Investigation of the Temperature and Density Dependences of the Effective Pair Potential Parameters Using Variational Theory

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A variational theory (VT), in which the potential energy of a real system is evaluated relative to the hard-sphere system, has been used to investigate the medium's effects on the pair potential parameters. By adding the medium's effects to the isolated pair potential, the concept of an "effective pair potential" (EPP) has been introduced. The advantage of such a potential (EPP) over the isolated pair potential is that the configurational energy can exactly be written as the sum of all EPP of all pairs available in the system. The parameters of such a pair potential will then show state dependence. The EPP parameters for different dense fluids at various temperatures have been obtained via the VT, and they have been shown to be density independent for densities greater than the Boyle density, $\rho_B \simeq 1.8\rho_c$, (where ρ_c is the critical density), while at lower densities the parameters depend on density as well as temperature. For any dense fluid, the depth of the EPP, ε, is found to be larger than its corresponding isolated pair. When the EPP parameters are used to reduce temperature and density, the cut-off parameter, $C = d/\sigma$ depends only on the reduced density, and this parameter shows a strong principle of corresponding states for different fluids. The resulting expression for the cut-off parameter has then been used to accurately predict the internal energy. Finally, the EPP parameters are compared with those of the average effective pair potential (AEPP) for Ar, to show the importance of the medium effects and the long-range interactions of the AEPP in dense fluids, individually. This comparison shows that the depth parameter of the AEPP is much larger than that of the EPP. Since the long-range interactions are mainly attractive, such a conclusion is reasonable.

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1. INTRODUCTION

The interaction potential of an isolated pair is quite different from that of the pair in the presence of other molecules. This difference can be attributed to the effect of the medium on the molecular charge distribution. In addition to the effect of the medium on the molecular charge distribution, which makes the configurational energy non-pair-wise additive, the long-range interactions have important contributions in dense fluids. Even in liquids with spherically symmetrical molecules, interactions of a given molecule with at least three molecular shells surrounding it must be taken into account. Recently, the concept of the ''average effective pair potential,'' (AEPP) is introduced [1], in order to write the configurational potential energy as the sum of only the nearest neighbor potential energies with the AEPP interactions, exactly. Such a pair potential (AEPP) is considered as an isolated pair potential to which the medium effect and all long-range interactions of a given pair with remaining molecules are both added. The mathematical form of the average effective pair potential is considered to be the same as that of the isolated pair potential, but the parameters of the former are state dependent.

Because at very high temperatures the equation of state of a fluid is mainly due to the repulsive potential among its molecules and the attractive part comes into effect at lower temperatures, Zwanzig [2] originally used a perturbation approach for the equation of state of fluids based on a simple system of hard spheres. Mansoori and Canfield [3] applied that idea via a variational approach, so that if one varies the attractive contribution of the partition function around the repulsive contribution, the hard-sphere contribution, the lower temperature properties of gases and liquids may be predicted satisfactorily.Such a method, which is known as a variational theory, has been used to successfully predict the thermodynamic properties of fluids [3–5]. A number of investigators have used the variational technique to calculate the thermodynamic properties of different fluids including liquid metals [6–13]. Jedrzejek and Mansoori [14] used the variational technique to develop analytic equations of state of a hard-core fluid with a Yukawa tail. They then extended their work to a two-tail Yukawa potential [15]. In the variational inequality minimizing (VIM) approach, Alem and Mansoori [16] have used the variational theory, along with the Lennard-Jones (LJ) pair potential function and the Axilrod–Teller three-body potential, to predict the thermodynamic properties of fluids. They also have obtained general expressions for the density and temperature dependences of the hard-sphere diameter, d.

Because there is no reason to limit the non-additive contribution of the configurational potential energy of dense fluids to three-body interactions

only, we have introduced an effective pair potential (EPP) similar to that in our previous work (i.e., AEPP) to present an exact expression for the configurational energy. The EPP is considered to be the isolated pair potential to which the medium effect is added. Since long-range interactions are not included in the EPP (unlike the case of AEPP), such interactions must be taken into account in the configurational energy.

