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The Direct Correlation Function and Its Interpretation via the Linear Isotherm Regularity

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The contributions of all non-ideally effects which arise from excluded volume, attractive and repulsive forces have been separated and investigated in the direct correlation function, DCF, using the Linear Isotherm Regularity, LIR for dense fluids. In such away we have shown that the core of the DCF ($0 < r < \sigma$) is related to the geometric effect which arises from the excluded volume, while the intermolecular interactions have an important role in the tail ($\sigma < r < \infty$). Also mathematical expressions for the core and tail of the DCF have been presented via the bulk modulus and the LIR. These new expressions beside of satisfying the experimental DCF can also generate the structural factor of fluids. The other issue that we discuss in this article and should be noticed separately, is the effective pair potential. The effective pair potential is the intermolecular pair interactions in presence of the other molecules of the system. We have shown that the well depth of such an effective pair potential is shallower than that of the isolated pair which is in accordance with the reported results in the literatures. Our results suggest that the net effect of the medium on interactions between two molecules is positive (repulsion).

KEYWORDS: direct correlation function, effective pair potential, linear isotherm regularity, structure factor

§1. Introduction

The DCF, $c(r)$, is an important function in the theory of structural liquids and has been studied extensively by many authors, for example Kambayashi and Hiwatari in a great deal.[1)] They have calculated the bridge function and therefore the DCF for soft shpere model. The DCF is related to the total pair correlation function, $h(r)$, which may be straightforwardly measured in diffraction experiments and by the computer simulations, and lies at the heart of the modern density functional theories.[2,3)] The total correlation function, $h(r)$, represents the total effect of molecule 1 on molecule 2 at a separation r and goes to zero in the limit of $r \to \infty$, in which there is no correlation. For normal spherical fluids both functions [$c(r)$ and $h(r)$] depend only on separation and may be related to each other by using Ornestion-Zernick equation, O.Z.[4,5)] In O.Z. equation the total correlation function between molecules 1 and 2 is separated into two contributions: 1) a direct effect of 1 on 2 which has a short range [roughly the same as that of the isolated pair potential, $\phi(r)$] and 2) an indirect effect by which molecule 1 is influenced by some other molecule 3 that in turn, affects on the correlation with the molecule 2. This indirect effect is the sum of all contributions due to all other molecules and should be averaged over the volume of the system. Therefore in the O.Z. equation the DCF is defined as,[6)]

$$h(r_{12}) = c(r_{12}) + \rho \int h(r_{23})c(r_{13})\mathrm{d}r_3 \qquad (1)$$

where the first term is the direct correlation and the second term is the indirect contribution, which includes direct effect between 1 and 3, 3 and 4, and so on. For a dilute gas all the indirect effects reduce to zero and $h(r) = c(r) = \exp(-\beta\phi(r)) - 1$, where $\beta = 1/kT$ and $\phi(r)$ is the isolated pair potential. Since $c(r)$ is a short range function [compare to $h(r)$] the result of the theory of liquids based on such a function is not very sensitive to the accuracy of the approximations involved. This function is always short range even in the critical region in which $h(r)$ is a long-range function and unlike the total correlation function, the direct correlation function has no bumping. Also it is possible to obtain the thermodynamic properties via $c(r)$ without using the pair wise additivity approximation for the configuration potential[6)] which is the main approximation in the theory based on the pair correlation function, $g(r)$. In spite of the mentioned advantages, the above definition, eq. (1), does not give any simple physical interpretation for $c(r)$ in terms of the probability concept. Even though it is clear that $c(r)$ goes to zero when $r \to \infty$, but the behavior of $c(r)$ when r goes to zero is unknown. Fisher[7)] said "in the absence of an independent theory enabling one to calculate $c(r)$ in terms of molecular parameters eq. (1) is really a definition of the DCF and we will adopt with that, although O.Z. had been regarded $c(r)$ as a more basic function, closer relation to the intermolecular forces." Therefore the formal definition of the DCF is just a mathematical expression and has no obvious physical interpretation, specially for $r < \sigma$, where σ is the molecular diameter. It is known that in a real fluid,

