Corresponding-states principle for two-dimensional hard models of molecular fluids

M. J. Maeso and J. R. Solana

Departamento de Física Aplicada, Universidad de Cantabria, 39005 Santander, Spain

This paper develops a theoretically based corresponding-states principle for the equation of state of athermal two-dimensional fluids consisting of rigid molecules. It is shown that the excess compressibility factor, reduced by means of a parameter which can be determined from the geometry of the molecules, is very nearly a common function of the excess compressibility factor of the hard-disk fluid. Existing simulation data show very good agreement with the corresponding-states principle, except for some molecules with very large bond length. [S1063-651X(97)04407-3]

PACS number(s): 61.20.Gy, 64.30.+t

I. INTRODUCTION

It is well known that the principle of corresponding states (CSP), as was introduced more than a century ago by van der Waals, establishes that the equation of state of all fluids has a common form when expressed in terms of the reduced adimensional variables p_r, T_r, and V_r. That is, the equation of state can be expressed in the form

$$f(p_r, T_r, V_r) = 0, \qquad (1)$$

f being a common function for all fluids. In the original formulation, the reducing quantities were the critical parameters p_c, T_c, and V_c of each fluid, so that $p_r = p/p_c$, $T_r = T/T_c$, and $V_r = V/V_c$, but more generally the reducing quantities can be taken as $(\epsilon/k)/\sigma^3$, ϵ/k, and σ^3, respectively, where ϵ is a characteristic energy parameter, σ is a characteristic distance parameter, and k is the Boltzmann constant.

Experimental evidence shows that many substances obey the corresponding-states principle not only for the equation of state, but also for other thermodynamic properties. However, there are many other substances which depart more or less from this principle. Sometimes this departure is due to quantum effects and more often to the polarity of the molecules, but in most cases the reason is the nonsphericity of the molecules.

In order to extend the applicability of the CSP to nonspherical nonpolar molecular fluids it is necessary to introduce an additional parameter which depends on the molecular shape, as stated by Kamerling Onnes in his *principle of mechanical equivalence*. For chain molecules this can be done [1,2] by introducing a parameter c accounting for the $3c$ external degrees of freedom which are volume dependent. For more complicated molecules, such as those having polarity, new parameters are needed in order to express a CSP.

Alternatively, the CSP can be extended to molecular fluids by introducing the *acentric factor* ω defined as [3,4]

$$\omega = -\log_{10} p_r - 1, \qquad (2)$$

where p_r is now the reduced pressure at $T_r = 0.7$. When this empirical parameter is introduced, the CSP becomes

$$f(p_r, T_r, V_r, \omega) = 0. \qquad (3)$$

The acentric factor depends on the shape of nonspherical molecules and the dipole moment of polar molecules so that, in principle, it can deal with complicated molecular fluids without needing additional parameters.

Although the acentric factor has been widely used, its empirical character prevents a clear and direct relation to the shapes of the molecules. Since the different contributions (molecular shape, polarity, etc.) to the departure of a fluid from the CSP behavior are not explicit in the acentric factor, it is difficult to introduce improvements to the performance of this formulation of the CSP. Function f itself is often of empirical character, the derivation of a simple analytical expression for f from theoretical arguments remaining as an open question.

In order to attempt to derive a theoretically based CSP for fluids, it is desirable to start by dealing with hard models of nonpolar molecular fluids, so that complications arising from the intermolecular forces vanish. This makes the search for an analytical expression for f easier. Moreover, in these fluids the shape of the molecules is well defined, which simplifies the task of relating the shape-dependent parameter in the CSP to molecular shape. Additionally, for this kind of fluids there exists a considerable amount of simulation data allowing the performance of the CSP to be tested exhaustively.

Thus, in several previous papers [5,6,] we developed a theoretically based CSP for three-dimensional hard models of hard body (HB) molecular fluids expressed in the form

$$\frac{Z^{\mathrm{HB}} - 1}{\alpha_{\mathrm{ef}}} = f(y_{\mathrm{ef}}), \qquad (4)$$

where $Z = pV/NkT$ is the compressibility factor, $y_{\mathrm{ef}} = \rho v_m^{\mathrm{ef}}$ is the effective packing fraction for a fluid at number density ρ consisting of molecules having an effective volume v_m^{ef}, α_{ef} is the corresponding effective nonsphericity parameter or shape factor, and $f(y_{\mathrm{ef}})$ is the excess compressibility factor of the hard-sphere fluid.