Our goal in the present work is to show how to use the EPP to predict the state dependences of its parameters, ε and σ. We have followed the VIM approach but with the EPP as an effective pair interaction potential energy in a real fluid. The parameters of the EPP have then been calculated at various temperatures at high densities ($\rho > \rho_B$). The calculated EPP parameters are used to obtain a precise expression for the cut-off parameter ($C = d/\sigma$) of different fluids in terms of the reduced density. The resulting expression has then been used to accurately predict the internal energy.

2. FORMULATION OF A VARIATIONAL THEORY BASED ON EPP

The equilibrium behavior of a fluid can be formulated using the canonical partition function. A fundamental relation for the statistical mechanical description of the canonical ensemble exists between the Helmholtz free energy and the canonical partition function Q of an N-particle system confined in volume V at temperature T [17]

$$A = -kT \ln Q \tag{1}$$

where

$$Q = Q_{\text{int}} Z \tag{2}$$

and

$$Z = \frac{1}{N!} \iint e^{-\phi/kT} \, dr_1 \cdots dr_N \tag{3}$$

in which Q_{int} is the partition function of the internal molecular motions, Z is the configurational integral, and ϕ is the intermolecular potential energy function. If we consider two systems with different potential energy functions, ϕ and ϕ_0, with the same volume, temperature, and particle number, the ratio of their configurational integrals will be [16]

$$\frac{Q}{Q_0} = \frac{\int \cdots \int e^{(\phi_0 - \phi)/kT} \, dr_1 \cdots dr_N}{\int \cdots \int e^{-\phi_0/kT} \, dr_1 \cdots dr_N}$$
$$= \langle e^{(\phi_0 - \phi)/kT} \rangle_0 \tag{4}$$

The right-hand side of Eq. (4) can be expanded about $\prec(\phi-\phi_0)\succ_0$ by a Taylor's series as

$$\prec e^{(\phi_0-\phi)/kT}\succ_0 = e^{\prec(\phi_0-\phi)/kT\succ_0} + \frac{1}{2}\prec[(\phi_0-\phi)/kT - \prec(\phi_0-\phi)/kT\succ_0]^2 e^{\xi}\succ_0 \tag{5}$$

where the higher-order terms are ignored and

$$(\phi_0-\phi)/kT \leqslant \xi \leqslant \prec(\phi_0-\phi)/kT\succ_0 \tag{6}$$

The second term on the right side of Eq. (5) is always positive. Omitting it and replacing the result in Eq. (4) will give

$$\frac{Q}{Q_0} \geqslant e^{\prec(\phi_0-\phi)/kT\succ_0} \tag{7}$$

which can be written in terms of the Helmholtz free energy as

$$A \leqslant A_0 + \prec\phi-\phi_0\succ_0 \tag{8}$$

The inequality of Eq. (8) is known as the Gibbs–Bogoliubov inequality [16]. According to such an inequality, if we know the intermolecular potential energy function for a real system relative to that of a reference system (0) and the thermodynamic properties of the reference system, we can then obtain the Helmholtz free energy and the other thermodynamic properties of the real system by minimizing the right side of Eq. (8).

We define the configurational energy of the real system in terms of the effective pair potential (EPP), ϕ_{eff}, so that we can consider the configurational energy of the real system as sum of all EPP pairs which include medium effects. Therefore, this potential for a pair is expected to depend on the thermodynamic state of the system, in addition to the intermolecular separation of the pair. Because the effect of the fluid medium on the molecular charge distribution of a pair is included in the pair interaction potential, we will have

$$\phi = \sum_{i,j} \phi_{\text{eff},ij} \tag{9}$$

The hard-sphere model is taken as the reference system (0). Hence,

$$\phi_0 = \begin{cases} \infty, & r_{ij} \leqslant d \\ 0, & r_{ij} > d \end{cases} \tag{10}$$

