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Calculation of the Pair Correlation Functions for Fluids Composed of Diatomic Polar Molecules Based on the Interaction Site Model

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A reference hypernetted chain (RHNC) like approximation of the interaction site model is proposed, which is the extension of Lado's RHNC equation of simple fluids to the case of molecular fluids. By using the proposed RHNC like integral equation, pair correlation functions, structure factors and some thermodynamic quantities for fluids composed of diatomic polar molecules are calculated, where the molecules consist of two fused hard-spheres with each center located at a distance l, and at each center charges $+q$ and $-q$ are sited. Calculated pair correlation functions are successful in showing well-marked characteristics of the fluid, such as cusps, not observed for simple fluids like argon. The isothermal compressibility at a constant reduced density and dipole moment has a weak l-dependence in sharp contrast to the total internal energy showing a strong l-dependence.

The statistical mechanical theory of fluids based on the interaction site model (ISM)[1–4] has turned out to be successful in studying the equilibrium properties of those composed of polyatomic molecules. It was also applied to fluids composed of molecules with electrostatic potentials. The theory of polar fluids based on the ISM was proposed first by Chandler and others.[5,6] We applied the ISM to ionic solutions.[7] These theories concern with general properties of dielectric constant, pair correlation functions and others for polar and ionic fluids. Recently, Morriss and Perram have obtained a formal solutions of the mean spherical approximation of RISM-1 (see below) for polyatomic polar fluids,[8] but numerical results have not been given yet.

As the method of obtaining site-site pair correlation functions, three modifications of reference interaction site model integral equations (RISM-1, RISM-2, and RISM-3) coupled with a certain approximation, such as the Percuss-Yevick (PY) like approximation, the hypernetted chain (HNC) like approximation and mean spherical approximation, are proposed.[1,4,9,10] These integral equations were solved for molecular fluids with short-ranged intermolecular forces,[11–13] and the RISM-1 equation gives the most accurate site-site pair correlation functions in comparison with computer simulation results or experimental results.[4] Since the differences between the results of the PY like approximation and the HNC like approximation are similar to those of simple fluids,[4] it is expected that the PY like and HNC like approximations are appropriated to fluids with short-ranged forces and with long-ranged forces, respectively.

For simple fluids composed of molecules with a short-ranged force and a long-ranged tail, the reference hypernetted chain (RHNC) approximation gives a fairly good result.[14–16] In the theory, the system without long-ranged tails is treated as a reference system whose properties are obtained from the PY approximation or computer simulations, and the correction due to the long-ranged tail is calculated by the HNC approximation. So, by considering the properties of the PY like and HNC like approximations, a similar treatment will also be appropriated to the case of polyatomic molecular fluids.

In this paper, we propose an RHNC like approximation of RISM-1 and solve it for diatomic polar fluids. In Theory section, the definition of a model is made and the RHNC like approximation is proposed.

Theory

Model. We assume that the molecule has n interaction sites and a charge q_α is sited on the α-th site of the molecule. The total potential energy for the molecular fluid is assumed to be the sum over all pairs of the intermolecular potentials. The pair interaction between the i-th molecule and the j-th molecule $U(i,j)$ is given by

$$U(i,j) = \sum_{\alpha=1}^{n} \sum_{\gamma=1}^{n} u_{\alpha\gamma}(|\boldsymbol{r}_i^\alpha - \boldsymbol{r}_j^\gamma|), \tag{1}$$

where $u_{\alpha\gamma}(|\boldsymbol{r}_i^\alpha - \boldsymbol{r}_j^\gamma|)$ is an interaction potential between the pair of the site α of the i-th molecule and the site γ of the j-th molecule, and $\boldsymbol{r}_i^\alpha$ the position of the site α of the i-th molecule. An illustration of the molecule is shown in Fig. 1. The site-site interaction can be divided into two parts,

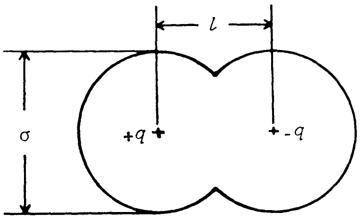

Fig. 1. The shape of the diatomic polar molecule considered in this paper.

$$u_{\alpha\gamma}(r) = u_{\alpha\gamma}^{(0)}(r) + u_{\alpha\gamma}^{(1)}(r). \tag{2}$$

Here, $u_{\alpha\gamma}^{(0)}(r)$ is a short ranged part of the site-site interaction, which is treated as a reference potential, and $u_{\alpha\gamma}^{(1)}(r)$ a long-ranged Coulomb tail, that is,

$$u_{\alpha\gamma}^{(1)}(r) = \frac{q_\alpha q_\gamma}{4\pi\varepsilon_0 r}, \tag{3}$$

where ε_0 is the dielectric constant of vacuum.

