

Prediction of the Temperature and Density Dependencies of the Parameters of the Average Effective Pair Potential Using Only the LIR Equation of State

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In this work we have studied the density and temperature dependencies of the parameters of the average effective pair potential using linear isotherm regularity (LIR). Such a potential is considered to be the interaction of two nearest neighbor molecules in which all of their longer range interactions are added to it, and also the effect of the medium on the charge distributions of two neighboring molecules is included. We have found that the density dependencies of the parameters of the average effective pair potential are negligible for densities greater than the Boyle density for which the LIR is valid. The parameter σ , the separation at which the potential is zero, increases with temperature while the depth of the potential well, ϵ , decreases. Furthermore, analytical expressions for ϵ and σ are obtained in terms of the LIR parameters. Using these parameters for the average effective pair potential, a strong principle of corresponding states is proposed.

Introduction

Many physical and chemical properties such as the compressibility factor, pressure, lattice energy, vapor pressure, Joule–Thomson coefficient, fugacity, and chemical potential of a system depend strongly on the molecular interaction potential. There have been many attempts to relate the molecular interaction potential to experimentally measurable properties, such as the second virial coefficient, transport properties, and the beam scattering data. Due to the fact that the relation between the (macroscopic) thermodynamic properties and the intermolecular interactions is very complicated, it has been impossible to introduce a unique function for the interaction potential which gives a satisfactory agreement with the experimental data of both the equilibrium and transport properties,¹ except for the noble gases for which accurate pair potential expressions are known.² The second virial coefficient B_2 has been found to be very insensitive to the analytical form of the pair potential unless the temperature range is very large.³ In fact, B_2 is related to the integral of the Mayer f -function times the square of the molecular separation and is independent of the detail of the interaction potential. The investigation of the pair potential is also complicated from the theoretical point of view. For instance at very short separations for which the overlapping of the electronic clouds of molecules is significant, the perturbation theory in which the separated molecules are considered as the unperturbed state is not suitable. For this reason another model known as the united atom perturbation theory has been used for such a case.⁴ The situation for the intermediate separations is even more complicated (see ref 4, p 86) so that for most cases there is no better approximation than adding the repulsion term to the attraction term to get the total pair potential for the entire separation. Theoretically, the most accurate information is available for the long-range attractive wall. For instance for

the noble gases it is obtained as⁵

$$U_{atr} = -\frac{c_6}{r^6} - \frac{c_8}{r^8} - \frac{c_{10}}{r^{10}} \quad (1)$$

where the term $-c_6/r^6$ arises from the summation of the dipole–dipole, dipole-induced dipole, and the London dispersion interactions. The following terms are due to the dipole–quadrupole and quadrupole–quadrupole interactions, respectively (see ref 4, p 62).

The investigation of the molecular interactions in dense systems are more complicated than those of the isolated pair. The complexity is mainly due to the nonadditive contribution of the potential. However, it is known that the major contribution is due to the additive pair potential. Even though the contributions due to nonadditive three-body, four-body, and so on may be significant individually, their algebraic sum is small compared to the additive pair potential contribution. In fact, it has been found that the overall nonadditive contribution is positive, so that an analysis based on pairwise additivity suggests a shallower intermolecular potential well than the true value (see ref 4, p 438).

It is possible to use an effective pair potential along with the pairwise-additive approximation for the potential to calculate the macroscopic properties of a dense system. Of course, one should expect that the parameters of the effective pair potential are different from those of an isolated pair. The effective pair potential of some molecules in a liquid phase is compared with their interaction potential in the gas phase, in which the former has a shallower depth (see ref 1, pp 322–5).

