

Improved perturbation theory of Kihara fluids

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An accurate perturbation theory for Kihara fluids is proposed. For several molecular models, agreement between calculated pressures and internal energies and their values from simulation is found to be good. The theory is not restricted to a given geometry and can be applied to any Kihara molecular fluid, even when the anisotropy of the molecule is high. Quality of the results is comparable to that obtained by perturbation theories for spherical models. The calculations can be carried out with a personal computer so that the theory can be useful for practical applications.

1. Introduction

Determination of thermodynamic properties of liquids from the basic principles of statistical mechanics yields results of considerable interest. For fluids made up of spherical molecules, progress made in the 1970s now permits a fast and accurate determination of their thermodynamic properties [1]. For nonpolar molecular fluids, there have been important advances during the last decade, especially on integral equations and perturbation theories [2]. Nevertheless, the accuracy of the calculations achieved for molecular fluids is not yet comparable to that of simple liquids. Therefore, an effort to develop fast and accurate theories for nonpolar fluids is desirable.

Kihara proposed in 1951 a potential [3] depending only on the shortest distance between the molecular cores $\rho(r, \omega_1, \omega_2)$. This potential model has been mainly applied to the study of the second virial coefficient [4–6]. Several simulation studies of the Kihara model [7–9] have shown, however, that the Kihara potential model constitutes a good effective pair-potential for modeling the liquid behavior of substances such as nitrogen or propane; hence, the interest in developing theories computationally less demanding than the simulation studies for this kind of fluids. Two perturbation theories have recently been proposed for Kihara fluids: The first theory, developed by Boublik [10], is based on the formalism

of convex bodies and on a semi-empirical surface-to-surface correlation function. The second one, developed in our laboratory [11–13], is an extension to Kihara fluids of the WCA-type perturbation theory formulated by Fischer [14] for the site-site potential model. The theory of Fischer for the site-site model presents the inconvenience that the reference system is difficult to simulate, which prevents a systematic improvement of the theory. However, when the theory is extended to Kihara fluids, the reference system has a very simple definition and it is easy to carry out simulations. Indeed, we have recently presented such simulations of the reference system for several Kihara models [7,9,12]. From these simulations, it is possible to obtain the exact value of the first perturbation terms of the expansion of free energy of the Kihara fluid about the reference system. Thus, a direct comparison between the perturbation terms obtained from the theory and those obtained from simulations of the reference fluid [9,12] could be performed. Such comparison has revealed that the main weakness of the theory is to neglect the orientational dependence of the background correlation function. Although the theory yields very accurate values of the zero- and second-order terms (A_0 and A_2), the values of the first-order term (A_1) are affected by error specially at high densities and anisotropies. In this work, we shall show that the error of the first-order term of the perturbation expansion has a systematic behavior with density and anisot-

ropy. We shall also show that it is possible to correct the first-order term in a systematic way, and how this correction brings theoretical results of the full Kihara model into close agreement with simulation data. The proposed perturbation scheme of this work improves the results obtained from Boublik perturbation theory of Kihara fluids [10], and constitutes an accurate theory to determine thermodynamic properties of this kind of model. The theory can be applied to any Kihara fluid without restriction of geometry, and the quality of the results holds even for high anisotropies.

In section 2, we shall briefly show the proposed perturbation theory of Kihara fluids. We shall illustrate its systematic deficiencies and we shall propose an improved version. In section 3, theoretical results obtained from this improved perturbation theory are compared with the results obtained from simulations of the model.

