PHYSICAL REVIEW A VOLUME 42, NUMBER 8 15 OCTOBER 1990

Analytical equation of state for molecular fluids: Kihara model for rodlike molecules

Yuhua Song and E. A. Mason
Brown University, Providence, Rhode Island 02912

(Received 1 June 1990)

We present an analytical equation of state for convex-molecule fluids in any number of dimensions, based on statistical-mechanical perturbation theory for hard convex bodies. The second virial coefficient is calculated exactly. Two temperature-dependent parameters in addition to the second virial coefficient arise, an effective molecular volume (or van der Waals covolume) and a scaling factor for the average contact pair distribution function of hard convex bodies. The equation is tested against computer simulations and perturbation calculations for the model of rodlike molecules interacting via a Kihara (12,6) potential. This model allows the two temperature-dependent parameters to be calculated from the intermolecular potential by simple quadrature, without further approximations for averaging over molecular orientations. The agreement is quite good.

I. INTRODUCTION

The calculation of the equilibrium properties of molecular fluids from intermolecular potentials is a basic theoretical problem of long-standing interest. The most successful statistical-mechanical theories of molecular fluids at present are perturbation theories based on reference systems consisting of hard bodies,[1,2] analogous to the perturbation theories of simple fluids based on hard spheres. Two main different methods are used in these perturbation theories, depending on the type of pair potentials used to characterize the molecular interactions: the multicenter potential (interaction-site model),[3] or the Kihara core potential.[4] The respective perturbation theories employ corresponding fused hard spheres or hard convex bodies as reference systems. Their main difference follows from the use of angle-dependent molecular distribution functions in the former and average distribution functions in the latter when evaluating the perturbation terms. Unfortunately, both types of theories require considerable numerical computation and no simple analytical equation of state for molecular fluids is forthcoming.

We present here a simple analytical equation of state for molecular fluids, using as a reference system a fluid of hard convex bodies, for which an analytical equation of state has recently been developed.[5] Although based on statistical-mechanical perturbation theory, our result differs from previous theories in two important features: the treatment of the second virial coefficient, and the determination of an effective hard-body volume. The second virial coefficient is calculated exactly rather than by perturbation theory, so that an accurate description of the fluid at low densities is automatically obtained. The effective hard-body volume is calculated according to a simple algorithm giving it as a function of temperature alone, rather than as a function of both temperature and density. It is largely these features that lead to a simple analytical result for the equation of state.

We compare the present equation of state with results for a system of rodlike molecules interacting according to a Kihara (12,6) core model.[6] This model tests the essentials of the theory, with no adjustable parameters as would be needed for a real fluid. The model also avoids having to make any additional approximations in separating the angular and radial parts of perturbation integrals, since the pair potential depends only on the shortest surface-to-surface distance of the molecular cores regardless of their relative orientation. Such additional approximations are needed in applying the present theory to real molecular fluids. We compare both with results from computer simulations[7] and from a previous perturbation theory.[4]

It is easy to keep the dimensionality d of the problem arbitrary, at least initially, because the equation of state for the hard-body reference system has been given for arbitrary d.[5] However, comparisons are possible at present only for $d=3$.

II. STATISTICAL-MECHANICAL DERIVATION

The present derivation is similar to that given earlier for fluids of spherical particles,[8] but molecular fluids are more difficult to treat because both the pair potential and the pair distribution function depend on molecular orientations as well as on positions. We begin with the pressure equation under the assumption that the intermolecular potentials are pairwise additive,[2]

$$\frac{p}{\rho kT}=1-\frac{\rho}{2dkT}\int\int\left[r\frac{\partial u(\mathbf{r},\omega)}{\partial r}\right]g(\mathbf{r},\omega)d\mathbf{r}\,d\omega\ , \qquad (1)$$

where p is the pressure, $\rho=N/V$ is the number density, kT has the usual meaning, d is the dimensionality, $\mathbf{r}$ and ω denote the vectors of relative position and orientation coordinates, respectively (ω is normalized so that $\int d\omega=1$), $u(\mathbf{r},\omega)$ is the intermolecular pair potential, and $g(\mathbf{r},\omega)$ is the molecular pair distribution function.