Our aim in this work is to predict the temperature and density dependencies of the parameters of the average effective Lennard-Jones (12, 6) (LJ(12,6)) pair potential for dense fluids. The obtained results have been used to present a strong principle of corresponding states. Assuming the pairwise-additivity approximation for the fluid potential and using the statistical

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mechanical expressions for the internal energy U and the compressibility factor $Z = p/\rho RT$, the following ratio

$$\frac{p/\rho RT}{U} = -\frac{2}{NkT} \frac{\int_0^\infty [(\sigma/r)^6 - 2(\sigma/r)^{12}]g(r)r^2 dr}{\int_0^\infty [(\sigma/r)^6 - (\sigma/r)^{12}]g(r)r^2 dr} \quad (2)$$

which depends only on the separation at which the potential is zero, σ , will be obtained, if the effective pair potential is assumed to be the LJ(12,6). $g(r)$ is the radial distribution function which can be obtained experimentally. Equation 2 was used to obtain the parameters of the effective pair potential for the liquid argon.⁶ However, such a method is limited to simple fluids and was used for a very short temperature range. We shall present a method which is much simpler and more practical to use for all types of dense fluids and gives analytical functions for temperature dependencies of the parameters of the average effective pair potential parameters. In our approach only the experimental p - v - T data are needed. One should note that the calculated potential in this work is different from the effective pair potential given in the previous works, and we shall see that the former is more practical to use and is more meaningful, physically.

Linear Isotherm Regularity in the Reduced Form

Using the LJ(12,6) potential for the effective pair potential along with the pairwise-additive approximation for the molecular interactions in dense fluids and considering only the nearest neighbor interactions, linear isothermal regularity (LIR) was derived from the exact thermodynamic relations as⁷

$$(Z - 1)v^2 = A + B\rho^2 \quad (3)$$

where $\rho = 1/v$ is the number density and A and B are the temperature dependent parameters. It was experimentally found that the regularity (LIR) holds for all types of fluids, including nonpolar, polar, hydrogen bonded, and quantum fluids, for densities greater than the Boyle density ($\rho_B \approx 1.8\rho_c$, where ρ_c is the critical density) and temperatures less than twice the Boyle temperature, the temperature at which the second virial coefficient is zero. According to the one-fluid approximation,⁸ the regularity holds for the dense fluid mixtures as well.^{9,10} LIR is able to predict many experimentally known regularities for dense pure fluids and fluid mixtures.¹¹⁻¹³ On the basis of a simple model, the temperature dependencies of the LIR parameters are found to be⁷

$$A = A_2 - \frac{A_1}{RT} \quad (4)$$

$$B = -\frac{B_1}{RT} \quad (5)$$

where A_1 and B_1 are related to the attraction and repulsion terms of the average effective pair potential and A_2 is related to the nonideal thermal pressure. It is assumed that the total potential energy among N molecules is proportional to $(N/2)\epsilon[(\sigma/\bar{r})^{12} - (\sigma/\bar{r})^6]$, where \bar{r} is the average nearest neighbor separation. The differentiation of the total potential energy with respect to volume gives the internal pressure as $A_1\rho^3 - B_1\rho^5$, where

$$A_1 \propto \epsilon\sigma^6 \quad (6)$$

$$B_1 \propto 2\epsilon\sigma^{12} \quad (7)$$

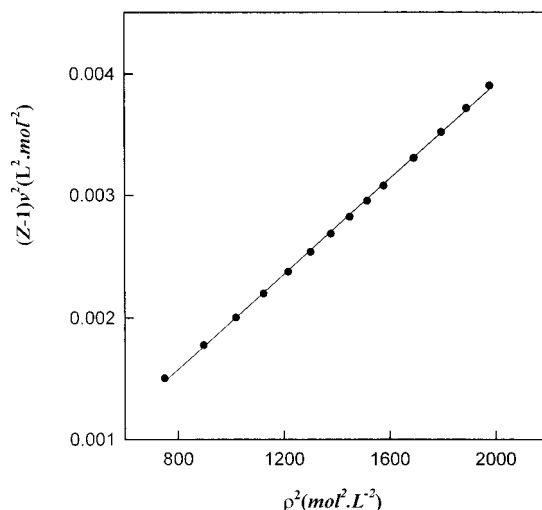


Figure 1. Checking the linearity of $(Z - 1)v^2$ versus ρ^2 , for Ar at 37 °C.