The effective volume accounts for the fact that for nonconvex molecules the volume that the molecule excludes to any point of another molecule is greater than the molecular volume v_m. Obviously, for convex molecules $v_m^{\mathrm{ef}} = v_m$, $y_{\mathrm{ef}} = y$, and $\alpha_{\mathrm{ef}} = \alpha$, where

$$\alpha = \frac{RS}{3v_m} \qquad (5)$$

is the nonsphericity parameter for convex molecules with volume v_m, and surface S, R being the $(1/4\pi)$ multiple of the mean curvature integral. All these quantities can be determined from the geometry of the molecules [7]. By contrast, for nonconvex rigid linear molecules consisting of fused hard spheres of diameter σ, the radius of the curvature is not well defined, so we used an alternative definition [8] in the form

$$\alpha_{\text{ef}} = \frac{1}{3\pi} \frac{(\partial v_m^{\text{ef}}/\partial \sigma)(\partial^2 v_m^{\text{ef}}/\partial \sigma^2)}{v_m^{\text{ef}}}, \qquad (6)$$

which can be obtained from the analytical expression derived [8] for v_m^{ef}. The existing simulation data for a great variety of hard molecular fluids showed [5,6] very good agreement with the CSP expressed in form (4), together with Eqs. (5) or (6).

In the present paper we will derive a two-dimensional counterpart of the CSP previously developed for three-dimensional hard-body fluids. The interest in the study of two-dimensional fluids is due to the fact that they constitute, at least as a first approximation, simple models of molecules adsorbed on surfaces as well as of thin films. From a theoretical viewpoint, apart from its intrinsic interest, the derivation of a CSP of form (4) for two-dimensional fluids is interesting because it is easier to determine the geometrical parameters involved for the case of complex molecules than in their three-dimensional counterparts.

II. CORRESPONDING-STATES PRINCIPLE FOR TWO-DIMENSIONAL HARD-BODY FLUIDS

The expression of the compressibility factor for a two-dimensional hard convex body (HCB) fluid which occupies a surface A at number density $\rho = N/A$, can be expressed in the form

$$Z^{\text{HCB}} = \frac{pA}{NkT} = 1 + \tfrac{1}{4}\rho S_{1+2} \sigma^{\text{av}} g^{\text{av}}(0), \qquad (7)$$

where S_{1+2} is the perimeter of the body formed by the center of molecule 2 moving around molecule 1, while both molecules remain in contact; $g^{\text{av}}(0)$ is the contact value of the pair correlation function, averaged over all possible orientations of the two molecules; and σ^{av} is the mean distance between the centers of the two molecules being in contact projected onto the direction normal to the perimeter at the contact point. Introducing the mean radius of the molecule $R = S/2\pi$, and taking into account the fact that for equal molecules $S_{1+2} = 2S = S + 2\pi R$, we obtain

$$Z^{\text{HCB}} = 1 + \tfrac{1}{4}\rho(S + 2\pi R)\sigma^{\text{av}} g^{\text{av}}(0). \qquad (8)$$

For a hard-disk fluid with diameter σ^{HD}, we have $\sigma^{\text{av}} = \sigma^{\text{HD}}$, $g^{\text{av}}(0) = g^{\text{HD}}(0)$, and $S = \pi\sigma^{\text{HD}}$, so that, for the same density, the preceding expression reduces to

$$Z^{\text{HD}} = 1 + \tfrac{1}{2}\pi\rho(\sigma^{\text{HD}})^2 g^{\text{HD}}(0), \qquad (9)$$

and thus

$$\frac{Z^{\text{HCB}} - 1}{Z^{\text{HD}} - 1} = \frac{(S + 2\pi R)\sigma^{\text{av}} g^{\text{av}}(0)}{2\pi(\sigma^{\text{HD}})^2 g^{\text{HD}}(0)}. \qquad (10)$$