2. Theory

In this section, we shall briefly describe a perturbation theory for Kihara fluids. More details of the theory can be found in ref. [13]. The Kihara potential is given by [3]

$$u(\rho) = 4\epsilon [(\sigma/\rho)^{12} - (\sigma/\rho)^6], \quad (1)$$

where $\rho(r, \omega_1, \omega_2)$ is the shortest distance between the molecular cores, which hereafter will be denoted simply as ρ , ϵ is an energetic parameter and σ a length parameter. Molecular cores are chosen to reproduce the molecular shape. The core may be convex as originally defined by Kihara [3–5] or not convex as defined by ourselves [9,13]. The full potential is divided into a reference (u_0) and a perturbation part ($u_1 = u - u_0$). The prescription of Mo and Gubbins [15] applied to eq. (1) yields for u_0 ,

$$u_0(\rho) = u(\rho) + \epsilon, \quad \rho < 2^{1/6}\sigma, \quad (2)$$

$$u_0(\rho) = 0, \quad \rho > 2^{1/6}\sigma. \quad (3)$$

The residual Helmholtz free energy of the Kihara fluid A^{res} is now expanded about the reference system to obtain to second order [2]

$$\frac{A^{\text{res}}}{NkT} = \frac{A_0^{\text{res}}}{NkT} + \frac{A_1}{NkT} + \frac{A_2}{NkT} + \dots \quad (4)$$

To evaluate the perturbation terms of eq. (4), the structure of the reference system as given by the pair-correlation function $g_0(r, \omega_1, \omega_2)$ is needed. Zero-order RAM theory [16] for the background correlation of the anisotropic reference system

$$y_0(r, \omega_1, \omega_2) = g_0(r, \omega_1, \omega_2) \exp[\beta u_0(r_{12}, \omega_1, \omega_2)]$$

is now used. The RAM potential, $\phi_{\text{RAM}}(r)$, is defined as

$$\begin{aligned} & \exp[-\beta \phi_{\text{RAM}}(r_{12})] \\ & = \langle \exp[-\beta u_0(r_{12}, \omega_1, \omega_2)] \rangle_g, \end{aligned} \quad (5)$$

where the brackets with the subscript g stand for unweighted orientational average. The function $y_0(r, \omega_1, \omega_2)$ is then approximated by

$$y_0(r_{12}, \omega_1, \omega_2) = y_{\text{RAM}}(r_{12}). \quad (6)$$

Therefore, $g_0(r, \omega_1, \omega_2)$ is written as

$$\begin{aligned} & g_0(r_{12}, \omega_1, \omega_2) \\ & = \exp[-\beta u_0(r_{12}, \omega_1, \omega_2)] y_{\text{RAM}}(r_{12}). \end{aligned} \quad (7)$$

The function $y_{\text{RAM}}(r)$ is obtained at every temperature and density by solving the Ornstein-Zernike (OZ) equation with the Percus-Yevick (PY) approximation [17] for the potential $\phi_{\text{RAM}}(r)$. A_0^{res} is identified with the free energy of a equivalent hard system $A_{\text{H}}^{\text{res}}$ whose diameter at every temperature and density is obtained by setting to zero the first-order term of the BLIP expansion [1,12–14]

$$\begin{aligned} & \frac{n}{2} \int [\exp(-\beta u_0) - \exp(-\beta u_{\text{H}})] \\ & \times y_{\text{RAM}}(r_{12}) dr_{12} d\omega_1 d\omega_2 = 0. \end{aligned} \quad (8)$$

$A_{\text{H}}^{\text{res}}$ can be obtained from integration of the equation of state of hard bodies proposed by Boublik [18]. Therefore, $A_{\text{H}}^{\text{res}}$ is given by

$$\frac{A_{\text{H}}^{\text{res}}}{NkT} = \frac{\eta(c_1 + c_2\eta)}{(1-\eta)^2} + c_3 \ln(1-\eta), \quad (9)$$

where the constants c_1 , c_2 and c_3 are given by $c_1 = 6\alpha^2 - 2\alpha$, $c_2 = 1.5\alpha(3 - 5\alpha)$ and $c_3 = 6\alpha^2 - 5\alpha - 1$. The nonsphericity parameter [19] α and the packing fraction η are defined as

$$\frac{B_{2\text{H}}}{V_{\text{H}}} = 1 + 3\alpha, \quad (10)$$

$$\eta = nV_H, \quad (11)$$

where B_{2H} and V_H are the second virial coefficient and the volume of the equivalent hard body, respectively.