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the DCF has a negative part for $r < \sigma$ and rises steeply around $r = \sigma$, and then looks very much like the Mayer-f function, although it is somewhat smaller. When the temperature is low, the positive part of $c(r)$, $r > \sigma$, is significant while for high temperatures, the negative part of $c(r)$ has the most contribution, similar to that of its hard core.$^{8)}$ The DCF for $r < \sigma$ is similar to that of the Percus Yevick, PY, approximation for the hard sphere fluid.$^{9)}$

In this article we try to interpret the DCF from the molecular viewpoint using the Linear Isotherm Regularity. We shall present mathematical expressions for the DCF and compare it with the experimental data. Although the agreement of our results with experimental data is so good, but we do not claim that the presented expression for the DCF is exact and completed. Our aim in this work is just the physical interpretation and presentation of a qualitative expression not quantitative for the DCF. Of course we show that the obtained DCF can generated the structural factor, $S(k)$ that is very sensitive function to small error in the DCF. Finally, the effective pair potential is introduced and calculated by using the obtained DCF.

Before to interpret DCF, which has been an obscure function among the correlation functions for about a century, we should introduce the LIR equation of state briefly.

§2. Linear Isotherm Regularity, LIR

A general regularity was reported for pure dense fluids,$^{10,11)}$ according to which $(Z-1)v^2$ is linear with respect to ρ^2 for each isotherm as,

$$(Z-1)v^2 = A + B\rho^2. \tag{2}$$

Where Z, is the compressibility factor, $\rho = 1/v$ is the molar density, and A and B are the temperature dependent parameters as follows,

$$A = A'' - \frac{A'}{RT}$$
$$B = \frac{B'}{RT}. \tag{3}$$

In which A' and B' are related to the intermolecular attractive and repulsive forces, respectively, while A'' is related to the non-ideal thermal pressure, and RT has its usual meaning. This regularity holds for densities greater than the Boyle density and temperatures lower than twice of the Boyle temperature.

§3. Physical Interpretation of the DCF

We know that the structure of a dense fluid is essentially a geometric packing problem. In fact the repulsive forces have important role in the determination of the fluid structure and the cohesive or attractive interactions in fluid just define the fluid volume.$^{12)}$ The consequent of these facts for the direct correlation function is also clear$^{9)}$ via the compressibility equation. To show that, it is convenient to spilt the compressibility equation of state into long- and short-range terms as,

$$B_{\rm r} = \frac{1}{kT}\left(\frac{\partial p}{\partial \rho}\right)_T$$
$$= 1 - 4\pi\rho\left[\underbrace{\int_0^\sigma c(r)r^2{\rm d}r}_{\rm core} + \underbrace{\int_\sigma^\infty c(r)r^2{\rm d}r}_{\rm tail}\right] \tag{4}$$

where $B_{\rm r}$ is the reduced bulk modulus. The first and second integrals respectively represent the contribution of the core and tail of the DCF in $B_{\rm r}$. At high temperatures the weak positive tail of the DCF is washed out and the behavior of the fluid is define essentially by the hard-core effects [first integral of eq. (4)]. In such a condition the Percus Yevick, PY, approximation is expected to give a good description of the equation of state for real fluid. In contrast at low temperatures the positive tail of the DCF becomes significant and the intermolecular interactions have an important role in determining the thermodynamic properties. To clarify these points we use the LIR and obtain $B_{\rm r}$ as,$^{12)}$

$$B_{\rm r} = 1 + 3A''\rho^2 - \frac{3A'}{RT}\rho^2 + \frac{5B'}{RT}\rho^4. \tag{5}$$