where r_{ij} is the intermolecular distance between i and j molecules and d is the effective hard-sphere diameter for the reference system which gives the same entropy as that for the real system. The Helmholtz free energy will then be

$$A \leqslant A_0 + A_{2b} \tag{11}$$

where A_0 is the Helmholtz free energy of the reference system, A is that for the real system with the EPP interaction between each pair, and

$$A_{2b} = (\rho^2/2) \iint g_{02}(r_{12}) \, \phi(r_{12}) \, dr_1 \, dr_2 \tag{12}$$

and g_{02} is the radial distribution function of a pair in the reference system. Note that the real system has no interaction other than the EPP for all pairs, since the medium effect is completely included. This is the main difference between the present work and previous studies [2–4], in which at most the three-body interactions were included.

In order to calculate the properties of fluids via Eq. (11), its right side should be minimized with respect to d as the variational parameter to satisfy the following conditions:

$$A' = (\partial A_0/\partial d)_\rho + (\partial A_{2b}/\partial d)_\rho = 0 \tag{13}$$

and

$$A'' = (\partial^2 A_0/\partial d^2)_\rho + (\partial^2 A_{2b}/\partial d^2)_\rho > 0 \tag{14}$$

The Helmholtz free energy of the hard-sphere (reference) system was fairly accurately obtained by Carnahan and Starling [18] as

$$A_0 = A^{ig} + \frac{RT\eta(4-3\eta)}{(1-\eta)^2} \tag{15}$$

where A^{ig} is the ideal gas Helmholtz free energy,

$$\eta = \frac{\pi}{6} N_A \rho d^3 \tag{16}$$

is a dimensionless density called the packing factor, and N_A is the Avogadro number. Substitution of Eq. (15), for A_0, in Eq. (11) gives

$$A \leqslant A^{ig} + \frac{RT\eta(4-3\eta)}{(1-\eta)^2} + A_{2b}(\rho, d) \tag{17}$$

As mentioned before, the minimization of the right side of Eq. (17) with respect to Eq. (13) gives the effective hard-sphere diameter at a given thermodynamic state. The right side with the resulting value of d gives the Helmholtz free energy of the real system at a given thermodynamic state. Hence, the inequality can now be replaced by an equality. All thermodynamic functions can be derived from Eq. (17) (but the inequality should be replaced with an equality in advance). For instance, for entropy using the thermodynamic equation of $S = -(\partial A/\partial T)_\rho$ with respect to Eq. (13) we obtain

$$S(\rho, T) = S^{\text{ig}} + \frac{R\eta(4-3\eta)}{(1-\eta)^2} = S_0(\eta) \tag{18}$$

which means that the entropy of the real system is equal to the entropy of the hard-sphere system with a hard-sphere diameter, d. At this stage, we assume that the EPP parameters are constants. Once the EPP parameters are calculated, that assumption should be corrected using an iterative procedure based on the condition of Eq. (13) to reach convergence for the EPP parameters. According to Eqs. (16) and (18), we can directly use the experimental values of entropy at any given thermodynamic state to calculate the value of d at that state. Actually, Eqs. (16) and (18) can be combined and solved for the d parameter, which gives

$$d(\rho, T) = \left\{ \frac{6}{\pi \rho N_{\text{A}}} \frac{\{2 - (S-S^{\text{ig}})/R + [4-(S-S^{\text{ig}})/R]^{1/2}\}}{[3-(S-S^{\text{ig}})/R]} \right\}^{1/3} \tag{19}$$

Such calculations have been done for Ar, CH_4, and C_2H_6 (the needed data are taken from Refs. 19–21) and the result are shown in Figs. 1 and 2 for a given isotherm and isochore, respectively.