(note that the proportionality constants of eqs 6 and 7 are the same, except for the factor of 2). Using the van der Waals equation of state, A_2 is equal to $4b^2$ (see ref 9), where b is the covolume; then

$$A_2 \propto \sigma^6 \quad (8)$$

where ϵ and σ are the parameters of the average effective LJ pair potential.

If we assume that the proportionality constants of eqs 6–8 are independent of the detail of molecular structure, then eqs 4 and 5 may be written in the reduced forms as

$$A^* = \frac{A}{\sigma^6} = a - \frac{b}{T^*} \quad (9)$$

$$B^* = \frac{B}{\sigma^{12}} = \frac{c}{T^*} \quad (10)$$

where a – c are independent of temperature and molecular structure and $T^* = kT/\epsilon$. According to eqs 9 and 10, we may expect that the reduced LIR parameters (A^* and B^*) would be linear with respect to $1/T^*$ and the same for all fluids. To test such an expectation, we have to find the parameters of the average effective pair potential.

Density Dependencies of the Parameters of the Average Effective Pair Potential

According to the LIR equation of state along with eqs 4 and 5

$$(Z - 1)v^2 = \left(A_2 - \frac{A_1}{RT}\right) + \frac{B_1}{RT}\rho^2 \quad (11)$$

The linear behavior of $(Z - 1)v^2$ versus ρ^2 for each isotherm indicates that the parameters of the average effective pair potential, σ and ϵ , are independent of density. This linearity is shown in Figure 1 for the supercritical isotherm of argon at 37 °C for the density range of 24–48 mol·L⁻¹ (the widest density range for which the experimental data exist). The linearity of $(Z - 1)v^2$ versus ρ^2 in such a wide density range is quite obvious (see Figure 1). Such linearity reveals the fact that the parameters of the average effective pair potential (ϵ, σ) are independent of density. As mentioned in ref 9, A_2 is given as $A_2 = b/\rho(1 - b\rho)$. According to the van der Waals equation of state (EOS),

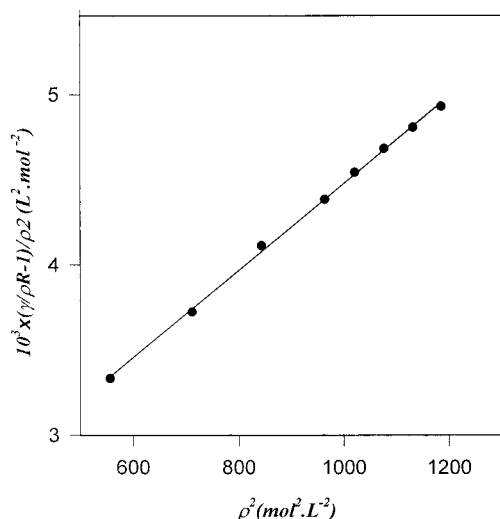


Figure 2. Linearity predicted according to eq 12 for Ar in the temperature range of 90–140 K.

the density range of interest occurs around the minimum of A_2 , $b\rho = 1/2$. The first approximation is to take A_2 as the bottom of the function $b/\rho(1 - b\rho)$, which is equal to $4b^2$. However, a better approximation is to take $A_2 = A_0 + B_0\rho^2$. The exact expression for A_2 is given as⁷ $A_2 = (1/\rho^2)((\gamma/R\rho) - 1)$, where γ is the thermal pressure coefficient, $(\partial p/\partial T)_v$, and R is the gas constant. Therefore, the combination of these two expressions for A_2 gives

$$\frac{1}{\rho^2} \left(\frac{\gamma}{R\rho} - 1 \right) = A_0 + B_0\rho^2 \quad (12)$$

Using the experimental data for γ and ρ , one can check the validity of eq 12. We have used the experimental data for Ar⁸ in a small temperature range (90–140 K) to test the validity. The result is shown in Figure 2. The small temperature range is used due to the fact that A_2 , and hence A_0 and B_0 , is expected to be temperature dependent. Using the expression $A_0 + B_0\rho^2$ for A_2 , LIR becomes

$$(Z - 1)v^2 = \left(A_0 - \frac{A_1}{RT} \right) + \left(B_0 + \frac{B_1}{RT} \right) \rho^2 \quad (13)$$

in which the linearity still holds, and the appearance of a small nonzero intercept in the plot of B against $1/T$ is in accordance with eq 13. However, the nonzero intercept becomes significant for mixtures.¹⁰ The linearity of $(Z - 1)v^2$ versus ρ^2 according to eq 13 again indicates the fact that the parameters σ and ϵ have no density dependencies.