When temperature is very high, the potential energy between molecules is negligible compare to the kinetic energy and consequently the contributions of $3A'\rho^2/RT$ and $5B'\rho^4/RT$ in $B_{\rm r}$ become negligible in comparison with $3A''\rho^2$. In such a condition we may write $B_{\rm r}$ as,

$$B_{\rm r} = 1 + 3A''\rho^2. \tag{6}$$

On the other hands, at such a condition the positive part of the DCF is very small and eq. (4) reduces to,

$$B_{\rm r} = 1 - 4\pi\rho\int_0^\sigma c(r)r^2{\rm d}r. \tag{7}$$

Comparison of eqs. (6) with (7) at such a condition, i.e. at that very high temperatures, gives,

$$-\frac{3A''\rho}{4\pi} = \int_0^\sigma c(r)r^2{\rm d}r. \tag{8}$$

In such a way the short-range form of the DCF which has been unknown quantity from the physical point of view, may be interpreted using the LIR. According to eq. (8), the core of the DCF is proportional to A''. Since A'' in the LIR is related to the covolume and geometric effects, we may conclude that the contribution of the core of the DCF depends on the excluded volume. This equation also shows that when the density increases the contribution of the core in the DCF also increases. We know that if the system were hard, the only contribution of the DCF would be such a covolume term. Although the real systems are not hard, but at very high temperature and densities, they show the hard like behavior. At very high densities, because of the hardness nature of fluid, the DCF doesn't depend on temperature (like the hard sphere fluid for which the DCF is density dependent only$^{9)}$).

It can also be shown that the A'' is proportional to b^2, where b is the van der Waals co volume.$^{11)}$ Hence we may say that with increasing the molecular size, the contribution of the core in the DCF also increases. According to our approach, the contribution of the DCF at short range ($r < \sigma$) is related to the geometric effect, which arises from the excluded volume. It is clear that such a contribution is both temperature and density dependent, except when the behavior of the system becomes similar to hard sphere (note that A'' is related to non-ideal thermal pressure and expected to be temperature dependent).

Now return to eq. (4) and consider the second integral, the tail contribution. This contribution of the DCF is very similar to the positive part of mayer-f function although it is somewhat smaller. At very low-density limit these two functions (the DCF and Mayer-f function) are completely identical. The similarity of these two functions is to some extend that Rushbrooke *et al.*[14] gave for the DCF a density expression of the Mayer-f function. However, the positive part of the DCF is related to the intermolecular interactions and becomes important when temperature decreases. Comparison of eqs. (4) and (5) shows that if the contribution of the excluded volume can be attributed only to the short range, then the tail of the DCF is merely related to the LIR potential parameters as,

$$\frac{-3A'}{RT}\rho^2 + \frac{5B'}{RT}\rho^4 = -4\pi\rho\int_\sigma^\infty c(r)r^2\mathrm{d}r. \tag{9}$$

As it is clear this contribution is both density and temperature dependent and it is easy to show that it decreases when temperature and density increases.[8] We know that for the thermodynamic states at which the system behaves like hard sphere fluid the tail contribution becomes negligible. In order to understand the physical meaning of that, let us use the LIR. At first we introduce an average nearest neighbors separation at any thermodynamic state for the system (like the assumption made in the LIR derivation,[11]) as $\bar{r} = (1/\rho N)^{1/3}$. Therefore we have,

$$-\frac{3A'}{kT(\bar{r})^6} + \frac{5B'}{kT(\bar{r})^{12}} = -4\pi\rho\int_\sigma^\infty c(r)r^2\mathrm{d}r. \tag{10}$$

It is also possible to define an average value for the DCF at each thermodynamic state, $\bar{c}(r)$ in such a way that eq. (10) can be written as,

$$-\frac{3A'}{RT(\bar{r})^6} + \frac{5B'}{RT(\bar{r})^{12}} = -4\pi\rho\bar{c}(r)\int_\sigma^\infty r^2\mathrm{d}r. \tag{11}$$

If we assume that the excluded volume is negligible compare to the fluid volume, the integral of eq. (11) gives volume and reduces to (this is just an assumption which is accurate when $\rho \to 0$. However, since we are looking for qualitative behavior of the DCF, such an assumption is reasonable),

$$\frac{-3A'}{(\bar{r})^6} + \frac{5B'}{(\bar{r})^{12}} = -RT\bar{c}(r). \tag{12}$$

