A Corresponding-States Principle for the Equation of State of Linear Homonuclear Fused-Hard-Sphere Fluids

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A theoretically based corresponding-states principle previously developed for the equation of state of hard-convex-body fluids is extended to rigid linear homonuclear fused-hard-sphere fluids. Effective volumes and shapes are introduced in order to account for the nonconvexity of the molecules. The excess compressibility factor, reduced by means of a parameter which can be determined analytically, is a common function of the effective packing fraction. The analytical expression for the function can be obtained from the equation of state of the hard-sphere fluid. Existing simulation data for diatomics, triatomics and tetraatomics show excellent agreement with the corresponding-states principle.

KEY WORDS: equation of state; corresponding states; fused-hard-sphere fluids; hard spheres.

1. INTRODUCTION

In its simplest form, the corresponding-states principle (CSP), introduced more than a century ago by van der Waals, establishes that, for all fluids, the equation of state has a common form when expressed in terms of the variables reduced by suitable parameters. Originally the reducing parameters were the critical constants, and these have also been used frequently since then. Thus, the reduced variables are defined as $p_r = p/p_c$, $T_r = T/T_c$, and $V_r = V/V_c$, and the universal equation of state can be expressed in the form

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

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Alternatively, if the molecules are assumed to interact by means of a potential function depending on two parameters such as the Lennard–Jones potential:

$$\varphi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] \tag{2}$$

the potential parameters σ and ε can be used as reducing quantities. The reduced variables are now $p^* = p\sigma^3/\varepsilon$, $T^* = kT/\varepsilon$, and $V^* = V/N\sigma^3$, where k is the Boltzmann constant and N the number of molecules.

Of course, other definitions for the reducing quantities are possible. In any case, the principle is applicable not only to the equation of state, but also to other thermodynamic properties. Experimental data show that, when plotted in terms of the reduced variables, such properties lie on a single curve for many classical substances with nonpolar and nearly spherical molecules. If molecules deviate appreciably from spherical shape, it is necessary to generalize the principle by introducing an additional parameter which depends on the shape of the molecule such as the *acentric factor* ω, defined by [1, 2]

$$\omega = -\log p_r - 1 \tag{3}$$

where p_r is the reduced vapor pressure at $T_r = 0.7$. The CSP is then expressed in the more general form

$$p_r = f(T_r, V_r, \omega) \tag{4}$$

For polar molecules, another parameter, related to the reduced dipole moment $\mu^* = \mu/\sqrt{\varepsilon\sigma^3}$, must also be introduced. Thus, the more complicated the molecules considered, the greater the number of parameters needed to express the CSP.

In order to increase the usefulness of the CSP for the equation of state of fluids, one of the unsolved questions is the derivation of a simple analytical expression for the function f if only for relatively simple molecular fluids. In this sense, it seems worthwhile to start by dealing with hard-body fluids, for which there is a considerable amount of simulation data suitable to test the accuracy of a CSP. Moreover, their well-defined shape and the absence of attractive forces between the molecules mean that they are simpler to deal with, from a theoretical viewpoint, than real fluids.

With this in mind, we extend to fluids consisting of linear homonuclear fused hard spheres a CSP previously developed [3] for hard-convex-body (HCB) fluids.

2. CORRESPONDING-STATES PRINCIPLE FOR THE EQUATION OF STATE OF HARD-BODY FLUIDS

In a previous paper [3], we derived, for the equation of state of hard-convex-body (HCB) fluids, a CSP of the form

$$Z^{HCB} = f(y, \alpha) \tag{5}$$

where $Z = pV/NkT$ is the compressibility factor, $y = pv_m$ is the packing fraction for a fluid of density p consisting of molecules of volume v_m, and $\alpha = RS/3v_m$ is the shape factor of the molecules which have a mean radius of curvature R and surface S.

Starting from the virial theorem for one-component HCB fluids [4], we showed that the excess compressibility factor $Z - 1$ reduced by the shape factor α is very nearly a common function of the packing fraction y. This function is the excess compressibility factor for the hard-sphere fluid, which can be obtained from the very accurate equation of state of Carnahan–Starling [5], so that in the final form, the CSP for HCB fluids is expressed as

$$\frac{Z^{HCB} - 1}{\alpha} = \frac{4y - 2y^2}{(1 - y)^3} \tag{6}$$

Furthermore, it was shown [3] that existing simulation data for HCB fluids are in very good agreement with this form of the CSP.