One may claim that the density dependencies of the parameters are in such a way that their dependencies cancel each other out exactly. Due to the fact that different powers of σ appears in A_1 and B_1 and only one parameter appears in A_2 (see eqs 6–8), we may rule out such a claim.

Temperature Dependencies of the Parameters of the Average Effective Pair Potential

According to the distribution function theory, the potential parameters of the effective pair potential are temperature independent only for a short temperature interval (about 30 °C) (see ref 6, p 187). This is also found to be true for the parameters of the average effective pair potential, ϵ and σ , which may be easily verified by the LIR. The parameters A and B of the LIR are plotted versus $1/T$ for some typical fluids Ar,¹⁴ N₂,¹⁵ CO₂,¹⁶

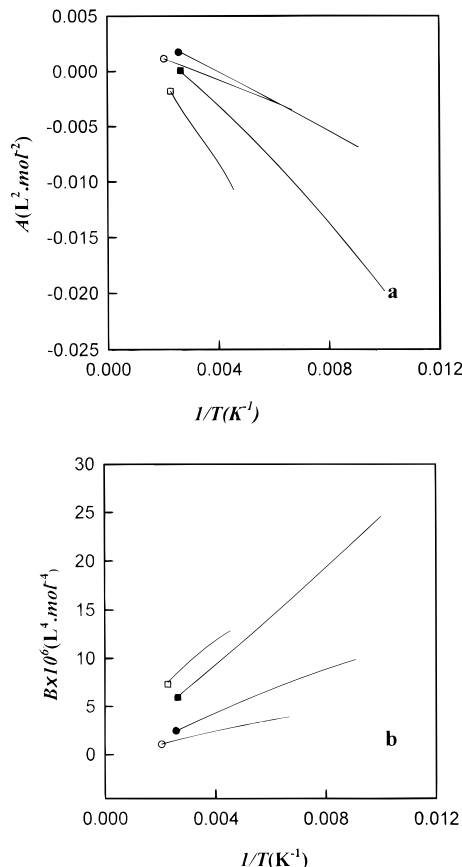


Figure 3. (a) Parameter A of LIR versus $1/T$ for Ar (O), N₂ (●), CO₂ (□), and CH₄ (■). (b) The same as a for the B parameter.

and CH₄,¹⁷ in Figure 3, which is linear for any short temperature range ($\Delta T \approx 30$ K) even though some deviations from linearity are obvious, for the wide temperature range shown in this figure. The values of A_0 , A_1 , B_0 , and B_1 obtained from such lines for a short given temperature interval may be attributed to the average temperature of that interval.

By knowing the values of A_1 and B_1 , the combination of eqs 6 and 7 gives

$$2A_1^2/B_1 = \epsilon \quad (14)$$

$$(B_1/2A_1)^{1/6} = \sigma \quad (15)$$

which helps us to find out the variation of ϵ and σ with temperature. These results are shown in Figure 4 for Ar, N₂, CO₂, and CH₄.

Strong Principle of Corresponding States

If we assume that the isolated pair potential parameters can be used instead of the parameters of the average effective pair potential and ignore the temperature dependency of A_2 , according to eqs 9 and 10, we would expect that A^* and B^* versus $1/T^*$ become linear and the lines become coincident for all different fluids. Since such assumptions are not true, when we use the parameters of the isolated pair potential to reduce A , B , and T , we will not observe such a coincidence and linearity. In order to observe such a coincidence, we have to use the parameters of the average effective pair potential. Since the temperature dependencies of A_0 and B_0 in eq 12 are ignored in LIR, we have plotted $(A - A_0)/\sigma^6$ and $(B - B_0)/\sigma^{12}$ against $1/T^*$ in Figure 5, which are quite linear and superimposed with zero intercepts as expected. Equations 3, 6, 7, and 13 may be