Comparing eq. (12) with the total potential energy, which is given by the LIR[11] as,

$$\frac{U}{N} = \frac{-A'}{2(\bar{r})^6} + \frac{B'}{4(\bar{r})^{12}} \tag{13}$$

shows that $-kT\bar{c}(r)$ is the representation of the intermolecular forces at high density, at which the LIR is valid. But one can see that the coefficients of the repulsion and attraction terms of eqs. (12) and (13), are not exactly the same. The differences between these coefficients may be considered as the screening effect of the potential in eq. (12) at high density. We may verify such a conclusion by considering the behavior of the DCF at very low density as,[8]

$$h(r) = c(r) = \exp(-\beta\phi(r)) - 1 \quad \rho \to 0. \tag{14}$$

At very high temperatures, the exponential term of eq. (14) may be expanded as,

$$\exp(-\beta\phi(r)) = 1 - \beta\phi(r) + \cdots$$

and then

$$c(r) = -\beta\phi(r)$$

or

$$-kTc(r) = \phi(r). \tag{15}$$

Therefore at very low density when temperature is high the term $-kTc(r)$ represents the isolated pair potential and now we have shown by some approximations that at very high density $-kT\bar{c}(r)$ is also a representation of the effective or screened pair potential. In such away we may conclude that the DCF at least for $r > \sigma$ is always related to the intermolecular interactions. But this intermolecular interactions at high densities are screened due to the medium effect and it is obvious that the screening effect reduces when density decreases and it becomes zero when $\rho \to 0$ [eq. (15)]. We shall investigate and explain the screening potential in more detail later in this work.

As a result, we can say that the core of the DCF is related to the geometric effect and its tail is the representation of the interactions between two molecules in presence of $N - 2$ other molecules. As we know at very high densities the core contribution is very important and therefore the excluded volume is the dominated factor in the DCF, while at low density and temperature the intermolecular interactions have an important role.

To interpret the DCF more clearly, consider a system at constant temperature and density and insert a molecule in a position at which the fluid is uniform, $g(r) = 1$. The insertion of this molecule may be considered as a perturbing factor for its neighboring molecules. If the density is high, the values of bulk modulus and consequently $(\partial p/\partial\rho)_T$ are large and such a condition corresponds to high stability of the medium against this perturbation. At such a high density and stability the intermolecular interactions between the inserted molecule and neighboring molecules do not have an important role, while the co volume effect has significant contribution. It means that at very high densities, the intermolecular interactions are highly and effectively screened, therefore the contribution of the tail is very small and the molecular ordering is mainly due to the excluded volume. In contrast, at very low densities when $(\partial p/\partial\rho)_T$ is small, the system is very sensible to small perturbation, and the insertion of a molecule will easily change the ordering of its neighboring molecules. In such a condition the little-screened potential has an important effect on its neighboring molecular ordering. But, because of the large volume of the system, the excluded volume is negligible. Therefore the core contribution in the DCF is very small and its positive part, which is related to the intermolecular interactions, is significant. It is clear that the variation of the DCF with the thermodynamic state may be understood from such an interpretation. By increasing the temperature and density the contribution of the intermolecular interactions in the DCF becomes less and the excluded volume has an important role, therefore the positive part of the DCF decreases and that of the core increases.

§4. Mathematical Expressions for the DCF

As we know, the DCF may be obtained experimentally by the neutron scattering or X-ray diffraction,[15] but we want to obtain this function using an easily available thermodynamic property such as bulk modulus. Since the behavior of the DCF in short range, $0 < r < \sigma$, is essentially different from its long range behavior, $\sigma < r < \infty$, in the molecular point of view (the behavior of the DCF at short range distances is mainly related to the co-volume while in the long distances to the intermolecular interactions). We consider two different expressions for the DCF, one for $0 < r < \sigma$, and the other for $\sigma < r < \infty$.