When the structure of the reference fluid is approximated by eq. (7), the first-order perturbation term A_1 is given by

$$\frac{A_1}{N} = 2n\pi \int_0^\infty \langle u_1 \exp(-\beta u_0) \rangle_g \times y_{RAM}(r_{12}) r_{12}^2 dr_{12}. \quad (12)$$

The second-order perturbation term A_2 is obtained from an extension to molecular systems [10,13] of the macroscopic compressibility equation [20]. The final expression is then

$$\frac{A_2}{NkT} = -\frac{\pi n}{kT} \left(\frac{\partial n}{\partial p} \right)_0 \int_0^\infty \langle u_1^2 \exp(-\beta u_0) \rangle_g \times y_{RAM}(r_{12}) r_{12}^2 dr_{12}, \quad (13)$$

where $(\partial n/\partial p)_0$ is the isothermal compressibility, which can be easily obtained from the equation of state of the reference system. Eqs. (2)–(13) constitute a perturbation theory for Kihara fluids. We shall denote this perturbation scheme as PT. Calculated values of A_0^{res} and A_2 from PT agree very well with simulations of the reference fluid [12,13]. Theoretical values of A_1 , however, deviate significantly from the values of simulation at high densities and anisotropies. The reason for this discrepancy arises from using the approximation of eq. (6). We have studied the behavior of the function ΔA_1 defined as

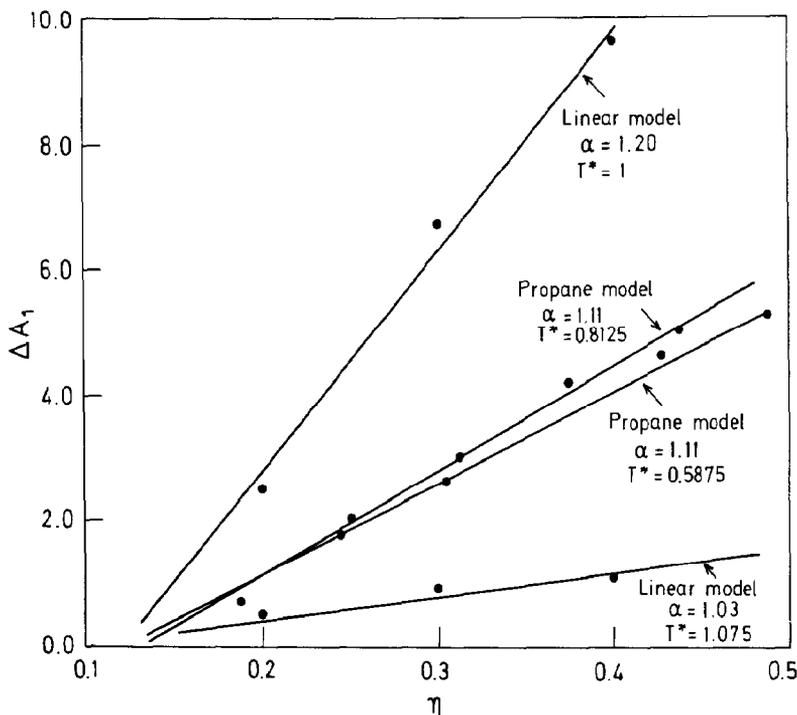


Fig. 1. Error in the estimation of the first-order perturbation term ΔA_1 (see eq. (14)) as a function of the packing fraction (eq. (11)) for several Kihara models. The A_1^{sim} values are from refs. [9,12]. The dots are the obtained values of ΔA_1 and the solid line is the fit to the data given by eq. (15). The upper and lowest curve are for linear models with $L^*=1$ and $L^*=0.29$, respectively. The two middle lines are for an angular propane-like model.