We first separate out the exact second virial coefficient B_2, and then rewrite the remaining integral in terms of the cavity distribution function $y(\mathbf{r},\omega)$,

$$\frac{p}{\rho kT}=1+B_2\rho+\rho I \ , \tag{2}$$

where

$$B_2(T)=-\frac{1}{2dkT}\int\int\left[r\frac{\partial u(\mathbf{r},\omega)}{\partial r}\right]e^{-u(\mathbf{r},\omega)/kT}d\mathbf{r}\,d\omega \ , \tag{3}$$

$$I(T)=\frac{1}{2d}\int\int f(\mathbf{r},\omega)[y(\mathbf{r},\omega)-1]r\,d\mathbf{r}\,d\omega \ , \tag{4}$$

$$f(\mathbf{r},\omega)\equiv-\frac{1}{kT}\left[\frac{\partial u(\mathbf{r},\omega)}{\partial r}\right]e^{-u(\mathbf{r},\omega)/kT} , \tag{5}$$

$$y(\mathbf{r},\omega)\equiv e^{u(\mathbf{r},\omega)/kT}g(\mathbf{r},\omega) \ . \tag{6}$$

The integral $I(T)$ is to be evaluated by perturbation theory. For spherical potentials, the function $f(r)$ is sharply peaked and $y(r)$ is slowly varying in the vicinity of the peak, so that the integral of the product $f(y-1)$ can be split into a product of two terms that are easily evaluated.[8] But for nonspherical potentials, the angular part of the integration must somehow be dealt with before such a split can be made. For general $u(\mathbf{r},\omega)$ this requires some sort of additional approximation. A virtue of the Kihara core model is that it allows the angular integration to be done exactly, so that the theory can be tested independently of any approximation for angular averaging.

The angular integration proceeds as follows for a system of convex bodies with the pair potential dependent only on the shortest surface-to-surface distance. The integral $I(T)$ is expressed in terms of variables characterizing convex-body geometries in three dimensions,[6] that is, two angles θ and ϕ are used to determine the normal of the supporting plane between the bodies, angles ω are used to determine the relative orientation of the two bodies, and s is used to determine the shortest surface-to-surface distance between the bodies. On performing this coordinate transformation one obtains[9,10]

$$I(T)=\tfrac{1}{2}\int_0^\infty f(s)[y_{\text{av}}(s)-1]V_{1+s+2}(s)ds \ , \tag{7}$$

where

$$f(s)=-\frac{1}{kT}\frac{du(s)}{ds}e^{-u(s)/kT} , \tag{8}$$

$$y_{\text{av}}(s)=e^{u(s)/kT}g_{\text{av}}(s) \ , \tag{9}$$

$$g_{\text{av}}(s)=\frac{1}{3V_{1+s+2}}\int\int\int g(\theta,\phi,s,\omega)\mathbf{r}\cdot\left[\frac{\partial\mathbf{r}}{\partial\theta}\times\frac{\partial\mathbf{r}}{\partial\phi}\right]\times d\theta\,d\phi\,d\omega \ , \tag{10}$$

$$V_{1+s+2}(s)=\tfrac{1}{3}\int\int\int\mathbf{r}\cdot\left[\frac{\partial\mathbf{r}}{\partial\theta}\times\frac{\partial\mathbf{r}}{\partial\phi}\right]d\theta\,d\phi\,d\omega \ . \tag{11}$$

Here $g_{\text{av}}(s)$ is the average pair distribution function and V_{1+s+2} is the volume of a body outlined by the center of molecule 2 when it is moved around molecule 1 with constant surface-to-surface distance s.[11] The behavior of $g_{\text{av}}(s)$ as a function of s is similar to that of the radial distribution function $g(r)$ of spherical-molecule fluids.[9] For example, molecular-dynamics simulations of $g_{\text{av}}(s)$ for hard ellipsoids give results much like those for hard spheres.[12]