4.1 The DCF for short distances, $0 < r < \sigma$

As it is clear, the Fourier transform of the DCF, $c(k)$, is not sensitive to the short-range form of the DCF.[9] Even from a simple model, called the empty core, all the principal thermodynamic properties and structural factor may be easily evaluated. Also, in the PY derivation of the DCF for hard cores, which is valid for the real fluids at very high densities, a Taylor expansion around $r = \sigma$ is used along with some other approximations. Therefore to obtain an analytical expression for the DCF at short distances, we may also expand the DCF around the average nearest neighbor's distance, $\bar{r}$, at any thermodynamic state as,

$$c(r) = c(\bar{r}) + \frac{1}{1!}\left(\frac{\partial c}{\partial r}\right)_{r=\bar{r}}(r-\bar{r}) + \frac{1}{2!}\left(\frac{\partial^2 c}{\partial r^2}\right)_{r=\bar{r}}(r-\bar{r})^2 + \cdots .$$

Due to the insensitivity of $c(k)$ to the mathematical form of the DCF at such distances, we retain only two terms of the above series as,

$$c(r) = a + br \quad r < \sigma \tag{16}$$

where a and b depend on the thermodynamic state. We have already shown in eq. (8) that the core of the DCF is related to the covolume and by using the LIR as,

$$-\frac{3A''\rho}{4\pi} = \int_0^\sigma c(r) r^2 \mathrm{d}r.$$

The upper limit of the integral at very high temperatures is the molecular diameter, σ. Even though at low temperatures the contribution of the covolume is also significant for $0 < r < \sigma$, however, its contribution for $\sigma < r < \infty$ is not negligible. In order to include the latter contribution we may change the upper limit of the integral from σ to the average nearest neighbor separation, $\bar{r}$. Owing to the fact that at very high densities, at which the positive part of the DCF vanishes and fluid behaves as hard spheres, $\bar{r}$ approaches to σ, which is corresponds to our approximation that the excluded volume can only effect in $0 < r < \sigma$. Substitution of the DCF from eq. (16) into eq. (8), and integration from $r = 0$ to $r = \bar{r}$, gives,

$$\frac{-3A''\rho}{4\pi} = \frac{a(\bar{r})^3}{3} + \frac{b(\bar{r})^4}{4}$$

or

$$\frac{-3A''\rho}{4\pi(\bar{r})^3} = \frac{a}{3} + \frac{b(\bar{r})}{4}. \tag{17}$$

To obtain the parameters of eq. (17) we need an extra relation between a and b. We assume that,

$$c(\sigma) = a + b\sigma = -1. \tag{18}$$

It means that the value of $c(r)$ at contact is equal to minus one. This is only an assumption which is accurate at very low densities. Since the exact form of the DCF are not important to obtain the thermodynamic function (because they related to the DCF by an integral and therefore the area is important). It is similar to the case of second virial coefficient that is not sensitive to the form of the pair potential.[2] Therefore we use eqs. (17) and (18) to obtain the value of the a and b parameters at each thermodynamic state just by knowing the density and A''. In such a way by using the linear expression for the DCF at distances less than σ, the DCF can be obtained.

4.2 The DCF for large distances, $\sigma < r < \infty$

As we mentioned before, the intermolecular interactions have a significant contribution in the DCF at such distances. Also, when the temperature and density are low the positive part of the DCF, behaves very much like the Mayer-f function. At high densities the behavior of the tail is similar to this function but its value is smaller (at high densities the pair potential energy becomes highly screened). In the other words, the interaction of the two particles in the dense systems is influenced very much by the medium. Therefore, we may consider the same mathematical expression for the DCF at high densities as that for its low density, $\exp(-\beta\phi(r)) - 1$, except that we use the effective pair potential, U_{eff}, instead of the isolated pair potential but just for $\sigma < r < \infty$, i.e.,

$$c(r) = \exp(-\beta U_{\text{eff}}) - 1 \quad r \geq \sigma. \tag{19}$$

In such away we have assumed that the analytical form of the effective pair potential is the same as that of the isolated pair which is reasonable at high densities (note that in such case a molecule is surrounded uniformly and symmetrically by its nearest neighbors). Because of the simplicity of the LJ $(12, 6)$ potential, we have used it as the effective pair potential in the DCF, however, its well depth is expected to be state dependent and different from that of the isolated pair. Since the separation at which $c(r) = 0$, which is nearly around $r = \sigma$, does not significantly vary with the thermodynamic state,[15] we supposed that the value of σ is the same as that of the isolated pair. Therefore the only unknown quantity in eq. (19) is the well depth of the effective pair potential, ε_{eff}. To obtain ε_{eff} we have used the bulk modulus given by the LIR, eq. (5), and eqs. (4) and (15) as,