$$\Delta A_1 = 100 \frac{A_1^{\text{simulation}} - A_1^{\text{PY}}}{A_1^{\text{simulation}}}, \quad (14)$$

as a function of the packing fraction η for several Kihara fluids for which there are accurate values of A_1 obtained from simulations of the reference fluid. We show in fig. 1 the function ΔA_1 for two linear models with elongations $L^* = l/\sigma = 0.29$ and 1 where l is the length of the rod and for an angular model of propane made up two connected rods. Fig. 1 shows that ΔA_1 increases linearly as a function of the density for every model. Furthermore, the slope of the straight line increases linearly with the anisotropy of the model, given by the nonsphericity parameter α , irrespective of the detailed molecular shape, at least in these cases. For $\eta < 0.12$, ΔA_1 is almost zero as expected since the approximation of eq. (6) becomes exact in the zero-density limit. Since the variations of ΔA_1 with η and α are smooth, we have fitted them to the function

$$\alpha < 1.03, \quad \Delta A_1 = 0,$$

$$\alpha > 1.03, \quad \eta < 0.12, \quad \Delta A_1 = 0,$$

$$\alpha > 1.03, \quad \eta > 0.12,$$

$$\Delta A_1 = (185.52 \alpha - 188.42)(\eta - 0.12). \quad (15)$$

This expression fits very well the values of ΔA_1 obtained for different models and densities. Therefore, theoretical values of A_1 can be corrected according to eqs. (14) and (15). When the A_1 term is corrected in this way, we obtain an improved perturbation theory which we shall denote as IPT. In section 3, we shall show the results obtained by the IPT for the pressure p and internal energy U of several Kihara fluids. A comparison with simulation results of these models will be carried out.

3. Results

Two different models of Kihara potential have

Table 1
Z and U for a linear Kihara model with $L^* = 1$

| T^* | η | $Z = pV/NkT$ | | | | U^{res}/NkT | | | |
|-------|--------|--------------|------|-------|--------------|---------------|-------|-------|--------------|
| | | MC | PT | IPT | Boublik [10] | MC | PT | IPT | Boublik [10] |
| 0.70 | 0.3351 | -0.62 | | -0.68 | -0.71 | -5.45 | | -5.23 | -5.14 |
| | 0.3879 | 0.22 | | 0.22 | -0.03 | -6.33 | | -6.14 | -6.05 |
| | 0.4460 | 2.47 | | 2.58 | 1.92 | -7.32 | | -7.12 | -7.05 |
| 0.85 | 0.1414 | 0.24 | 0.31 | 0.22 | 0.26 | -2.08 | -1.44 | -1.70 | -1.68 |
| | 0.2245 | 0.10 | 0.20 | -0.11 | -0.02 | -3.04 | -2.45 | -2.69 | -2.67 |
| | 0.3351 | 0.28 | 1.44 | 0.33 | 0.29 | -4.33 | -3.89 | -4.22 | -4.13 |
| | 0.3879 | 1.24 | | 1.36 | 1.15 | -5.08 | | -4.95 | -4.86 |
| | 0.4460 | 3.72 | | 3.78 | 3.20 | -5.81 | | -5.71 | -5.64 |
| 1.00 | 0.1414 | 0.47 | 0.55 | 0.45 | 0.51 | -1.60 | -1.21 | -1.40 | -1.38 |
| | 0.2245 | 0.41 | 0.60 | 0.32 | 0.40 | -2.42 | -2.06 | -2.24 | -2.21 |
| | 0.3351 | 1.02 | 1.99 | 1.01 | 0.98 | -3.60 | -3.27 | -3.50 | -3.43 |
| | 0.3879 | 2.05 | | 2.13 | 1.95 | -4.18 | | -4.09 | -4.03 |
| | 0.4460 | 4.60 | | 4.55 | 4.05 | -4.79 | | -4.69 | -4.66 |
| 1.15 | 0.1414 | 0.62 | 0.73 | 0.65 | 0.68 | -1.30 | -1.05 | -1.20 | -1.17 |
| | 0.2245 | 0.64 | 0.89 | 0.64 | 0.70 | -2.04 | -1.78 | -1.91 | -1.88 |
| | 0.3351 | 1.62 | 2.38 | 1.51 | 1.48 | -3.05 | -2.81 | -2.98 | -2.91 |
| | 0.3879 | 2.74 | | 2.68 | 2.52 | -3.56 | | -3.47 | -3.42 |
| | 0.4460 | 5.00 | | 5.07 | 4.63 | -4.05 | | -3.96 | -3.94 |
| 1.35 | 0.1414 | 0.83 | 0.90 | 0.83 | 0.85 | -1.05 | -0.89 | -0.99 | -0.96 |
| | 0.2245 | 1.02 | 1.17 | 0.95 | 1.00 | -1.66 | -1.50 | -1.59 | -1.56 |
| | 0.3351 | 1.97 | 2.75 | 1.98 | 1.95 | -2.52 | -2.35 | -2.50 | -2.41 |
| | 0.3879 | 3.46 | | 3.19 | 3.05 | -2.93 | | -2.90 | -2.82 |
| | 0.4460 | 5.57 | | 5.56 | 5.16 | -3.29 | | -3.29 | -3.22 |