It is interesting to apply Eqs. (2)–(11) to hard convex bodies, since in this case $f(s)$ is a δ function,

$$f(s)=\delta(s^+) \ . \tag{12}$$

We get immediately

$$\frac{p}{\rho kT}=1+b\rho G \ , \tag{13}$$

where b is the second virial coefficient of the hard bodies and

$$G=y_{\text{av}}(0)=g_{\text{av}}(0^+) \tag{14}$$

is the average pair distribution function at contact for the hard bodies, for which an accurate approximation is available.[5]

For convex-molecular fluids other than hard bodies we can evaluate $I(T)$ by perturbation theory, using the results of Eqs. (13) and (14) for the reference fluid. The physical basis for the derivation is the same as for spherical molecules, namely, that the structure of the fluid is largely determined by the repulsive interactions. We follow the same approximations used for spherical molecules because the important features of $f(s)$ and $y_{\text{av}}(s)$ are similar to those of spherical molecules, and use the method of Weeks, Chandler, and Andersen[13] (WCA) in which $u(s)$ is divided at its minimum into a region of repulsive force and a region of attractive force. The result is

$$I(T)\approx\alpha(T)[G(\eta)-1] \ , \tag{15}$$

$$\alpha(T)=-\frac{1}{2kT}\int_0^{s_m}\frac{du_0(s)}{ds}e^{-u_0(s)/kT}V_{1+s+2}(s)ds \ , \tag{16}$$

where $\alpha(T)$ is a scaling factor that accounts for the softness of the repulsion and $G(\eta)$ is the average contact pair distribution function for hard convex bodies at a density corresponding to the packing fraction η. The packing fraction is related to the volume v_0 of a single hard convex body by

$$\eta=v_0\rho \ . \tag{17}$$

In Eq. (16), $u_0(s)$ is the repulsive part of $u(s)$,

$$u_0(s)=\begin{cases}u(s)+\varepsilon, & s<s_m\\ 0, & s>s_m\end{cases} \tag{18}$$

in which ε is the depth of the potential well and s_m is its minimum position.

On combining Eqs. (2) and (15) we obtain an equation of state of the form

$$\frac{p}{\rho kT}=1+B_2\rho+\alpha\rho[G(\eta)-1] \ , \tag{19}$$

which contains the two temperature-dependent quantities $B_2(T)$ and $\alpha(T)$, and the still unspecified quantity v_0, the effective volume of a single nonhard convex molecule. The functional form of $G(\eta)$ must also be determined.

Notice that $\alpha(T)$ is just the contribution of the repulsive forces to $B_2(T)$; in this sense Eq. (19) is valid for any dimensionality, although the particular coordinate transformations of Eqs. (10) and (11) that involve V_{1+s+2} are specific for $d=3$.

It remains to specify $G(\eta)$ and to choose an algorithm for determining v_0. For $G(\eta)$ we adopt our equation of state for hard convex bodies in any number of dimensions,[5]

$$G(\eta)=\frac{1-\gamma_1\eta+\gamma_2\eta^2}{(1-\eta)^d}\ , \tag{20}$$

where γ_1 and γ_2 are chosen to reproduce the correct third and fourth virial coefficients, B_3 and B_4, respectively, of the hard convex bodies (HCB):

$$\gamma_1=d-2^{d-1}\left[\frac{B_3}{b^2}\right]_{\text{HCB}}F\ , \tag{21}$$

$$\gamma_2=\tfrac{1}{2}d(d-1)-2^{d-1}d\left[\frac{B_3}{b^2}\right]_{\text{HCB}}F+2^{2(d-1)}\left[\frac{B_4}{b^3}\right]_{\text{HCB}}F^2\ . \tag{22}$$

The shape of the convex bodies is contained entirely in γ_1 and γ_2, inasmuch as η depends only on the volume but not the shape. The second virial coefficient b and the shape factor F are related to the molecular volume by

$$b=2^{d-1}v_0F\ , \tag{23}$$

so that F is unity for spheres. Thus the hard-body reference fluid requires knowledge of its first three virial coefficients in order to characterize the size and shape of its molecules.