For fused-hard-sphere (FHS) fluids, an expression of the virial theorem similar to that for HCB fluids has been derived [6]. Thus, we can arrive at Eq. (6) for the CSP for linear homonuclear FHS fluids following the same procedure as that used to derive the CSP for HCB fluids in [3]. However, we must take into account that since FHS are not convex molecules, the volume that a molecule excludes to any point of another molecule is greater than the molecular volume [7], as illustrated in Fig. 1, and this affects the pressure. Thus, we must introduce the "effective molecular volume" v_m^{ef} instead of the molecular volume v_m, the effective packing fraction $y_{ef} = pv_m^{ef}$ instead of the packing fraction y, and consequently, an effective shape factor α_{ef} instead of the shape factor α.

Then, the corresponding-states principle must be generalized in the form

$$\frac{Z - 1}{\alpha_{ef}} = \frac{4y_{ef} - 2y_{ef}^2}{(1 - y_{ef})^3} \tag{7}$$

which, for HCB fluids, with $\alpha = \alpha_{ef}$ and $v_m = v_m^{ef}$, reduces to Eq. (6). In the form of Eq. (7), the CSP is in fact applicable to any hard-body fluid,
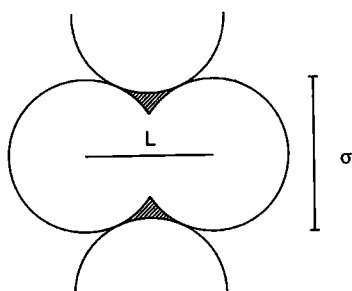
Fig. 1. The shaded area illustrates the difference between effective volume and real volume for homonuclear diatomics.

provided that we are able to determine the corresponding effective values of molecular volume and shape.

The effective molecular volume of an n-sites linear homonuclear FHS body can be expressed [7] in the form

$$v_{\mathrm{m}}^{\mathrm{ef}} = \frac{\pi\sigma^3}{6} \left[1 + (n-1)(3L - L^3/2 - 3h\theta) \right] \tag{8}$$

where $h = (1 - L^2/4)^{1/2}$, $\theta = \sin^{-1}(L/2)$, and L is the distance between the centers of two adjacent spheres of the molecule, all distances being expressed as units of the diameter σ of the spheres.

The effective shape factor can be obtained [7] from

$$\alpha_{\mathrm{ef}} = \frac{(\partial v_{\mathrm{m}}^{\mathrm{ef}}/\partial\sigma)(\partial^2 v_{\mathrm{m}}^{\mathrm{ef}}/\partial\sigma^2)}{v_{\mathrm{m}}^{\mathrm{ef}}} \tag{9}$$

where, from Eq. (8),

$$\frac{\partial v_{\mathrm{m}}^{\mathrm{ef}}}{\partial\sigma} = \frac{\pi\sigma^2}{2} \left[1 + (n-1)\left(\frac{5}{2}L - 3h\theta - \frac{L^2\theta}{4h}\right) \right] \tag{10}$$

and

$$\frac{\partial^2 v_{\mathrm{m}}^{\mathrm{ef}}}{\partial\sigma^2} = \pi\sigma \left[1 + (n-1)\left(2L - 3h\theta - \frac{3L^2\theta}{8h} + \frac{L^3}{16h^2} + \frac{L^4\theta}{32h^3}\right) \right] \tag{11}$$

3. RESULTS AND DISCUSSION

According to Eq. (7), the excess compressibility factor, reduced by the effective shape factor α_{ef}, must be a universal function of the effective

packing fraction y_{ef}. Thus, in order to test the accuracy of the principle, we have plotted the left-hand side of Eq. (7) as a function of the effective packing fraction for several linear homonuclear FHS fluids. For Z we have taken the simulation data [8–12] for diatomics, triatomics, and tetra-atomics with different values of the center-to-center distance L. The values of v_m^{ef}, v_m (from which we can obtain $y_{ef} = y v_m^{ef}/v_m$), and α_{ef} corresponding to the different shapes considered are listed in Table I. Results are shown in Figs. 2–4, from which it is clear that all the fluids considered obey very accurately the proposed corresponding-states principle.

In summary, with the generalization introduced here, the two-parameter CSP derived in Ref. 3 can in principle be applied to any hard-body fluid for which we can obtain the effective volume and shape, except perhaps for very elongated molecules. Of course, the problem of determining the parameters from geometrical considerations becomes increasingly difficult as the shape of the molecule becomes more complicated. Thus, an expression equivalent to Eq. (8) has not been derived yet, for example, for unequal fused hard spheres, although we are currently working in this direction.