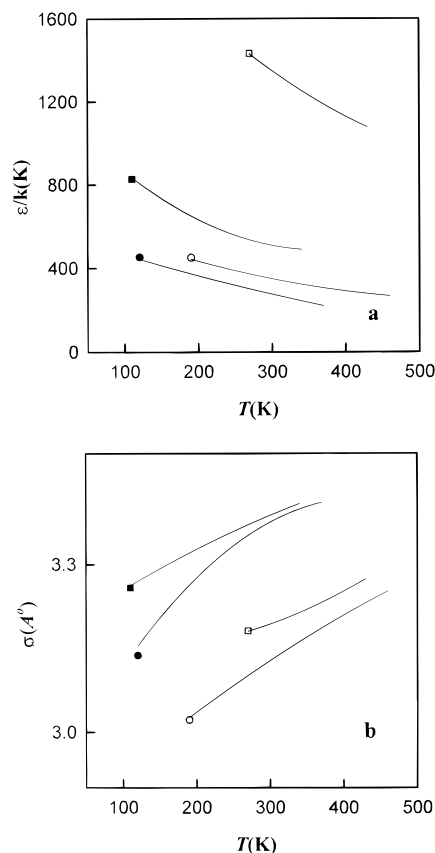


Figure 4. (a) Potential well of the average effective pair potential, ϵ , versus T for Ar (○), N₂ (●), CO₂ (□), and CH₄ (■). (b) The same as a for the separation at which the potential is zero, σ .

combined to give

$$(A - A_0)/\sigma^6 = \alpha/T^* \quad (16)$$

$$(B - B_0)/\sigma^{12} = 2\beta/T^* \quad (17)$$

where α and β are constants. The values of α and 2β are found from Figure 5 to be -8.30 and $+8.30$, respectively. Note that according to LIR, the total potential, U , is given by $(U/2)z(\rho) - \{4\epsilon[(\sigma/r)^9 - (\sigma/r)^3]\}$ (see ref 7), where $z(\rho)$ is the coordination number, in which $z(\rho) \propto \rho$ and $\bar{r} \propto \rho^{-1/3}$. All proportionality factors which appear in the first term and hence in B_1 will exactly appear in the second term and hence in A_1 . For this reason, we may expect that the magnitudes of α and 2β are the same. Such behavior (Figure 5) suggests a strong principle of corresponding states for dense fluids.

Calculation of the Potential Parameters Using the Strong Principle of Corresponding States

Now, by having the universal eqs 16 and 17, we may calculate the parameters of the average effective pair potential for any dense fluid at any temperature. Equations 16 and 17 may be combined as

$$\sigma = \left[\frac{\alpha(B - B_0)}{2\beta(A - A_0)} \right]^{1/6} \quad (18)$$

$$\epsilon/k = \frac{T}{\alpha} \frac{(A - A_0)}{\left[\frac{\alpha(B - B_0)}{2\beta(A - A_0)} \right]} \quad (19)$$

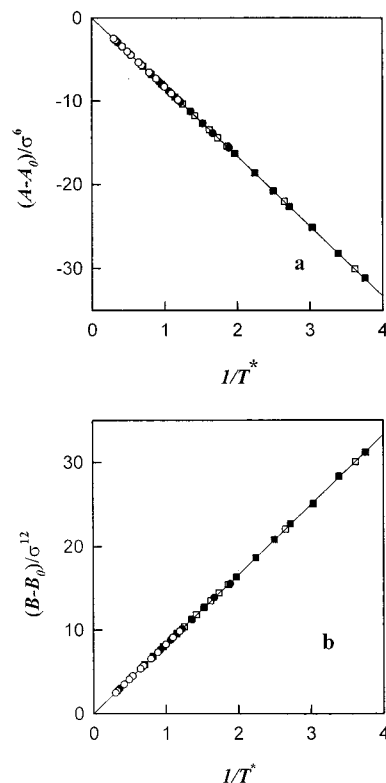


Figure 5. (a) Strong principle of corresponding states in accordance with eq 16 for Ar (○), N₂ (●), CO₂ (□), and CH₄ (■). (b) Similar behavior for B^* according to eq 17.