Then, introducing the shape factor

$$\alpha = S^2/2\pi A_m, \qquad (11)$$

where A_m is the molecular area, and considering disks with area $A_m = \tfrac{1}{4}\pi(\sigma^{\text{HD}})^2$ equal to that of the HCB molecule, we have

$$\frac{Z^{\text{HCB}} - 1}{Z^{\text{HD}} - 1} = \frac{1}{2}\left(\frac{\alpha}{2} + \frac{\pi R^2}{A_m}\right)\frac{\sigma^{\text{HD}}}{2R}\frac{\sigma^{\text{av}} g^{\text{av}}(0)}{\sigma^{\text{HD}} g^{\text{HD}}(0)}. \qquad (12)$$

In a previous work [9], we showed that

$$\frac{\sigma^{\text{av}} g^{\text{av}}(0)}{\sigma^{\text{HD}} g^{\text{HD}}(0)} \simeq 1, \qquad (13)$$

and

$$\frac{1}{2}\left(\frac{\alpha}{2} + \frac{\pi R^2}{A_m}\right)\frac{\sigma^{\text{HD}}}{2R} \simeq \frac{1}{2}\left(1 + \frac{\alpha}{2}\right). \qquad (14)$$

Moreover, it was shown that the small error introduced by approximation (13) was largely canceled out by the small error introduced by approximation (14), which acts in the opposite direction. With these approximations expression (12) becomes

$$\frac{Z^{\text{HCB}} - 1}{Z^{\text{HD}} - 1} \simeq \frac{1}{2}\left(1 + \frac{\alpha}{2}\right), \qquad (15)$$

which allows us to obtain the equation of state of a two-dimensional fluid consisting of hard convex molecules from the compressibility factor of a fluid of hard disks having the same surface area as the convex molecule, and the nonsphericity parameter of the latter.

For the equation of state of the hard-disk fluid we can use the Henderson equation [10]

$$Z^{\text{HD}} = \frac{1 + y^2/8}{(1-y)^2}, \qquad (16)$$

where $y = \rho A_m$ is the packing fraction.

The equation of state (15) can easily be extended to two-dimensional fluids consisting of rigid fused hard-disk molecules by simply replacing the packing fraction y by the effective packing fraction $y_{\text{ef}} = \rho A_m^{\text{ef}}$, where A_m^{ef} is the effective molecular area (see Fig. 1), defined as the area from which any point of a molecule is excluded due to the presence of another molecule. Correspondingly, the nonsphericity parameter α must be replaced by the effective nonsphericity parameter α_{ef}. This can be obtained from the two-dimensional equivalent of Eq. (6), namely,

$$\alpha_{\text{ef}} = \frac{2}{\pi} \frac{(\partial A_m^{\text{ef}}/\partial \sigma)^2}{A_m^{\text{ef}}}, \qquad (17)$$
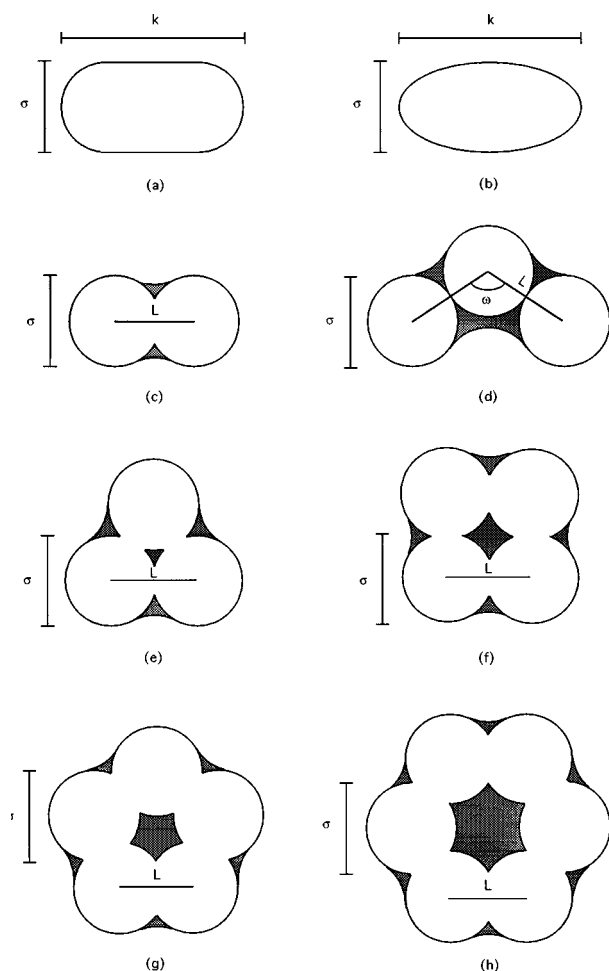
FIG. 1. Molecular models considered in this paper. For nonconvex molecules, the shaded area represents the difference between effective and real areas.