RHNC like Approximation. In the following formulation, we attempt to extend Lado's formalism of simple fluids[14,15] to polyatomic molecular fluids. We start with the Ornstein-Zernike type equation[1,4] as follows,

$$\boldsymbol{h}(r) = \boldsymbol{\omega}*\boldsymbol{c}*\boldsymbol{\omega}(r) + \rho\boldsymbol{\omega}*\boldsymbol{c}*\boldsymbol{h}(r), \tag{4}$$

where the $*$ denotes a convolution, ρ the number density of molecules and $\boldsymbol{h}(r)$, $\boldsymbol{\omega}(r)$, and $\boldsymbol{c}(r)$ are matrices with elements $h_{\alpha\gamma}(r)$, $\omega_{\alpha\gamma}(r)$, and $c_{\alpha\gamma}(r)$, respectively. The site-site total correlation function $h_{\alpha\gamma}(r)$ and the intramolecular pair correlation function $\omega_{\alpha\gamma}(r)$ are defined as reported,[7] and the site-site direct correlation function $c_{\alpha\gamma}(r)$ is defined in Eq. 4. The Fourier transform of Eq. 4 is

$$\tilde{\boldsymbol{h}} = \tilde{\boldsymbol{\omega}}\tilde{\boldsymbol{c}}\tilde{\boldsymbol{\omega}} + \rho\tilde{\boldsymbol{\omega}}\tilde{\boldsymbol{c}}\tilde{\boldsymbol{h}}, \tag{5}$$

where $\tilde{\boldsymbol{A}}$ denotes a matrix with the element $\tilde{A}_{\alpha\gamma}(k)$ and $\tilde{A}_{\alpha\gamma}(k)$ the Fourier transform of $A_{\alpha\gamma}(r)$,

$$\tilde{A}_{\alpha\gamma}(k) = \int \mathrm{d}\boldsymbol{r} A_{\alpha\gamma}(r)\mathrm{e}^{-i\boldsymbol{k}\cdot\boldsymbol{r}}.$$

The function, $\tilde{\omega}_{\alpha\gamma}(k)$, for rigid molecules is expressed as

$$\tilde{\omega}_{\alpha\gamma}(k) = \delta_{\alpha\gamma} + (1-\delta_{\alpha\gamma})\frac{\sin kl_{\alpha\gamma}}{kl_{\alpha\gamma}}, \tag{6}$$

where $\delta_{\alpha\gamma}$ is the Kronecker delta and $l_{\alpha\gamma}=|\boldsymbol{r}_i^{\alpha}-\boldsymbol{r}_i^{\gamma}|$ the distance between the α-th site and γ-th site of the same molecule.

The Ornstein-Zernike type equation for a reference system is

$$\tilde{\boldsymbol{h}}^{(0)} = \tilde{\boldsymbol{\omega}}\tilde{\boldsymbol{c}}^{(0)}\tilde{\boldsymbol{\omega}} + \rho\tilde{\boldsymbol{\omega}}\tilde{\boldsymbol{c}}^{(0)}\tilde{\boldsymbol{h}}^{(0)}, \tag{7}$$

where superscript (0) denotes the reference system quantity. From Eqs. 5 and 7, we obtain

$$\delta\tilde{\boldsymbol{h}} = (\tilde{\boldsymbol{\omega}}+\rho\tilde{\boldsymbol{h}}^{(0)})\{\boldsymbol{1}-\rho\delta\tilde{\boldsymbol{c}}(\tilde{\boldsymbol{\omega}}+\rho\tilde{\boldsymbol{h}}^{(0)})\}^{-1}\delta\tilde{\boldsymbol{c}}(\tilde{\boldsymbol{\omega}}+\rho\tilde{\boldsymbol{h}}^{(0)}), \tag{8}$$

where $\boldsymbol{A}^{-1}$ denotes the matrix inverse of matrix $\boldsymbol{A}$, $\boldsymbol{1}$ the unit matrix. $\delta\tilde{\boldsymbol{h}}$ and $\delta\tilde{\boldsymbol{c}}$ are the matrices with elements $\delta\tilde{h}_{\alpha\gamma}(k)$ and $\delta\tilde{c}_{\alpha\gamma}(k)$, the Fourier transforms of $\delta h_{\alpha\gamma}(r)$ and $\delta c_{\alpha\gamma}(r)$, respectively, which are defined as follows,

$$\delta h_{\alpha\gamma}(r) = h_{\alpha\gamma}(r) - h^{(0)}_{\alpha\gamma}(r) \tag{9}$$

and

$$\delta c_{\alpha\gamma}(r) = c_{\alpha\gamma}(r) - c^{(0)}_{\alpha\gamma}(r). \tag{10}$$

$\delta h_{\alpha\gamma}(r)$ and $\delta c_{\alpha\gamma}(r)$ are the perturbation corrections to $h_{\alpha\gamma}(r)$ and $c_{\alpha\gamma}(r)$, respectively, due to the perturbation potential $u^{(1)}_{\alpha\gamma}(r)$.