The statistical-mechanical derivation does not give a definite prescription for the determination of the effective volume v_0, but it suggest limiting behaviors at low and high temperatures from which a suitable algorithm for the calculation of v_0 as a function of T alone can be devised. This algorithm is most conveniently expressed in terms of an effective value of b, which plays the role of a van der Waals covolume, and has the same appearance as for spherical molecules:

$$b(T)=2^{d-1}v_0(T)F=\alpha+T\frac{d\alpha}{dT}\ . \tag{24}$$

This expression holds for arbitrary d; the explicit expression for $d=3$ is

$$b(T)=-\frac{1}{2(kT)^2}\int_0^{s_m}u_0(s)\frac{du_0(s)}{ds}e^{-u_0(s)/kT}V_{1+s+2}(s)ds\ . \tag{25}$$

This complete the specification of the equation of state.

To summarize, once the shape of the convex molecules is given, it is only an exercise in geometry (perhaps complicated) to calculate the dimensionless coefficients F, γ_1, and γ_2 from the first three virial coefficients of the corresponding hard convex bodies, via Eqs. (21)–(23). The real potential is then used to calculate the second virial coefficient $B_2(T)$ via Eq. (3), the repulsive contribution $\alpha(T)$ to the second virial coefficient via Eq. (16), and the effective molecular volume $v_0(T)$, or equivalently the effective covolume $b(T)$, via Eqs. (24) or (25). This completely defines the equation of state, Eq. (19), with $G(\eta)$ given by Eq. (20).

III. COMPARISONS

Although the foregoing results should be applicable in any number of dimensions, results for comparison are available only for $d=3$, for a Kihara (12,6) core potential,

$$u(s)=\varepsilon\left[\left[\frac{s_m}{s}\right]^{12}-2\left[\frac{s_m}{s}\right]^{6}\right]\ . \tag{26}$$

The available results include computer simulations,[7] and a previous perturbation theory[4] that gives numerical rather than analytical results. Comparisons can be made not only with the equation of state itself, but also with the internal energy and the Helmholtz free energy.

We deal first with the geometrical part of the calculation, involving the first three virial coefficients of the effective hard convex body. In three dimensions a hard convex body can be characterized by its volume v_0, its surface area S, and an integrated mean radius of curvature R.[11] In terms of these quantities the volume V_{1+s+2} is

$$V_{1+s+2}=v_{01}+v_{02}+S_1R_2+S_2R_1+(S_1+S_2+8\pi R_1R_2)s+4\pi(R_1+R_2)s^2+\tfrac{4}{3}\pi s^3\ . \tag{27}$$

The second virial coefficient b is determined by a single dimensionless combination of v_0, S, and R,

$$\gamma\equiv RS/3v_0\ , \tag{28}$$

which is unity for spheres. Then b and F are given by

$$b=(1+3\gamma)v_0\ , \tag{29}$$

$$F=(1+3\gamma)/4\ . \tag{30}$$

A single parameter γ is not sufficient to determine B_3 and B_4 uniquely, but for the present purposes adequate approximations exist.[5] They lead to the following expressions for γ_1 and γ_2:

$$\gamma_1=3-\frac{1+6\gamma+3\gamma^2}{1+3\gamma}\ , \tag{31}$$

$$\gamma_2=3-\frac{2+[21-(B_4/v_0^3)_{\text{HS}}]\gamma+7\gamma^2}{1+3\gamma}\ , \tag{32}$$

where $(B_4/v_0^3)_{\text{HS}}=18.36\ldots$ is the fourth virial coefficient for hard spheres. The resulting expression for $G(\eta)$ is

$$G(\eta)=\frac{(1+3\gamma)-(2+3\gamma-3\gamma^2)\eta+\{1+[(B_4/v_0^3)_{\mathrm{HS}}-12]\gamma-7\gamma^2\}\eta^2}{(1+3\gamma)(1-\eta)^3} . \tag{33}$$

This completes the geometric part of the problem involving the hard-body cores.