where σ is the diameter of one of the disks of the molecule. This expression gives the correct value $\alpha_{ef} = \alpha = 2$ for hard disks. Then Eq. (15) transforms into

$$\frac{Z^{FHD}(y_{ef}) - 1}{Z^{HD}(y_{ef}) - 1} = \frac{1}{2}\left(1 + \frac{\alpha_{ef}}{2}\right), \qquad (18)$$

which in fact applies to both convex and nonconvex molecular fluids provided that we take into account that for the former $y_{ef} = y$ and $\alpha_{ef} = \alpha$. Then, we can write, for two-dimensional hard body (HB) fluids,

$$\frac{Z^{HB}(y_{ef}) - 1}{\frac{1}{2}(1 + \alpha_{ef}/2)} = f(y_{ef}), \qquad (19)$$

where $f(y_{ef}) = Z^{HD}(y_{ef}) - 1$ is a universal function of y_{ef}, so that Eq. (19) is the mathematical expression of the two-dimensional corresponding-states principle.

III. DETERMINATION OF THE PARAMETERS

The molecular models considered are those of Fig. 1, where shaded areas represent the difference between effective and real molecular areas for nonconvex molecules. In

TABLE I. Parameters involved in the CSP expression (19) for the molecules considered. Lengths are in units of σ, and areas in units of σ^2.

|	A_m	A_m^{ef}	α_{ef}
Model (a)			
$k = 3$			2.9142
Model (b)			
$k = 2$			2.3805
$k = 4$			3.7813
$k = 6$			5.4009
Model (c)			
$L = 0.3$	1.0808	1.0820	2.0668
$L = 0.5$	1.2637	1.2695	2.1846
$L = 0.7$	1.4230	1.4411	2.3737
$L = 0.924$	1.5513	1.6049	2.7077
$L = 1$	1.5708	1.6514	2.8636
Model (d)			
$\omega = 60°$	2.3562	2.5174	2.7587
$\omega = 75°$	2.3562	2.6173	2.9675
$\omega = 90°$	2.3562	2.6514	3.3325
$\omega = 105°$	2.3562	2.6173	3.9479
$\omega = 120°$	2.3562	2.5174	5.0248
$\omega = 180°$	2.3562	2.5174	3.8071
Model (e)			
$L = 0.5$	1.6111	1.6198	2.1619
$L = 1$	2.3562	2.5174	2.7586
$L = \sqrt{2}$	2.3562	3.1514	4.2204
Model (f)			
$L = 0.5$	1.9920	2.0036	2.1538
$L = 1$	3.1416	3.5174	2.7250
$L = \sqrt{2}$	3.1416	4.7854	4.1285
Model (g)			
$L = 0.5$	2.4113	2.4258	2.1493
$L = 1$	3.9270	4.6709	2.7081
$L = \sqrt{2}$	3.9270	6.7264	4.0864
Model (h)			
$L = 0.5$	2.8698	2.8873	2.1463
$L = 1$	4.7124	5.9816	2.6980
$L = \sqrt{2}$	4.7124	8.9816	4.0627
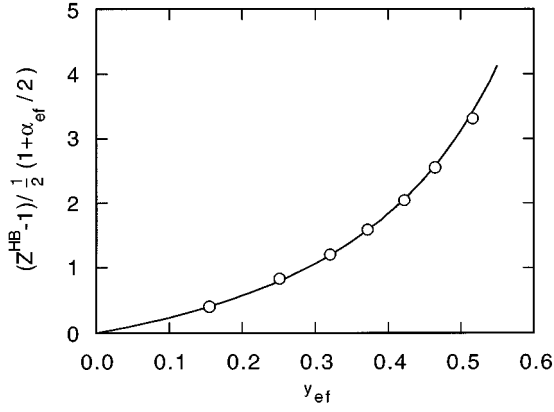
FIG. 2. Reduced excess compressibility factor for hard dis-corectangles (model a) with a length to breadth ratio $k=3$ as a function of the effective packing fraction y_{ef} or, equivalently, the packing fraction y. Points: simulation data from Ref. [11]. Continuous line: $f(y_{\mathrm{ef}})=Z^{\mathrm{HD}}-1$, with Z^{HD} given by Eq. (16).