3. CALCULATION OF THE EPP PARAMETERS

Substitution of Eq. (9) in Eq. (12), and using the (12-6) LJ potential as an effective pair potential, we will have

$$A_{2b} = 48\eta N_{\text{A}} \varepsilon [I_{12}(\eta)/C^{12} - I_6(\eta)/C^6] \tag{20}$$

where $I_n(\eta)$ is defined as [3]

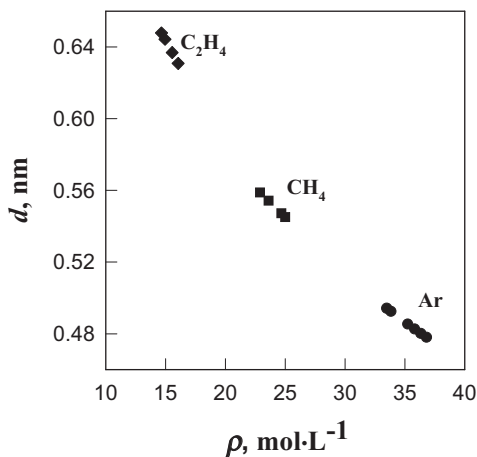$$I_n(\eta) = \int_0^\infty g_{02}(x, \eta) \, x^{2-n} \, dx \tag{21}$$

Fig. 1. Calculated hard-sphere diameter d versus ρ, for Ar (●) at $T = 100$ K, CH_4 (■) at $T = 150$ K, and C_2H_6 (◆) at $T = 260$ K, using Eq. (19).
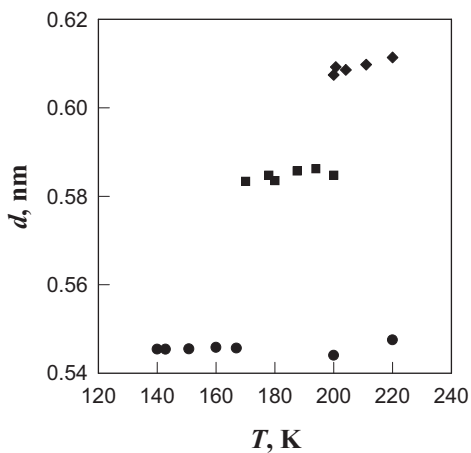

Fig. 2. The calculated hard-sphere diameter d in terms of T, for Ar (●) at $\rho = 25.30$ mol·L^{-1}, CH_4 (■) at $\rho = 20.21$ mol·L^{-1}, and C_2H_6 (◆) at $\rho = 17.62$ mol·L^{-1}.

Table I. Calculated I_6 and I_{12} via Eq. (21) in Terms of η, using g_{02} Values from Refs. 23 and 24

η	I_6 [23][a]	I_{12} [23][a]
0.2	0.379830	0.137530
0.3	0.405096	0.153022
0.4	0.432894	0.172019
0.5	0.461725	0.193219
0.6	0.492349	0.217700
0.7	0.523744	0.245060
0.8	0.557696	0.277233
0.9	0.593070	0.313957

[a] Reference from which the values of g_{02} are taken is indicated in the column heading.

in which g_{02} is the radial distribution function for the reference system, $C = d/\sigma$, and $x = r/d$. Mansoori and Ali [22] have shown that $I_n(\eta)$ can be expressed as a polynomial in terms of η as

$$I_n(\eta) = \sum_{i=0}^{5} C_{ni}\eta^i \tag{22}$$

We have calculated I_ns for $n = 6$ and 12 for various values of η, using the reported values of g_{02} [23], and then we have computed the C_{ni}s coefficients for them via Eq. (22). The calculated I_ns are given in Table I in terms of η. On the basis of data given in Table I, values of C_{ni}s coefficients of Eq. (22) are calculated and given in Table II.