$$\begin{aligned} B_{\mathrm{r}} &= 1 + 3A''\rho^2 - \frac{3A'}{RT}\rho^2 + \frac{5B'}{RT}\rho^4 \\ &= 1 - 4\pi\rho\left[\int_0^{\sigma}(a+br)r^2\mathrm{d}r \right. \\ &\quad \left. + \int_{\sigma}^{\infty}\exp\left(-4\beta\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]\right) - 1\right) r^2\mathrm{d}r\right]. \end{aligned} \tag{20}$$

Solving the above equation gives the ε_{eff} for each thermodynamic state. We did such a calculation for Ar as follows: At each thermodynamic state using the LIR parameters[15] the bulk modulus have obtained and by using eqs. (17) and (18), we have obtained the values of a and b parameters. Then the values of a, b, and $\sigma = 3.41$ Å for Ar[16] have been inserted in eq. (20) to obtain the value of ε_{eff} is calculated. The results for Ar are presented in Table I. Then the values of the σ, ε_{eff}, a, and b have been inserted in eqs. (16) and (19) to obtain the DCF at each thermodynamic state. Figure 1 shows the obtained DCF for Ar at 143.15 K and 24.58 mol·L^{-1}. In Table II, we have compared the experimental values[15] of the DCF for several distances with our calculated values for Ar. The agreements between the calculated and experimental values are quite remarkable. In summery, we have used the analytical expressions for the DCF as,

$$c(r)\begin{cases} a + br & r < \sigma \\ \exp(-\beta U_{\text{eff}}) - 1 & r \geq \sigma. \end{cases} \tag{21}$$

As it is clear in our definition for the DCF there is a discontinuity at $r = \sigma$, but because of the fact that the experimental value of DCF in this region rises steeply and the thermodynamic properties like B_{r} is related to the DCF by an integral, such a discontinuity is not important.

To test our result, we have also done the Fourier transform of eq. (21), to obtain $c(k)$, and the structural factor, $S(k)$, as,

$$\begin{aligned} c(k) &= 4\pi\left[\int_0^{\sigma}(a+br)\frac{\sin kr}{kr}r^2\mathrm{d}r \right. \\ &\quad \left. + \int_{\sigma}^{\infty}(\exp(-\beta U_{\text{eff}}) - 1)\frac{\sin kr}{kr}r^2\mathrm{d}r\right] \end{aligned} \tag{22}$$

Table I. The calculated values for a, b, B_{r}, and $\varepsilon_{\text{eff}}/k$ for Ar at several thermodynamic states.

T (K)	ρ (mol·L^{-1})	$\varepsilon_{\text{eff}}/k$(K)	B_{r}	a	b (Å^{-1})
143.15	24.58	84.9	2.80	−7.5238	1.91373
148.15	24.58	88.8	2.94	−7.5238	1.91373
148.15	26.94	86.38	3.33	−12.7372	3.44202

Table II. Comparison of the calculated and experimental values for the DCF at some given distances.

T (K)	ρ (mol·L^{-1})	$[r(\text{Å})]_{\text{exp}}$	$c_{\text{exp}}(r)$	$[r(\text{Å})]_{\text{cal}}$	$c_{\text{cal}}(r)$
143.15	24.58	3.45	0	3.41	0
143.15	24.58	3.82	0.84	3.83	0.81
148.15	24.58	3.38	0	3.41	0
148.15	26.94	3.72	0.86	3.83	0.82