order to apply the CSP, we must determine the parameters that appear in Eq. (19). For nonconvex molecules we need A_m, A_m^{ef}, and α_{ef}, since $y_{\mathrm{ef}}=\rho A_m^{\mathrm{ef}}=y A_m^{\mathrm{ef}}/A_m$. For convex molecules we only need $\alpha_{\mathrm{ef}}=\alpha$, since $A_m^{\mathrm{ef}}=A_m$. From geometrical considerations, one obtains the following expressions for these parameters:

Model (a)

$$\alpha=\frac{[2(k-1)+\pi]^2}{2\pi[(k-1)+\pi/4]}, \tag{20}$$

where k is the length to breadth ratio, that is, the length in units of σ.

Model (b)

$$\alpha=\frac{8k}{\pi^2}[E(1-1/k^2)]^2, \tag{21}$$

where k is the semiaxis ratio, and

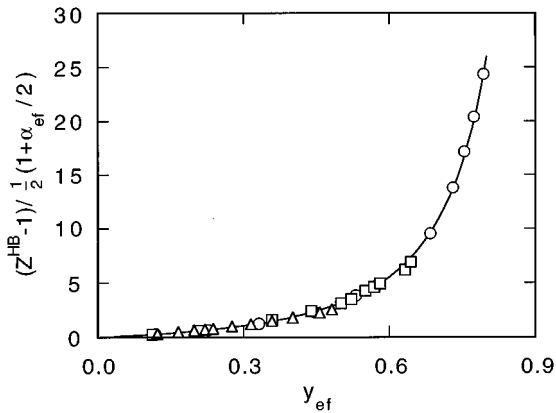FIG. 3. As in Fig. 2 for hard ellipses (model b), with a maximum length to maximum breadth ratio k. Points: simulation data from Ref. [12] for $k=2$ (circles), $k=4$ (squares), and $k=6$ (triangles).
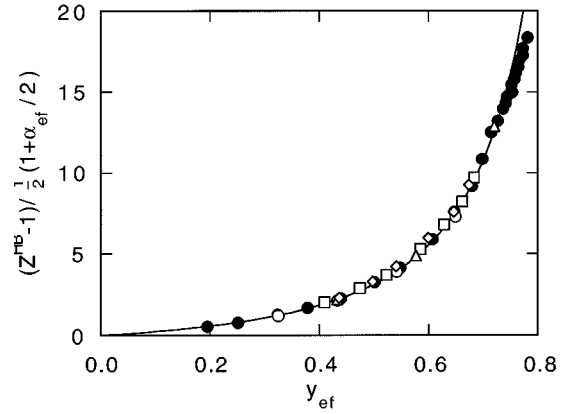
FIG. 4. Reduced excess compressibility factor for hard dumbbells (model c) with bond length L in units of σ, the diameter of one of the disks, as a function of the effective packing fraction y_{ef}. Points: simulation data from Refs. [13–15] for $L=0.3$ (circles), $L=0.5$ (squares), $L=0.7$ (triangles), $L=0.924$ (black circles), and $L=1$ (diamonds). Continuous line as in Fig. 2.

$$E(x)=\int_0^{\pi/2}dt(1-x\sin^2 t)^{1/2}, \tag{22}$$

is the complete elliptic function of the second kind.