A. Equation of state

Vega and Frenkel[7] have carried out Monte Carlo simulations for a system of rodlike molecules interacting via the Kihara (12,6) core potential of Eq. (26), in order to test the perturbation theory of Boublik.[4] They chose the core to be thin rods of length L. For this model we can calculate exact values of $B_2(T)$, $\alpha(T)$, and $b(T)$ from Eqs. (3), (16), and (25), respectively; after integration by parts the formulas become

$$B_2(T)=2\pi\int_0^{\infty}(1-e^{-u/kT})\left[\frac{L^2}{8}+Ls+s^2\right]ds , \tag{34}$$

$$\alpha(T)=2\pi\int_0^{s_m}(1-e^{-u_0/kT})\left[\frac{L^2}{8}+Ls+s^2\right]ds , \tag{35}$$

$$b(T)=2\pi\int_0^{s_m}\left[1-\left[1+\frac{u_0}{kT}\right]e^{-u_0/kT}\right] \times\left[\frac{L^2}{8}+Ls+s^2\right]ds , \tag{36}$$

where $u_0(s)$ is the repulsive branch of $u(s)$ as defined in Eq. (18). Notice that these expressions reduce to those for a spherical (12,6) potential if $L=0$.

Rather than calculate third and fourth virial coefficients to determine $G(\eta)$, we use the approximation of Eq. (33); this requires the choice of a reference system of hard convex bodies in order to determine the parameter γ. Following Boublik[4] and Vega and Frenkel,[7] we choose the reference system to be hard prolate spherocylinders of length L and diameter σ, where $\sigma=s_m/2^{1/6}$ is the parameter of the (12,6) potential such that $u(\sigma)=0$. Then γ is given by

$$\gamma=\frac{[1+(L/\sigma)][2+(L/\sigma)]}{2+3(L/\sigma)} , \tag{37}$$

and the packing fraction η by

$$\eta=v_0\rho=b\rho/4F =\frac{2\pi\rho}{1+3\gamma}\int_0^{s_m}\left[1-\left[1+\frac{u_0}{kT}\right]e^{-u_0/kT}\right] \times\left[\frac{L^2}{8}+Ls+s^2\right]ds . \tag{38}$$

Vega and Frenkel carried out simulations for both the repulsive potential $u_0(s)$ and the full potential $u(s)$. For the repulsive potential we have $B_2(T)=\alpha(T)$ and Eq. (19) reduces to

$$\frac{p_0}{\rho kT}=1+\alpha\rho G(\eta) , \tag{39}$$

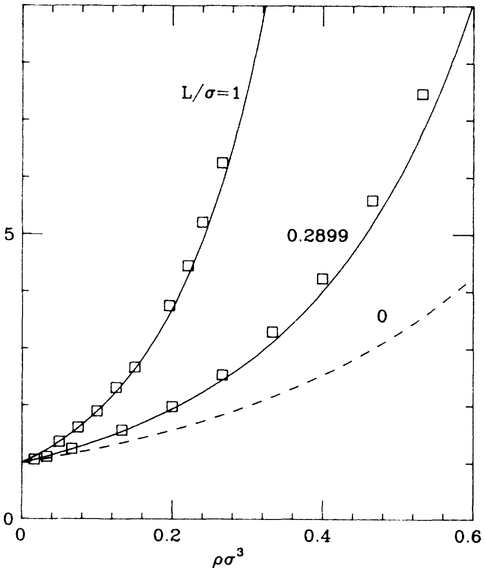

FIG. 1. Compressibility factor as a function of reduced density for rodlike molecules interacting via a Kihara (12,6) repulsive potential. The curves are *a priori* calculations from the potential and the points are computer simulations. The dashed curve for $L/\sigma=0$ corresponds to a Lennard-Jones (12,6) repulsive fluid. The reduced temperature is $kT/\varepsilon=1$ for $L/\sigma=0$ and 1, and $kT/\varepsilon=1.075$ for $L/\sigma=0.2899$.