been recently simulated. Boublik and Kantor [8] have performed Monte Carlo (MC) simulations for a linear model with $L^*=l/\sigma=1$. We have recently performed molecular dynamics (MD) simulations of an angular Kihara model of propane [9]. Therefore, the improved perturbation theory of section 2 can be directly tested against simulation data for these two models.

In table 1, we show the results for the residual internal energy U^{res} and the compressibility factor Z as obtained from the theory of this work (PT or IPT), from MC simulations [8] and from Boublik perturbation theory [10] for a Kihara model with $L^*=1$. PT yields too-high values of pressure and internal energy. IPT, however, gives very good agreement with the "pseudo-experimental" results of the model for all the studied densities and temperatures. This holds not only for pressure but also for internal energy. At high densities, the values obtained from the IPT treatment agree better with the values from simulation than those from Boublik perturbation theory

Table 2

First-order perturbation term A_1 as obtained from perturbation theory, PT, from the improved perturbation theory of this work, IPT, and from the simulation results of refs. [9, 11]. The results are for two linear models with $L^*=0.29$ and $L^*=1$ and for the angular Kihara model of propane defined in ref. [9]

| T^* | n^* | $A_1^{simulation}$ | A_1^{PT} | A_1^{IPT} |
|--------------------------|--------|--------------------|------------|-------------|
| linear model, $L^*=0.29$ | | | | |
| 1.075 | 0.2662 | -2.08 | -2.07 | -2.075 |
| 1.075 | 0.3993 | -3.37 | -3.34 | -3.36 |
| 1.075 | 0.5324 | -4.74 | -4.69 | -4.73 |
| linear model, $L^*=1$ | | | | |
| 1 | 0.1528 | -1.96 | -1.91 | -1.96 |
| 1 | 0.2292 | -3.27 | -3.05 | -3.25 |
| 1 | 0.3056 | -4.68 | -4.23 | -4.68 |
| propane model | | | | |
| 0.5875 | 0.15 | -2.77 | -2.75 | -2.78 |
| 0.5875 | 0.20 | -3.97 | -3.89 | -3.98 |
| 0.5875 | 0.25 | -5.28 | -5.12 | -5.29 |
| 0.5875 | 0.30 | -6.67 | -6.39 | -6.69 |
| 0.5875 | 0.35 | -8.11 | -7.70 | -8.15 |