Model (c)

For values of the ratio of the center-to-center distance $L\leqslant\sqrt{3}$, in units of the diameter σ of a disk, we have

$$A_m=\frac{\sigma^2}{2}[\arcsin L+L(1-L^2)^{1/2}+\pi/2], \tag{23}$$

$$A_m^{\mathrm{ef}}=\frac{\sigma^2}{2}[L(4-L^2)^{1/2}+\pi/2], \tag{24}$$

$$\alpha_{\mathrm{ef}}=\frac{2}{\pi}\frac{[L(1-L^2/4)^{1/2}+\pi/2]^2}{A_m^{\mathrm{ef}}}. \tag{25}$$
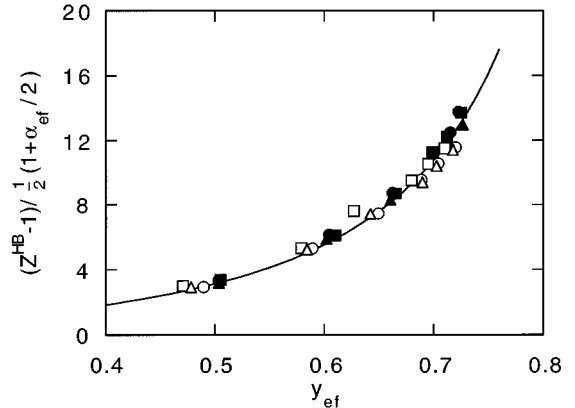
Model (d)

FIG. 5. As in Fig. 4 for nonlinear triatomics (model d) with bond length $L=1$ in units of σ. Points: simulation data from Ref. [14] for $\omega=60°$ (black circles), $\omega=75°$ (black squares), $\omega=90°$ (black triangles), $\omega=105°$ (open circles), $\omega=120°$ (open squares), and $\omega=180°$ (open triangles). Continuous line as in Fig. 2.
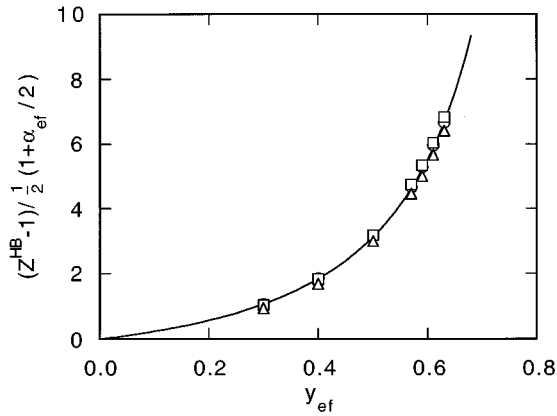
FIG. 6. As in Fig. 4 for cyclic trimers [model (e)]. Points: simulation data from Ref. [16] for $L=0.5$ (circles), $L=1$ (squares), and $L=\sqrt{2}$ (triangles). Continuous line as in Fig. 2.

For $L=1$ we have

$$A_m = 3\pi\sigma^2/4. \tag{26}$$

On the other hand, for $60° \leq \omega < 120°$,

$$A_m^{\mathrm{ef}} = \sigma^2\left(\frac{\pi}{4} + \sqrt{\frac{3}{2}} + \sin\omega\right), \tag{27}$$

$$\alpha_{\mathrm{ef}} = \frac{2}{\pi}\frac{\left(\frac{2}{\sqrt{3}} + \frac{\pi}{2} + \tan\frac{\omega}{2}\right)^2}{A_m^{\mathrm{ef}}}, \tag{28}$$

and, for $\omega \geq 120°$,

$$A_m^{\mathrm{ef}} = \sigma^2\left(\frac{\pi}{4} + \sqrt{3}\right), \tag{29}$$

$$\alpha_{\mathrm{ef}} = \frac{2}{\pi}\frac{\left(\frac{4}{\sqrt{3}} + \frac{\pi}{2}\right)^2}{A_m^{\mathrm{ef}}}. \tag{30}$$