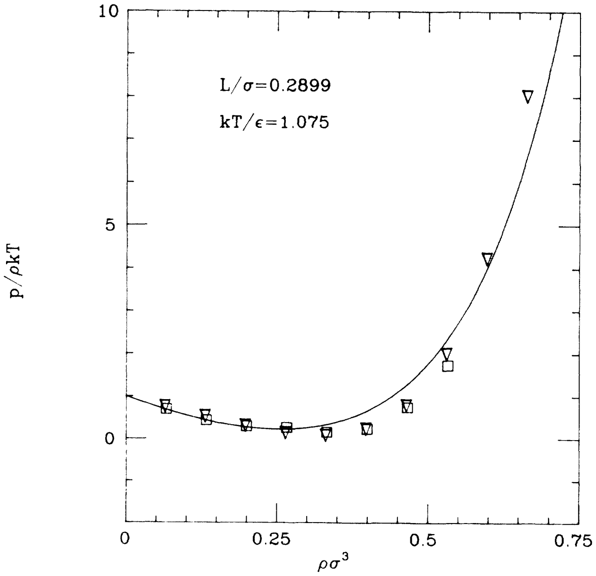

FIG. 2. Compressibility factor as a function of reduced density for the full Kihara (12,6) model for rodlike molecules. The curve is an *a priori* calculation from the potential, the squares are Monte Carlo calculations (Ref. 7), and the triangles are perturbation-theory calculations (Ref. 4).

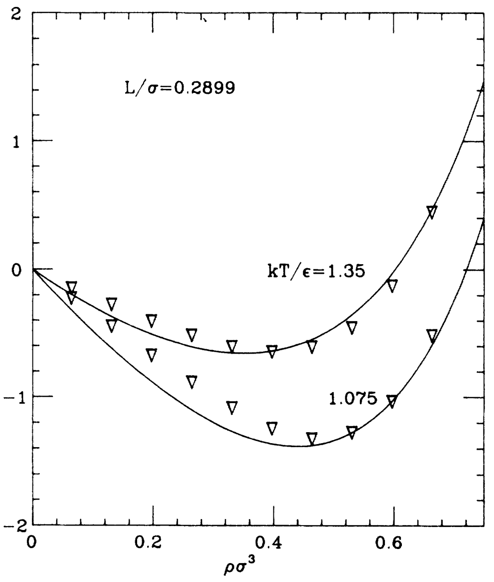

FIG. 3. Excess Helmholtz free energy as a function of reduced density for the same system as in Fig. 2.

where p_0 represents the pressure associated with u_0. The comparison of the results for the repulsive potential with the present equation of state are shown in Fig. 1 for temperatures near $kT/\varepsilon=1$. The agreement is comparable to that found previously for the spherical (12,6) repulsive potential,[8] which corresponds to $L/\sigma=0$.

Figure 2 shows results for the full Kihara (12,6) potential, including both the computer simulations[7] and the perturbation calculation by Boublik[4] based on the WCA method. The comparisons are again comparable to those found previously for the spherical potential ($L/\sigma=0$). Notice that the present equation of state is slightly better than the perturbation calculation at low densities, and slightly poorer at high densities. This is the result of our treating B_2 exactly, but taking b to be a function only of T rather than of both T and ρ.