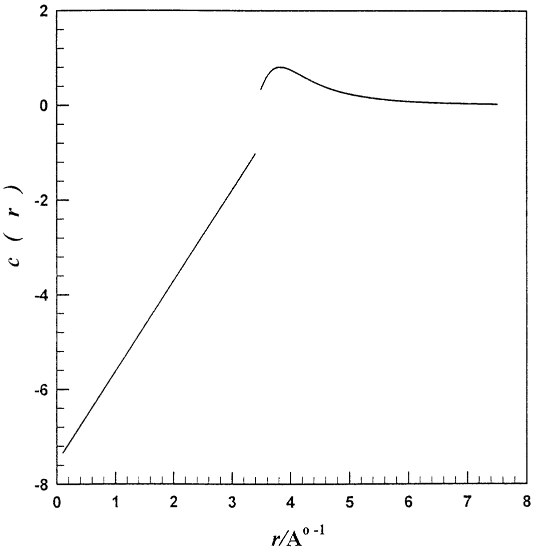

Fig. 1. The calculated DCF versus r for Ar at 143.15 K and 24.58 mol·L^{-1}.

and

$$S(k) = \frac{1}{1 - \rho c(k)} \tag{23}$$

where k is the wave vector. The obtained values of $S(k)$ are given in Figs. 2 and 3 for three different thermodynamic states of Ar. As it is clear, the qualitative form of the $S(k)$ is correctly generated and the number and heights of the bumping is increased with density, which is expected.[9]

§5. Effective Pair Potential

The interesting point to note in Table I is the values of the well depth of the effective pair potential. As it is clear its value is lower than that of the isolated pair, which is $\varepsilon/k = 125$ K, for Ar.[17] Before any discussion about this difference let us make clear the physical concept of the effective pair potential. Consider a very dilute fluid, the average separation between any two molecules is much greater than the range of the potential, $\phi(r)$, and two molecules can be moved toward each other almost without observing any other molecule (they are isolated and not effected by the other molecules). Thus at very low densities, $\phi(r)$ is also just the work required to bring two molecules at a separation r from the infinite separation. Now consider a dense system, in this case there are many molecules within the range of the pair potential and we cannot imagine any pair of molecules

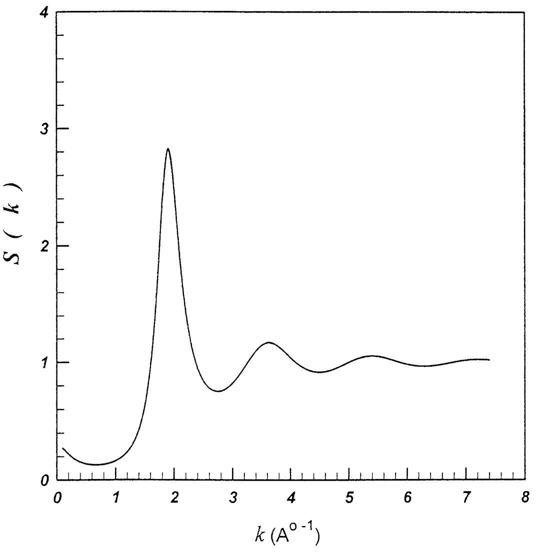

Fig. 2. The structural factor versus k for Ar, calculated from the purposed DCF, eq. (21), at 143.15 K and 24.58 mol·L^{-1}.

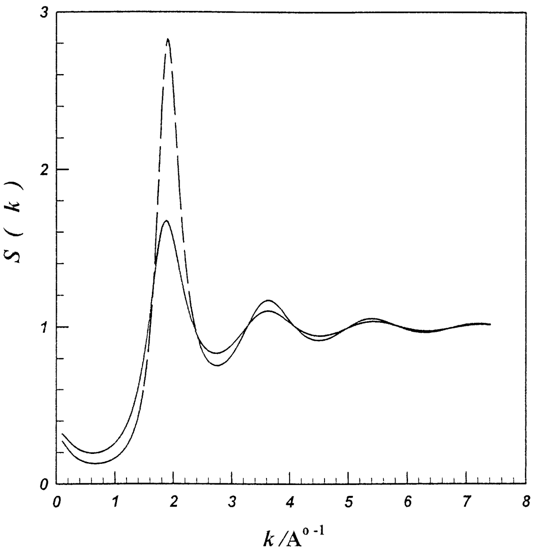

Fig. 3. Same as Fig. 2 for 148.15 K and 24.58 mol·L^{-1} (——) and for 94.4 K and 26.94 mol·L^{-1} (-----).