Models (e)–(h)

For cyclic molecules consisting of n hard disks with $L \leq \sqrt{3}$, we have
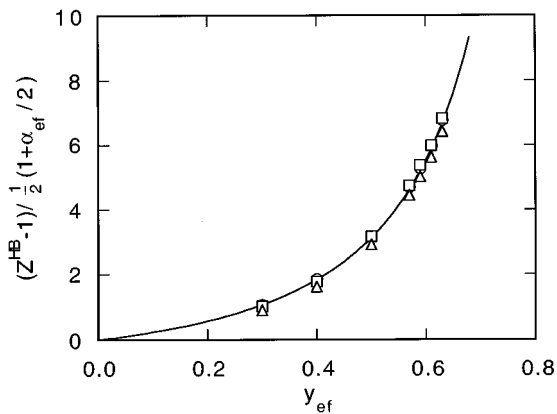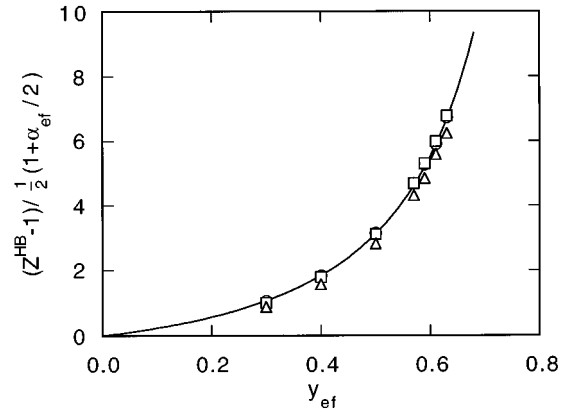
FIG. 8. As in Fig. 6 for cyclic pentamers [model (g)].

$$A_m^{\mathrm{ef}} = n\frac{\sigma^2}{4}\left[L^2\cot\left(\frac{\pi}{n}\right) + L(4-L^2)^{1/2} + \frac{\pi}{n}\right], \tag{31}$$

$$\alpha_{\mathrm{ef}} = \frac{2}{\pi}\frac{\left[\dfrac{nL}{(4-L^2)^{1/2} + \dfrac{\pi}{2}}\right]^2}{A_m^{\mathrm{ef}}}. \tag{32}$$

On the other hand, for $L \leq \sin(\pi/n)$,

$$A_m = n\frac{\sigma^2}{4}\left[\arcsin L + L(1-L^2)^{1/2} + L^2\cot\left(\frac{\pi}{n}\right) + \frac{\pi}{n}\right], \tag{33}$$

for $\sin(\pi/n) \leq L \leq 1$,

$$A_m = n\frac{\sigma^2}{2}[\arcsin L + L(1-L^2)^{1/2}], \tag{34}$$

and, for $L \geq 1$,

$$A_m = n\pi\sigma^2/4. \tag{35}$$

Values of the parameters for the types of molecules considered in this paper are listed in Table I.

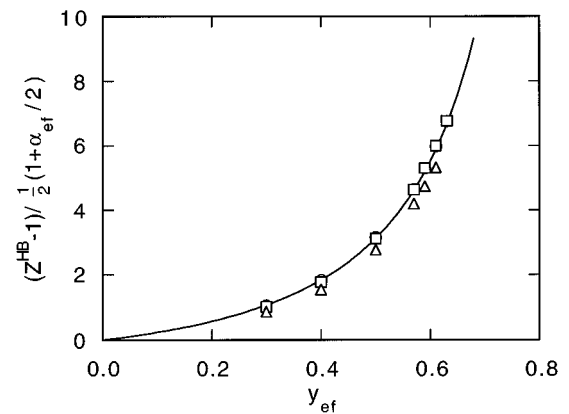FIG. 7. As in Fig. 6 for cyclic tetramers [model (f)].

FIG. 9. As in Fig. 6 for cyclic hexamers [model (h)].

