}, and rearranging, we obtain

$$\frac{Z^{\mathrm{HCB}} - 1}{\alpha} = \frac{4y - 2y^2}{(1-y)^3} \tag{13}$$

Thus, the excess compressibility factor $Z^{\mathrm{HCB}} - 1$, reduced by the shape factor α, must be a universal function of the packing fraction y. In other words, we have obtained a corresponding-states principle for HCB fluids which can be expressed in the form

$$Z = f(y, \alpha) \tag{14}$$

where parameter α can be determined from geometry by using standard formulae [11].

3. RESULTS AND DISCUSSION

In order to test the reliability of the principle, we have plotted the left-hand side of Eq. (13) as a function of the packing fraction for a variety of HCB fluids. For Z^{HCB} we took the simulation data for prolate [12–15] and oblate [6] spherocylinders, prolate and oblate ellipsoids of revolution [16], and prolate and oblate hard-Gaussian-overlap [17] fluids. The values of α corresponding to the different shapes considered are listed in

Table I. Shape Factors α for the HCB Fluids Considered

	Prolate spherocylinders			
γ	2.	3.	4.	6.
α	1.2	1.5	1.82	2.47
	Oblate spherocylinders			
γ	2.	2.5	3.	3.5
α	1.13	1.23	1.35	1.47
	Prolate ellipsoids of revolution			
κ	1.25	2.		3.
α	1.02	1.18		1.48
	Oblate ellipsoids of revolution			
κ	1/1.25	1/2		1/3
α	1.02	1.18		1.48
	Prolate hard Gaussian overlap			
κ		2.	3/2	
α		1.18	1.06	
	Oblate hard Gaussian overlap			
κ		1/2	2/3	
α		1.18	1.06	

Table I. For hard-Gaussian-overlap fluids, the shapes of the molecules are not well defined. Therefore, we took the shape factors of hard ellipsoids of revolution with equal axis ratios, which have rather similar properties, and molecular volumes from the equality of the second virial coefficients of both types of molecules [5]. Results are shown in Figs. 2–6, where one can see that the corresponding-states principle holds very well for all the cases considered.

As with other corresponding-states principles, the one presented here is, of course, only approximate, since from Eq. (13) it is clear that the principle gives the same functional dependence, on the packing fraction y, of the excess compressibility factor reduced by α, for different molecules having the same value of the shape factor. This occurs, in particular, for prolate and oblate ellipsoids with values of the length-to-breadth ratio $\kappa = x$ and $\kappa = 1/x$, respectively, which have the same values of α. Simulation data [16] show that this is not the case, although the difference is small. The same occurs for hard-Gaussian-overlap fluids.

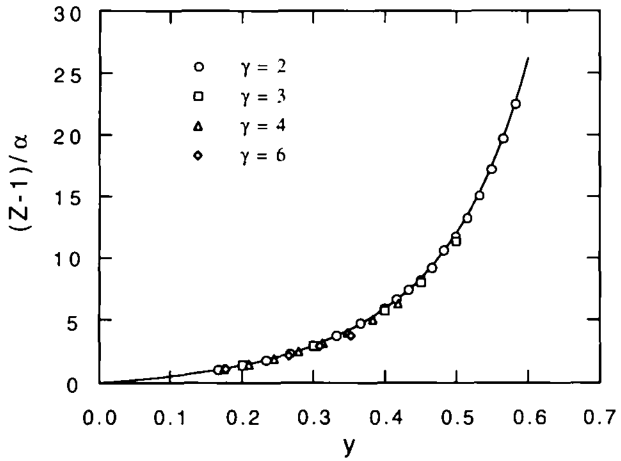

Fig. 2. Reduced excess compressibility factor for hard prolate spherocylinders as a function of the packing fraction y. Points: Simulation data from Refs. 12–15. Solid line: Eq. (13).