Now, by substitution of Eq. (20) in Eq. (17) (with the equal sign), we can obtain the Helmholtz free energy of the real system as

$$A = A^{ig} + \frac{RT\eta(4-3\eta)}{(1-\eta)^2} + 48\eta N_A \varepsilon[\{I_{12}(\eta)/C^{12} - I_6(\eta)/C^6] \tag{23}$$

**Table II.** Calculated C_{6i} and C_{12i} Coefficients of Eq. (22), using the Data of Table I

| i	C_6	C_{12}
0	0.33248	0.00000
1	0.22149	0.12357
2	0.07131	0.04786
3	4.692e-3	0.07375

In order to calculate the EPP parameters, Eq. (23) can be rearranged to

$$\frac{\left[A - A^{\mathrm{ig}} - \dfrac{RT\eta(4-3\eta)}{(1-\eta)^2}\right]d^6}{48\eta I_6(\eta)} = \varepsilon\sigma^{12}\frac{I_{12}(\eta)}{d^6 I_6(\eta)} - \varepsilon\sigma^6 \tag{24}$$

In Eq. (24), A could be calculated using experimental data of U and S via the relation of $A = U - TS$ and the d parameter could be obtained through Eq. (18). If the EPP parameters of dense fluids are independent of density, then, according to Eq. (24), we expect that the quantity on the left side of this equation becomes linear versus $I_{12}/d^6 I_6$ for each isotherm. Moreover, the slope and intercept of each isotherm give $\varepsilon\sigma^6$ and $\varepsilon\sigma^{12}$, respectively, at that temperature. Figure 3 shows the results of such calculations for some given isotherms of argon with densities greater than the Boyle density, ρ_{B} (its value for Ar is 24 mol·L^{-1}). As shown in this figure, the parameters are independent of density for such high densities. However, as shown in Fig. 4, the parameters are significantly density dependent at low densities. Also, if we calculate the EPP parameters by fitting the experimental data of argon in Eq. (24) for a wide density range and then illustrate them against ρ, such density dependences can be seen obviously. (See Figs. 5 and 6.)
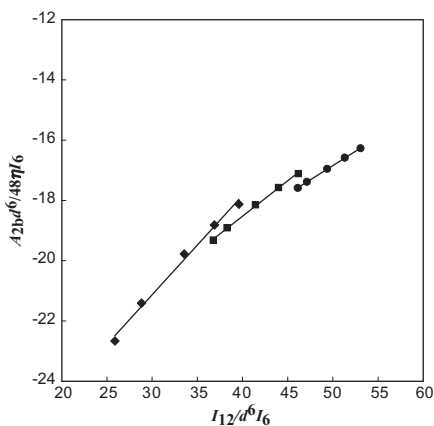
Fig. 3. Search for the density independencies of the EPP parameters for: 100 K (●), 120 K (■), and 140 K (◆), isotherms of argon for densities greater than the Boyle density.
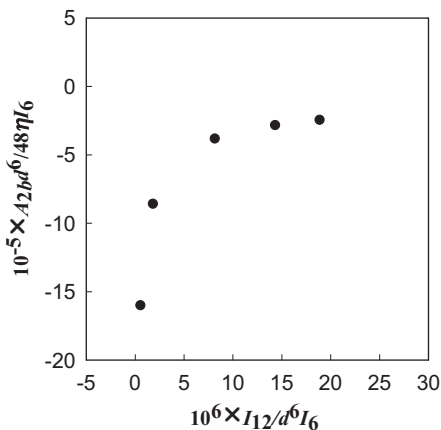
Fig. 4. Search for the density dependence of the EPP parameters for Ar at $T = 200$ K, and the density range of 3.74 to 21.70 mol·L^{-1}. (Note the significant deviation of the curve from linearity.)
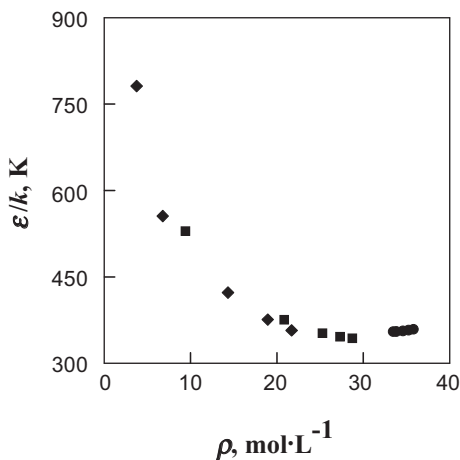
Fig. 5. Search for the density dependence of the ε/k parameters for Ar at $T = 100$ K ($\bullet$), $T = 160$ K ($\blacksquare$), and $T = 220$ K ($\blacklozenge$).
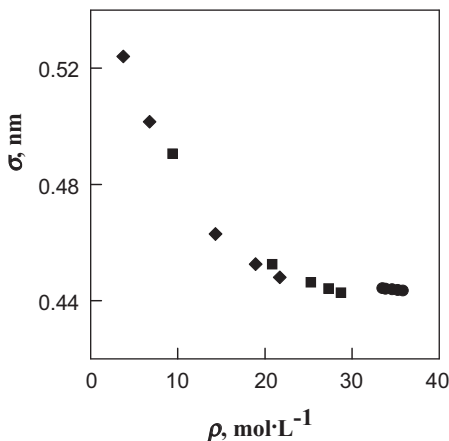
Fig. 6. Search for the density dependences of the σ parameters for Ar at $T = 100$ K ($\bullet$), $T = 160$ K ($\blacksquare$), and $T = 220$ K ($\blacklozenge$).