IV. RESULTS AND DISCUSSION

Figures 2–9 compare the simulation data [11–16] with the results obtained with the CSP expression (19), using Eq. (16) for the equation of state of the two-dimensional hard-disk fluid, together with the parameters listed in Table I. As can be seen, agreement is very good except for 5-mer and 6-mer cyclic molecules with $L = \sqrt{2}$. However, it should be noted that molecular models with values of L considerably greater than the diameter of one of the monomers, that is $L \geqslant 1$, are somewhat unrealistic.

Of course the corresponding-states principle developed here is only approximate, as occurs with other formulations of this principle. In particular, the low-density limit of Eq. (19) requires that

$$\frac{B_2^{\text{HB}}(y_{\text{ef}})}{\frac{1}{2}(1 + \alpha_{\text{ef}}/2)} = B_2^{\text{HS}}(y_{\text{ef}}), \qquad (36)$$

where $B_2^{\text{HB}}(y_{\text{ef}})$ is the second virial coefficient in the expansion of the compressibility factor in the power series of y_{ef}, and $B_2^{\text{HS}}(y_{\text{ef}}) = 2$ the second virial coefficient of the hard-disk fluid. This is certainly true for convex molecules, since for them the second virial coefficient is given exactly by $B_2^{\text{HCB}}(y_{\text{ef}}) = 1 + \alpha_{\text{ef}}/2$. However, for fused hard-disk molecules the ratio of the left-hand side of Eq. (36) increasingly underestimates the value of 2, corresponding to the right-hand side, with increasing bond length. This partial failure of our formulation of the CSP at low densities is not surprising, since generally the extensions of the CSP to nonspherical molecules applies only to dense gases and liquids.

In summary, we have formulated a simple corresponding-states principle for two-dimensional molecular fluids consisting of rigid molecules which depends on two parameters, the effective molecular area A_m^{ef} and the effective nonsphericity parameter or shape factor α_{ef}, which can be determined from the geometry of the molecules. The principle states that the reduced excess compressibility factor is a single function of the effective packing fraction y_{ef}. Comparison with simulation data for a great variety of two-dimensional fluids shows that the performance of the CSP is very good, for moderate to high densities except for some fluids which have molecules formed by fused hard-disks with extreme bonding distances. The principle could be extended to fluids with intermolecular potentials which include attractive interactions by introducing a suitable energy parameter.

[1] I. Prigogine, N. Trappeniers, and V. Mathot, J. Chem. Phys. **21**, 559 (1953).

[2] I. Prigogine, *Molecular Theory of Solutions* (North-Holland, Amsterdam, 1957).

[3] K. S. Pitzer, J. Am. Chem. Soc. **77**, 3427 (1955).

[4] K. S. Pitzer, D. Z. Lippmann, R. F. Curl, C. M. Huggins, and D. E. Petersen, J. Am. Chem. Soc. **77**, 3433 (1955).

[5] M. J. Maeso and J. R. Solana, Int. J. Thermophys. **15**, 933 (1994).

[6] M. J. Maeso and J. R. Solana, Int. J. Thermophys. **16**, 1413 (1995).

[7] T. Boublík and I. Nezbeda, Collect. Czech. Chem. Commun. **51**, 2301 (1986).

[8] J. L. F. Abascal and S. Lago, J. Mol. Liq. **30**, 133 (1985).

[9] M. J. Maeso and J. R. Solana, J. Chem. Phys. **102**, 8562 (1995).

[10] D. Henderson, Mol. Phys. **30**, 971 (1975).

[11] I. Nezbeda, T. Boublík, and O. Trnka, Czech. J. Phys. B **25**, 119 (1975).

[12] J. A. Cuesta and D. Frenkel, Phys. Rev. A **42**, 2126 (1990).

[13] J. Talbot and D. J. Tildesley, J. Chem. Phys. **83**, 6419 (1985).

[14] C. W. Goulding and M. Rigby, Mol. Phys. **75**, 623 (1992).

[15] K. W. Wojciechowski, Phys. Rev. B **46**, 26 (1992).

[16] A. C. Branka and K. W. Wojciechowski, Chem. Phys. **181**, 29 (1994).