Table I. Molecular Volumes, Effective Molecular Volumes, and Effective Shape Factors for the FHS Fluids Considered[a]

			Homonuclear diatomics		
L	0.2	0.4	0.6	0.8	1.0
v_m	0.6786	0.8210	0.9383	1.0179	1.0472
v_m^{ef}	0.6791	0.8253	0.9530	1.0538	1.1203
α_{ef}	1.0177	1.0660	1.1434	1.2549	1.4140
			Linear homonuclear triatomics		
L	0.4559	0.8	1.0		
v_m	1.1901	1.5122	1.5708		
v_m^{ef}	1.2028	1.5839	1.7170		
α_{ef}	1.2119	1.5529	1.8546		
			Linear homonuclear tetraatomics		
L	1.0				
v_m	2.0944				
v_m^{ef}	2.3138				
α_{ef}	2.3013				

[a] All volumes are expressed in units of σ^3, where σ is the diameter of a sphere. L is in units of σ.
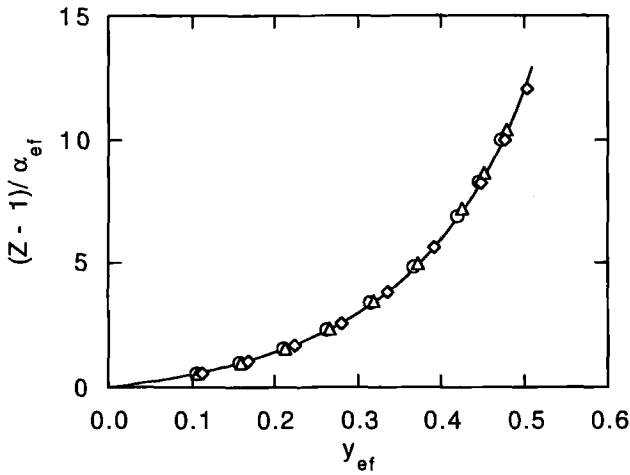
Fig. 2. Reduced excess compressibility factor for hard homonuclear diatomics ($n = 2$) as a function of the effective packing fraction y_{ef}. Points: simulation data from Ref. 8 for $L = 0.2$ (circles), $L = 0.4$ (triangles), and $L = 1.0$ (diamonds). Solid line: Eq. (8).
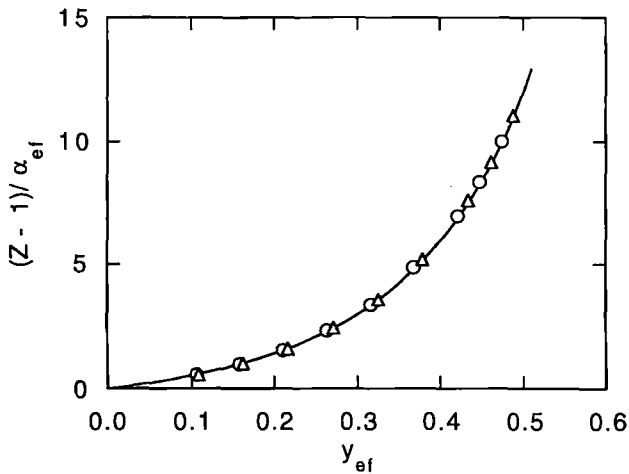

Fig. 3. As in Fig. 2 for center-to-center distances of $L = 0.4$ (circles) and $L = 0.8$ (triangles).
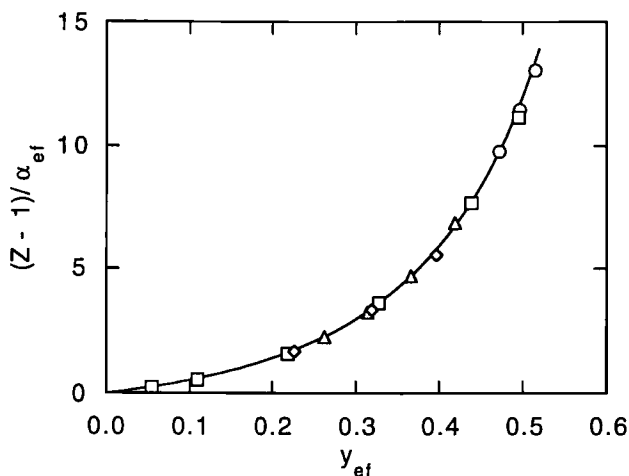
Fig. 4. As in Fig. 2 for hard linear homonuclear triatomics ($n = 3$) and tetraatomics ($n = 4$). Points: simulation data for $n = 3$, $L = 0.4559$ (circles), from Ref. 9; $n = 3$, $L = 0.8$ (triangles), from Ref. 10; $n = 3$, $L = 1.0$ (squares), from Ref. 11; and $n = 4$, $L = 1.0$ (diamonds), from Ref. 12.

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