If we denote the slope and intercept of a line with s and i, respectively, for an isotherm of dense fluid, then the EPP parameters, ε and σ, can be calculated from

$$\varepsilon/k = i^2/s \tag{25}$$

and

$$\sigma = (-s/i)^{1/6} \tag{26}$$

for that isotherm. Once the EPP parameters are calculated, an iterative procedure based on the condition of Eq. (13) should be applied to reach the convergence for the obtained EPP parameters. The results of such calculations are given in Table III for dense argon, along with those for CH_4 and C_2H_6.

In order to evaluate the calculated EPP parameters, they have been used to calculate the internal energy, U, of some given fluids via the following relation which can be derived from Eqs. (18) and (23) for the entropy and Helmholtz free energy of the fluid. Using the thermodynamic equation of $U = A + TS$ one obtains,

$$U = U^{ig} + 48\eta N_A \varepsilon [I_{12}(\eta)/C^{12} - I_6(\eta)/C^6] \tag{27}$$

Table III. EPP Parameters, ε and σ, for Ar, CH_4, and C_2H_6 at Given Temperatures Calculated from Eqs. (25) and (26). (The isolated pair potential parameters of Ar, CH_4, and C_2H_6 are $\varepsilon/k = 125$ K, $\sigma = 0.341$ nm; $\varepsilon/k = 159.7$ K, $\sigma = 0.3706$ nm; and $\varepsilon/k = 227.9$ K, and $\sigma = 0.4407$ nm, respectively [24].)

	Ar		CH_4		C_2H_6	
T (K)	ε/k (K)	σ (nm)	ε/k (K)	σ (nm)	ε/k (K)	σ (nm)
100	365.01	0.440	–	–	–	–
120	331.94	0.451	–	–	–	–
140	291.86	0.469	–	–	–	–
150	–	–	351.56	0.474	–	–
160	253.66	0.492	340.46	0.472	–	–
170	–	–	332.47	0.470	–	–
180	236.21	0.497	330.75	0.465	–	–
200	204.44	0.522	386.33	0.446	746.00	0.524
220	179.10	0.548	–	–	691.76	0.525
240	–	–	–	–	692.63	0.514
260	–	–	–	–	848.60	0.483

where

$$I_n(\eta) = \sum_{i=0}^{4} C_{ni}\eta^i \tag{28}$$

The results of such calculations are given in Table IV. The agreement between the calculated and reported values is satisfactory. The absolute deviation is less than 1.5%.