isolated from the other molecules. Therefore the work required to bring two molecules at a separation r from the infinite distance, denoted as $\psi(r)$, is different from the $\phi(r)$. The point is that in a dense system moving two molecules toward each other causes some rearrangements in the positions of other molecules and also the medium (other molecules) influence on the interactions between two molecules. Thus, when two molecules are brought at separation r from an infinitely large separation, there are uncontrolled changes in the configuration of the rest of molecules. In general, $\psi(r)$ is both temperature and density dependent. The $\psi(r)$ is known as the potential of average forces and also related to the $g(r)$ as,[18)]

$$g(r) = \exp(-\beta\psi(r)).$$

It is to be noted that the medium can effect on the charge distribution of the two molecules and hence on their interactions. The magnitude of such an effect depends on the molecular polarizability. If entire effect of the medium, which includes the change in the charge distribution and possibly the molecular shape, is considered on two molecules and then the interaction of these two effected molecules, free from the physical existence of $N-2$ molecules is studied, we call it the effective pair potential energy. Therefore the work, which is done to bring these two effected molecules at distance r from infinity, is not affected from the physical presence of any other molecule. Therefore the effective pair potential is expected to be quite different from $\phi(r)$ and also $\psi(r)$. In fact the entire effect of the medium is included in the effective pair potential expect for the effect of the excluded volume which leads to the bumping in $\psi(r)$ (unlike the $\psi(r)$, the effective pair potential has no bumping). This effective pair potential is also both temperature and density dependent.

As we mentioned before the well depth of the effective pair potential energy is always shallower than that of the isolated pair, because the net effect of the other molecules is positive or repulsion.[19)] We expect that the well depth decreases with increasing density. Because by increasing the density the hardness behavior of system increases, therefore ε_{eff} should be lower than that of the isolated pair. It is also to be noted that in such a way the entire effect of medium is included in the well depth of the potential and the molecular diameter, σ, considered to be unchanged.

§6. Conclusion

The objective of this work, is that just by using an equation of state, LIR, we have been able to interpret the DCF, which has been an unknown quantity for about one century. As mentioned before because of the nature of short range of the DCF even in the critical region, it has been very noticeable in the theory of liquids. Also there isn't any bumping in this function and the compressibility equation may be obtained from it without using pair wise additivity approximation for the configuration potential. However, we have shown that the core of the DCF is related to the covolume and geometric effect, which is the only contribution involved in the DCF for the hard sphere fluid. The amount of this contribution increases by increasing density and temperature means when the behavior of the system is similar to the hard sphere. But the tail of the DCF is supported by the intermolecular interactions which its contribution increases when the hardness of the system decreases. We may conclude from the arguments given in this article that at very high density and temperature the intermolecular interactions do not have any important role in the DCF, while the size of molecules (excluded volume) dose have a significant contribution.

As we have shown in Table II, the calculated DCF has a good agreement with the experimentally reported values and satisfies the temperature and density dependencies of the core and tail. Also the oscillatory function, the structural factor, is generated by the obtained DCF and its height and the number of the bumping increase with density.

The interesting quantity which obtained in this work is the effective pair potential. As we mentioned, the well depth of the potential is different and shallower than that of the isolated pair. Since the effective pair potential is the interaction between two molecules that are affected by $N-2$ other molecules, the difference between this potential and the isolated pair potential shows that the net effect of the other molecules on a given pair is repulsion (positive). This conclusion is in agreement with the previous works reported in the literature.6, 9, 20)

The other point that we want to mention is the wonderful ability of the LIR regularity in the interpretation of thermodynamic properties. Because all the no ideal effects which arise from the excluded volume, repulsive, and attractive forces, are considered in this regularity separately, therefore it is possible to observe the effect of each of them in any interested thermodynamic properties of dense fluids. In spite of the simplicity of this regularity it has been successful to interpret some phenomena such as, the metal-non-metal transition,21) chemical potential22) and Joule-Thomson inversion curve.23)

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