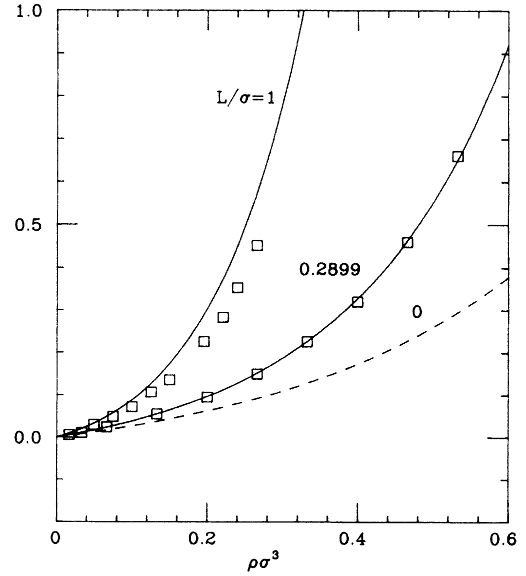

FIG. 4. Excess internal energy as a function of reduced density for the same system as in Fig. 1 (Kihara repulsive potential).

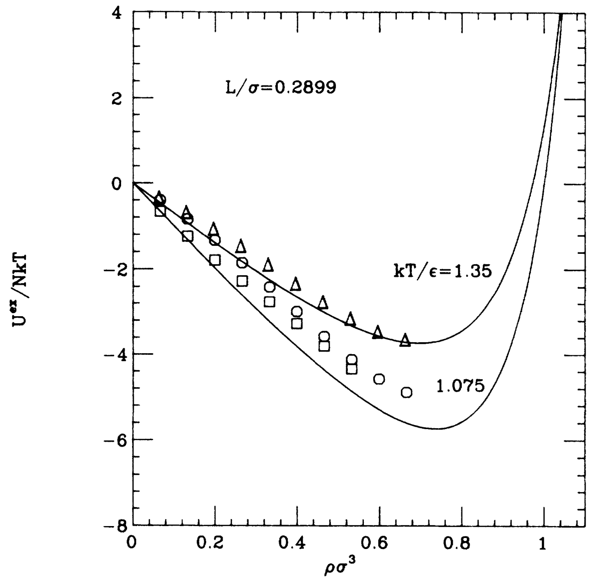

FIG. 5. Excess internal energy as a function of reduced density for the same system as in Figs. 2 and 3 (full Kihara potential). The squares are Monte Carlo calculations, and the triangles and circles are perturbation-theory calculations.

B. Helmholtz free energy

Once the equation of state is known, one can easily calculate the density dependence of the thermodynamic functions. For T and ρ as independent variables, the fundamental thermodynamic function is the Helmholtz free energy $A=U-TS$. The excess free energy, relative to the ideal gas at the same temperature and density, is found by integration of the equation of state,

$$\begin{aligned}\frac{A^{\mathrm{ex}}(\eta)}{NkT} &= \frac{1}{NkT}\int_{\infty}^{V}(p-p^{\mathrm{ideal}})dV\,,\\ &= \frac{4(B_2-\alpha)F}{b}\eta\\ &\quad+\frac{4\alpha F}{b}\left[\frac{[2-(1+\gamma_1)\eta-\gamma_2(2-3\eta)]\eta}{2(1-\eta)^2}\right.\\ &\qquad\left.-\gamma_2\ln(1-\eta)\right]. \qquad (40)\end{aligned}$$

Although there are no computer simulations for A^{ex}, results are available from the perturbation calculation of Boublik. The comparison with the results from the present equation of state is shown in Fig. 3. The agreement is comparable to that found previously for the spherical (12,6) potential.[8]

C. Internal energy

The excess internal energy can be found by differentiation of Eq. (40):

$$\frac{U^{\text{ex}}(\eta)}{NkT} = -\frac{4F}{b}\left[T\frac{dB_2}{dT}\right]\eta + 4\left[1-\frac{\alpha F}{b}\right]\left[\eta+\gamma_2\ln(1-\eta)-\frac{[2-(1+\gamma_1)\eta-\gamma_2(2-3\eta)]\eta}{2(1-\eta)^2}\right]$$
$$-\frac{4\alpha F}{b}\left[T\frac{db}{dT}\right]\left[\gamma_2\ln(1-\eta)+\frac{(3-\gamma_1)\eta^2-(1+\gamma_1)\eta^3+\gamma_2(2-5\eta+5\eta^2)\eta}{2(1-\eta)^3}\right]. \tag{41}$$

Comparisons are shown in Fig. 4 for the repulsive potential u_0, and in Fig. 5 for the full potential u. The agreement is again comparable to that for a spherical potential.