Table IV. Comparison of the Calculated Internal Energy, U_{cal}, from Eq. (27) with the Reported Values, U_{exp}, for Given Fluids along with the Absolute Percent Deviation for Given Thermodynamic States

| Fluid	p Range (MPa)	T Range (K)	No. of Data points	AAD for internal energy (%)
Ar	6–40	100–180	9	0.60
CH_4	5–25	150–170	9	0.24
C_2H_6	5–25	200–240	9	0.05

4. COMPARISON OF THE AEPP PARAMETERS WITH THOSE OF THE EPP

As mentioned before, differences between the interaction energy of a pair in a dense fluid and that in vacuum can be attributed to the medium's effect on the molecular charge distribution and the long-range interactions among molecules. Because the long-range interactions are included in the AEPP but not in the EPP, comparison of these potentials can explore the effects of the medium and long-range interactions on a given pair in dense fluids, individually. For this reason, the temperature dependences of the potential parameters of Ar are compared in Fig. 6. As shown in this figure, the depth parameter of the AEPP is much larger than that of the EPP at each temperature. Because the long-range interactions are mainly attractive, such a conclusion is reasonable. Since the ε parameter decreases with T in both cases, we may conclude that its temperature dependence is mainly due to the medium effect. When temperature increases, molecules behave more like hard spheres, then the medium effects on charge distribution of each molecule become less important. The parameter σ increases with T for both cases. This parameter for the AEPP is larger than that for the EPP at each temperature. Such a difference is reasonable due to the long-range attractions of the AEPP. Also, we may conclude that the temperature dependence of the parameter σ of AEPP is mainly due to the temperature dependence of the long-range interactions. This is because the temperature dependence of this parameter for the EPP is insignificant (see Fig. 7).

5. A CORRELATION FOR THE CUT-OFF PARAMETER IN TERMS OF THE REDUCED DENSITY

In the Alem and Mansoori approach [16], the hard-sphere diameter d was obtained as a function of density and temperature. By reducing the d with σ as $C = d/\sigma$ (which is called the cut-off parameter), they gave a general expression in terms of the reduced temperature, T^* $(=kT/\varepsilon)$, and density, ρ^* $(=\rho\sigma^3)$ for C. Their reducing parameters are the pair potential parameters. However, we have used the temperature-dependent EPP parameters to reduce T, ρ, and d, for which the results are shown in Fig. 8 for different fluids. There are two important points shown in this figure: first, when the EPP parameters are used to reduce the above mentioned quantities, the cut-off parameter depends on ρ^* only, and second, such a parameter shows a strong principle of corresponding states. The points shown in Fig. 8 are well fitted into the following cubic expression:

$$C = 2.35140 - 1.57421\rho^* + 0.68806\rho^{*2} - 0.10976\rho^{*3} \tag{29}$$
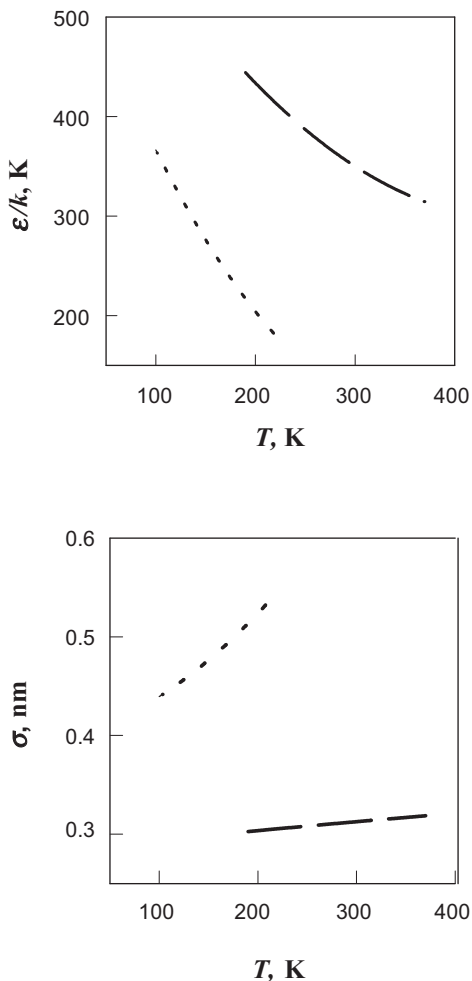
Fig. 7. Comparison of the parameters of the AEPP (– – –) and the EPP (- - -) for Ar at different temperatures.