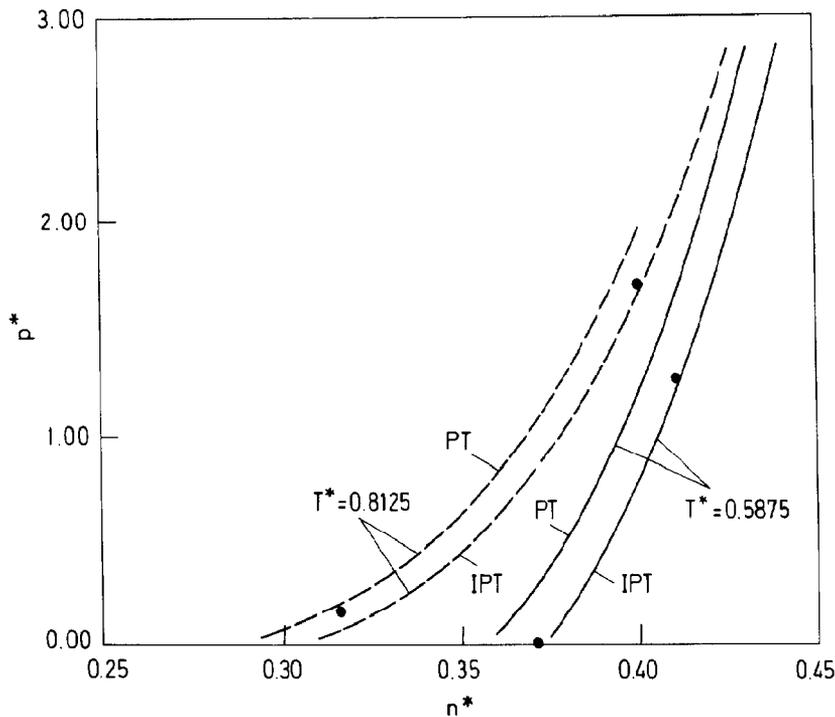


Fig. 2. Reduced pressure $p^*=p/(kT/\sigma^3)$ as a function of the numerical density $n^*=n\sigma^3$ for an angular Kihara model of propane as obtained from perturbation theory, PT, from the improved perturbation theory of this work, IPT, and from molecular dynamics of ref. [9] of the main text. Results are for the isotherms $T^*=T/(\epsilon/k)=0.5875$ (solid line) and $T^*=0.8125$ (dashed line).

[10]. It should be noted that the linear model with $L^*=1$ corresponds to a very high anisotropy. The elongation of real linear molecules is usually smaller than this value, being $L^*\approx 0.55$ for Cl_2 or $L^*\approx 0.80$ for CO_2 . Therefore, the results of table 1 for $L^*=1$ constitute a severe test of the theory.

Boublik has not provided values of A_1 . Nevertheless, A_1 as obtained from PT and IPT in comparison with our MC results can be seen in table 2 and, again, values from IPT agree considerably better than those from PT.

In fig. 2, the reduced pressure ($p^*=p/(kT/\sigma^3)$) for the Kihara model of propane as obtained from the theory (PT or IPT) and from MD [9] is shown. The IPT results are practically coincident with the values from simulation whereas the PT scheme gives too-high values of the pressure. It is again clear that the main error of PT is contained in the A_1 term due to the use of the approximation of eq. (6). When this error is corrected (IPT), the theoretical values are in close agreement with simulation results.

From a theoretical point of view, the approximation of eq. (6) should be directly improved. One possibility is to use first-order RAM theory [16] for $\nu_0(r, \omega_1, \omega_2)$. Although this would be convenient from a purely theoretical point of view, this route has the drawback of a considerable increase of computational time. It could still be done for linear models, but for nonlinear models it would at present become an almost impossible task. We have shown, however, that the IPT of this work yields very good results for highly anisotropic linear and nonlinear models without consuming a huge amount of computer time. For instance, the numbers shown in table 1 can be obtained in about 4 h of CPU time on a personal computer IBM PS/2 80-041. Indeed it is remarkable that similar results can be obtained by the direct solution of the PY integral equation for the linear Kihara [21] system. For instance, for a linear model with $L^*=1$ at $T^*=1$ and $\eta=0.3351$, the integral equation yields $U/NkT=-3.48$ and $Z=1.08$ in close agreement with both MC and IPT of this work (see table 1). However, the time consumed to solve the integral equation for the linear system at a given temperature and density is larger than the time required to obtain all the data of table 1 with the IPT of this work.

The IPT of Kihara fluids presented in this work constitutes a reliable approach for the determination of thermodynamic properties of this kind of fluids. From previous simulation studies, it has been shown that the Kihara potential model is a good effective pair potential for nonpolar molecular fluids in the liquid state. Consequently, we believe that the application of the IPT of Kihara fluids developed in this work will supply a good description of the thermodynamic behavior of real nonpolar fluids in the liquid state.

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