from which the parameters of the average effective pair potential may be calculated. For such a calculation we need only the experimental $p-v-T$ data to obtain the values of A , B , A_0 , and B_0 from LIR. The results for two fluids are summarized in Table 1.^{18,19} This is an easy and remarkable approach from which one can calculate the microscopic parameters (ϵ, σ) from the measurable macroscopic properties, i.e., $p-v-T$ data.

As an experimental test, the density at the common compression factor point, ρ_{oz} , which is related to σ , can be used as an efficient support for the validity of the temperature dependency of σ . Any fluid shows a common intersection point for the compression factor, Z , versus ρ for different isotherms. The ρ_{oz} is related to σ by the following relation¹¹

$$\rho_{oz} = (A_1/B_1)^{1/2} = (1/2^6)N\sigma^{-3} \quad (20)$$

where N is the Avogadro number. The calculated value of σ at any temperature is used to calculate $\rho_{oz,calc}$, which is compared with the experimental value in Table 2. As is shown, the differences are less than 1.4%.

Discussion

The LIR equation of state has been used to find the parameters of the average effective pair potential. In LIR, it is assumed that only the nearest neighbor interactions exist. In other words, the entire potential energy of the fluid is attributed to its nearest neighbor interactions. It means that the longer range interactions of a given neighboring pair with other molecules, which are mainly attractions, and the effect of fluid medium on the charge distributions of the pair are both added to the potential energy of the isolated nearest neighbor pair. We have considered such a pair potential as the average effective pair potential. For the defined average effective pair potential in this work the

TABLE 1: Parameters of the Average Effective Pair Potential, ϵ and σ , for R152a and C₂H₄ at Some Given Temperatures, Calculated from Equations 18 and 19

R152a ¹⁸			C ₂ H ₄ ¹⁹		
T, K	$\epsilon/k, K$	$\sigma, \text{\AA}$	T, K	$\epsilon/k, K$	$\sigma, \text{\AA}$
233	2386	3.88	115	1660.2	3.49
248	2279.8	3.90	130	1636.4	3.50
263	2179.6	3.91	175	1513.0	3.56
278	2066.6	3.91	212	1338.8	3.58
293	1985.6	3.94	266	1122.2	3.58
323	1799.6	3.94	278	1070.6	3.60

TABLE 2: Comparison of the Density of the Calculated Common Compression Point $\rho_{\text{oz,calc}}$ from Equations 18 and 20, with the Experimental Value, $\rho_{\text{oz,expt}}$ for Argon at Different Temperatures

T, K	$\rho_{\text{oz}}, \text{mol}\cdot\text{L}^{-1}$		T, K	$\rho_{\text{oz}}, \text{mol}\cdot\text{L}^{-1}$	
	calc	expt		calc	expt
190	42.54	41.95	340	37.22	37.22
225	41.49	41.47	400	35.46	35.27
270	39.08	39.08			

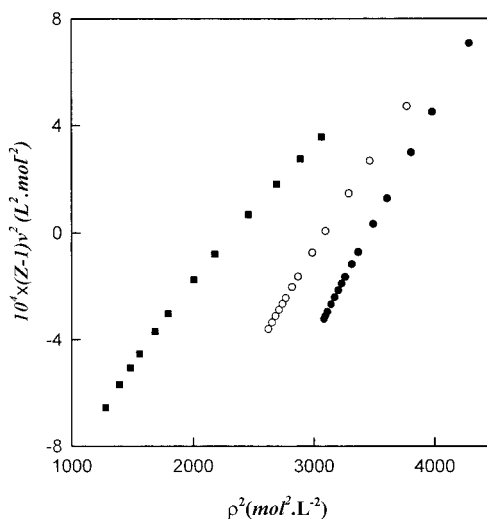
following points are expected: (1) The fact that all the long-range interactions are included, we expect that the potential well depth becomes deeper than that of the isolated pair potential, which is in accordance with our results in Figure 4. (2) Since the effect of fluid medium on the electronic distribution of molecules is included, the total potential energy of the fluid can be written as the sum of all average effective pair interaction energies, exactly. Therefore, the pairwise additivity of the potential energy in terms of the average effective pair potential is an exact treatment. (3) Since the total potential energy of fluid can exactly be written as