Having a general relation for the cut-off parameter, along with Eqs. (18) and (23), the thermodynamic properties of a fluid can be calculated, if we know its EPP parameters. Such a calculation has been carried out for Ar, CH_4, and C_2H_6 at different thermodynamic states, and the results are listed in Table V. As shown, the agreement between the calculated and experimental internal energies is quite satisfactory.
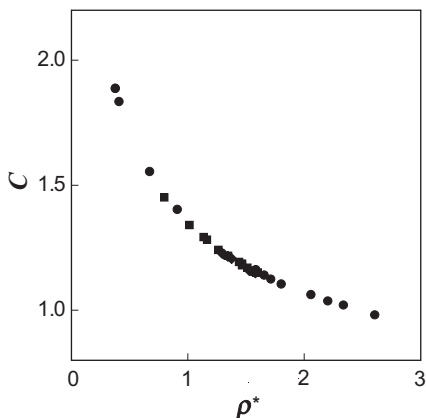
Fig. 8. Cut-off parameter in terms of ρ^* for Ar ($\bullet$), CH_4 ($\blacksquare$), and C_2H_6 ($\blacklozenge$) for different reduced temperatures. The curve is plotted based on Eq. (29).

6. DISCUSSION

In the variational theory (VT), the real system is compared with a hard-sphere model, as the reference system, whose entropy is taken to be exactly equal to that of the real system. In order to have such equality, an appropriate state-dependent molecular diameter has to be attributed to the spheres. Such a diameter may be considered as an "effective hard-sphere diameter," for the real system. In order to not restrict ourselves merely to the non-additive three-body interactions (which is unreasonable for the case of dense fluids) and to obtain the exact configurational energy, we have introduced the concept of "effective pair potential," in which the medium effect is included. We have shown that the EPP parameters for dense fluids are temperature dependent but independent of density.

Table V. Calculated Internal Energy, U_{cal}, via Eqs. (27)–(29), for Given Fluids Compared to Experimental Data, U_{exp}, and the Absolute Percent Deviation, at Given Thermodynamic States

Fluid	p Range (MPa)	T Range (K)	No. of Data points	AAD for internal energy (%)
Ar	6–40	100–180	9	
CH_4	5–25	150–170	9	0.38
C_2H_6	5–25	200–240	9	0.10

However, at low densities the parameters depend on density as well as temperature. Since a part of the repulsive interaction of the real system is excluded and is related to the hard-sphere model, it is expected that the repulsive effect in the EPP becomes smaller than that of the isolated pair, and hence two molecules can approach each other at a closer distance. Also, the well depth of the EPP, ε, is deeper than that of the isolated pair and the intermolecular distance that corresponds to the zero potential, σ, is shorter than that of the isolated pair. These expectations are in accordance with the calculated values of the EPP parameters given in Table III.

The remarkable point is that when the depth parameter of the AEPP and the EPP are compared at a given temperature, as shown in Fig. 7, the former has a much larger depth. Because the long-range interactions are mainly attractive, such a behavior is reasonable. These effects are included in the AEPP but not in the EPP. The other result is that the hard-sphere diameter d decreases with increasing density for each isotherm (Fig. 1). Such a result seems to be reasonable, because the hard spheres cannot penetrate in each other, and the only way to hold more molecules in a given volume is to reduce their diameters.

When the EPP parameters are used to reduce temperature and density, the cut-off parameter, C, depends on ρ^* only and such a parameter shows a strong principle of corresponding states for different fluids at various reduced temperatures. Using the general relation for the cut-off parameter (of Eq. (29)) along with the EPP, the thermodynamic properties of any fluid, such as internal energy, can be calculated, accurately.

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