IV. CONCLUSIONS

The present equation of state, Eq. (19), represents a first step towards the realization of the old van der Waals dream of a general analytical equation of state for real fluids that is based on fundamental theory. It is a first step because the evaluation of the quantities $\alpha(T)$ and $G(\eta)$ has been carried out here only for the Kihara core model of the molecular interactions. The good agreement with both computer simulations and perturbation calculations for rodlike Kihara-model molecules indicates that the approximations of the statistical-mechanical theory underlying Eq. (19) are accurate.

Application to real molecular fluids requires further approximations for averaging over molecular orientations, and is considered in the following paper.[14] The important point is that the Kihara model tests the present theory in a form uncontaminated by such further approximations.

There are some inherent restrictions on Eq. (19), which can be summarized as follows.

(1) Repulsion forces dominate the structure of the dense fluids: this is the fundamental assumption of the theory.

(2) The intermolecular potentials are pairwise additive: no explicit account is taken of many-body forces.

(3) The repulsive molecular core is convex; if it is not, we do not have a suitable general representation of $G(\eta)$.

(4) The fluid must remain isotropic: the theory does not describe liquid-crystal phases.

(5) No freezing transition is predicted: at best, Eq. (19) continues smoothly into the metastable liquid region.

(6) The entire pair potential must be known to evaluate the parameters $B_2(T)$, $\alpha(T)$, and $b(T)$. The relaxation of this restriction for real molecular fluids is taken up in the following paper.[14]

Finally, we note that the mathematical form of Eq. (19) is, after clearing fractions, a quintic polynomial in the density for three dimensions (generally a polynomial of order $d+2$), the same as for spherical molecular fluids.[8] As such, it exhibits a first-order phase transition (on maing the Maxwell construction through the van der Waals–like loop), and a critical point. Although these features were not investigated here for the Kihara model, they are considered for real molecular fluids in the following paper.

ACKNOWLEDGMENTS

This work was supported in part by the National Science Foundation under Grant No. CHE 88-19370.

---

[1] C. G. Gray and K. E. Gubbins, *Theory of Molecular Fluids. Vol. 1: Fundamentals* (Oxford University Press, Oxford, 1984), Chaps. 4 and 5.

[2] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, New York, 1986), Chap. 12.

[3] B. M. Ladanyi and D. Chandler, J. Chem. Phys. **62**, 4308 (1975).

[4] T. Boublik, Mol. Phys. **32**, 1737 (1976).

[5] Y. Song and E. A. Mason, Phys. Rev. A **41**, 3121 (1990).

[6] T. Kihara, Rev. Mod. Phys. **25**, 831 (1953); Adv. Chem. Phys. **5**, 147 (1963).

[7] C. Vega and D. Frenkel, Mol. Phys. **67**, 633 (1989).

[8] Y. Song and E. A. Mason, J. Chem. Phys. **91**, 7840 (1989).

[9] T. Boublik, I. Nezbeda, and O. Trnka, Czech. J. Phys. B **26**, 1081 (1976).

[10] T. Boublik, Mol. Phys. **51**, 1429 (1984).

[11] T. Boublik and I. Nezbeda, Coll. Czech. Chem. Commun. **51**, 2301 (1986).

[12] J. Talbot, D. Kivelson, M. P. Allen, G. T. Evans, and D. Frenkel, J. Chem. Phys. **92**, 3048 (1990).

[13] J. D. Weeks, D. Chandler, and H. C. Andersen, J. Chem. Phys. **54**, 5237 (1971).

[14] Y. Song and E. A. Mason, following paper, Phys. Rev. A **42**, 4749 (1990).