In summary, the correlation we have developed here allows the compressibility factor for all convex body fluids, except perhaps for extreme elongations, to be reduced to a single curve with a simple functional form in terms of the packing fraction y. This may be useful for the prediction of the compressibility factors of other HCB fluids. The

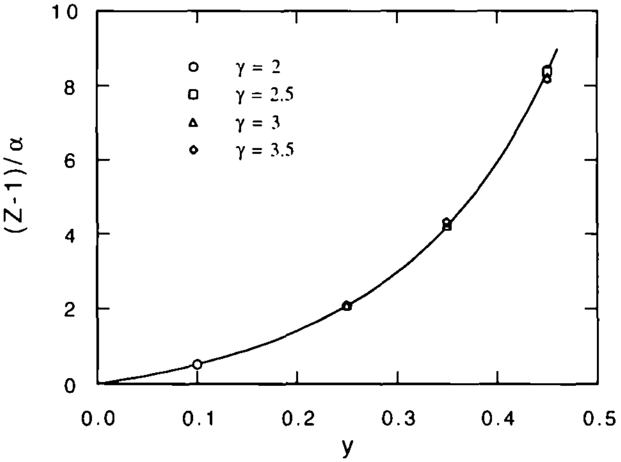

Fig. 3. As in Fig. 2 for hard oblate spherocylinders. Points: Simulation data from Ref. 6. Solid line: Eq. (13).

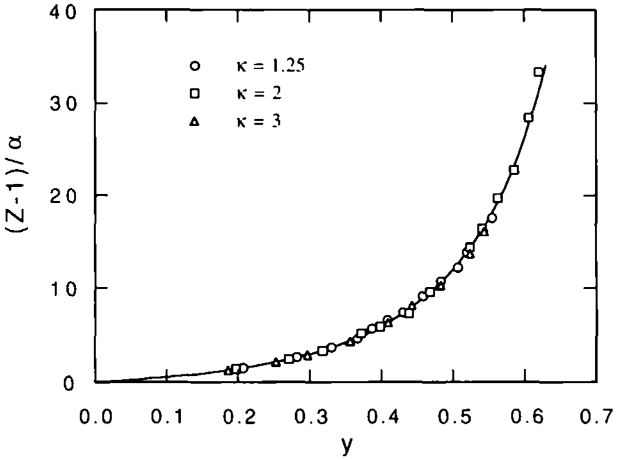

Fig. 4. As in Fig. 2 for hard prolate ellipsoids of revolution. Points: Simulation data from Ref. 16. Solid line: Eq. (13).

correlation might be extended to real fluids with approximately convex molecules, provided that (1) we obtain an effective molecular volume and, correspondingly, an effective shape factor, and (2) we include the effect of attractive forces through, for example, second virial coefficient data [18, 19]

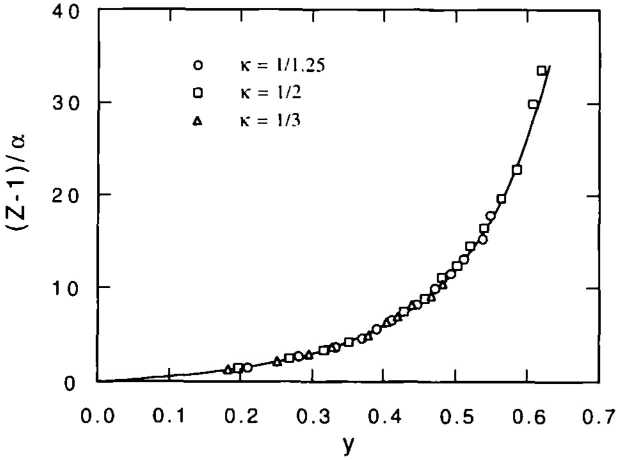

Fig. 5. As in Fig. 2 for hard oblate ellipsoids of revolution. Points: Simulation data from Ref. 16. Solid line: Eq. (13).

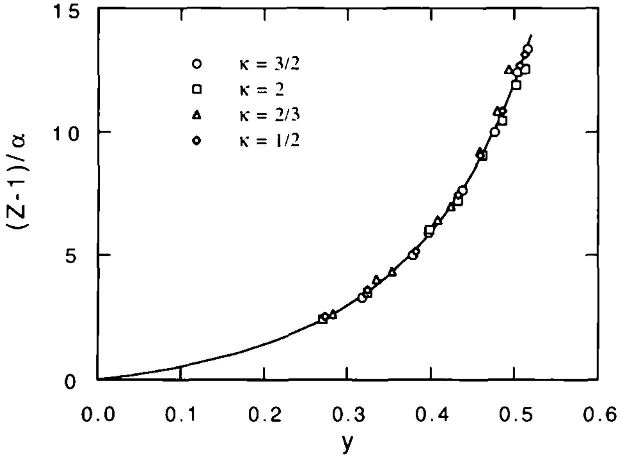

Fig. 6. As in Fig. 2 for prolate and oblate hard-Gaussian-overlap fluids. Points: Simulation data from Ref. 17. Solid line: Eq. (13).

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