$$U = \frac{N}{2} \bar{u}_z$$

where \bar{u} is the average effective pair potential, N is the number of molecules, and z is the average coordination number, \bar{u} sounds quite meaningful.

There have been many attempts to obtain the effective pair potential.⁶ One sample of such an attempt is eq 2, in which the macroscopic properties are formulated in terms of the pair correlation function. Such a formulation is based on the pairwise additive approximation for the potential energy in terms of the isolated pair potential. Due to the interaction of the many-body forces in the condensed system, the deviation from such an approximation is expected to be significant. To force such a formulation to give accurate macroscopic properties, one has to consider a state dependent pair potential which is called the effective pair potential. For another type of such works one may refer to the work of Mikolaj and Pings (see ref 6, p 237), in which the PY approximation is used to obtain the state dependent effective pair potential. It seems that such an effective pair potential is simply defined in such a way that the errors do compensate, exactly. Unlike the average effective pair potential introduced in this work, we may conclude that the effective pair potential has no physical sense.

In this work we have investigated the density and temperature dependencies of the parameters of the average effective pair potential for the dense fluids. As we mentioned before, these parameters are density independent for densities larger than the Boyle density. However, only in the case of the strongly hydrogen bonded systems such as water, especially at high temperatures for which the deviation of $(Z-1)v^2$ versus ρ^2 from the linearity is obvious (see Figure 6), we may expect

**Figure 6.** Obvious deviation from LIR linearity at some temperatures for the strongly hydrogen bonded fluid (H₂O) which reveals the density dependencies of the parameters of the average effective pair potential. The isotherms are 273.15 (○), 423.15 (●), and 623.15 K (■).

that the parameters of the average effective pair potential depend on density as well as temperature.

Equations 18 and 19 provide us with a useful tool for obtaining the potential parameters. These equations predict the temperature dependency of the ϵ and σ parameters. As shown in Figure 4, the parameter σ increases with temperature. If we treat the electrons of an atom as an electron gas which is uniformly and spherically distributed around the nucleus, we may expect that the volume of the electron gas (atom) increases with temperature at any given pressure. Such a simple argument predicts that the radius of the atom, and hence σ , increases with temperature. Furthermore, the separation at the minimum of the average effective potential well, r_m , can be calculated from the density of the common compression point, ρ_{oz} .¹¹ Such a calculation predicts that r_m increases with temperature [note that for the LJ(12,6) potential $r_m = 2^{1/6}\sigma$]. For instance the value of ρ_{oz} for Ar is 44.1 mol·L⁻¹ for the temperature range of 100–140 K, while its value is 33.6 mol·L⁻¹ for the range of 400–600 K; see Table 1 in ref 11. [Note that $r_m^3 \propto 1/\rho_{\text{oz}}$]. All of these results are qualitatively in agreement with our result presented in Figure 4b.

When the parameter σ increases, the repulsive branch of the potential shifts toward the longer separations. Hence, it will intersect with the attractive branch at a longer separation, which gives a shallower well. Therefore, we may expect that as σ increases with T, the potential well, ϵ , decreases. Such an expectation is in accordance with our result given in Figure 4a.

We have presented the parameters of the average effective pair potential by eqs 18 and 19. In previous paragraphs, we have shown that the results obtained from these equations are satisfactory (at least qualitatively). In order to test these equations, quantitatively, we have compared the common compression factor point obtained from these equations with the experiment; the results are summarized in Table 2, which shows excellent agreement. However, a severe test is to use our calculated potential parameters, given by eqs 18 and 19, to calculate the transport properties and then compare them with the experimental data. This remains for the future.

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