A closure relation between $\delta h_{\alpha\gamma}(r)$ and $\delta c_{\alpha\gamma}(r)$ is derived as follows. We consider the following relation as

$$c_{\alpha\gamma}(r) = h_{\alpha\gamma}(r) - \ln g_{\alpha\gamma}(r)\mathrm{e}^{\beta u_{\alpha\gamma}(r)} + B_{\alpha\gamma}(r), \tag{11}$$

where $g_{\alpha\gamma}(r)=h_{\alpha\gamma}(r)+1$ is the site-site radial distribution function, $\beta=(k_{\mathrm{B}}T)^{-1}$, k_{B} the Boltzmann constant and T the absolute temperature. $B_{\alpha\gamma}(r)$ defined in Eq. 11 is the residual term. If we put $B_{\alpha\gamma}(r)=0$, we obtain the HNC like approximation for RISM-1.[4,17] Different from the case of simple fluids, $B_{\alpha\gamma}(r)$ cannot be expressed as a sum of allowed cluster diagrams.[17] Subtraction of the similar equation for the reference system yields

$$\delta c_{\alpha\gamma}(r) = \delta h_{\alpha\gamma}(r) - \ln\frac{g_{\alpha\gamma}(r)}{g^{(0)}_{\alpha\gamma}(r)}\mathrm{e}^{\beta u^{(1)}_{\alpha\gamma}(r)} + \delta B_{\alpha\gamma}(r), \tag{12}$$

where

$$\delta B_{\alpha\gamma}(r) = B_{\alpha\gamma}(r) - B^{(0)}_{\alpha\gamma}(r).$$

Here, we assume that $\delta B_{\alpha\gamma}(r)=0$. Then we have a new approximation as follows

$$\delta c_{\alpha\gamma}(r) = \delta h_{\alpha\gamma}(r) - \ln\frac{g_{\alpha\gamma}(r)}{g^{(0)}_{\alpha\gamma}(r)}\mathrm{e}^{\beta u^{(1)}_{\alpha\gamma}(r)}, \tag{13}$$

which we call an RHNC like approximation for RISM-1. Combining Eq. 8 with Eq. 13, we can solve the integral equation when the reference system quantities are given. The RHNC like integral equation for RISM-1, that is, Eqs. 8 and 13, is the extension of Lado's RHNC integral equation for simple fluids[14,15] to the case of polyatomic molecular fluids.

Computational Procedures

A system calculated is a fluid composed of diatomic polar molecules which is shown in Fig. 1. A fluid composed of fused hard-spheres with the same diameter σ is considered as a reference system, so the reference potential is given as

$$u^{(0)}_{\alpha\gamma}(r) = \begin{cases} \infty, & r<\sigma \\ 0, & r>\sigma. \end{cases} \tag{14}$$

Because of the symmetry, we have $g_{++}(r)=g_{--}(r)$, $g_{+-}(r)=g_{-+}(r)$ and $g^{(0)}_{++}(r)=g^{(0)}_{--}(r)=g^{(0)}_{+-}(r)=g^{(0)}_{-+}(r)\equiv g^{(0)}(r)$ for the systems considered here.

The functions $\delta h_{\alpha\gamma}(r)$ and $\delta c_{\alpha\gamma}(r)$ have a discontinuity at $r=\sigma$. Thus, we define a new function $H_{\alpha\gamma}(r)$ as follows,

$$H_{\alpha\gamma}(r) = \delta h_{\alpha\gamma}(r) - \delta c_{\alpha\gamma}(r). \tag{15}$$

$H_{\alpha\gamma}(r)$ is a continuous function of r. By the use of this, Eqs. 8 and 13 can be written as

$$\tilde{\boldsymbol{H}} = (\tilde{\boldsymbol{\omega}}+\rho\tilde{\boldsymbol{h}}^{(0)})\{\boldsymbol{1}-\rho\delta\tilde{\boldsymbol{c}}(\tilde{\boldsymbol{\omega}}+\rho\tilde{\boldsymbol{h}}^{(0)})\}^{-1}\delta\tilde{\boldsymbol{c}}(\tilde{\boldsymbol{\omega}}+\rho\tilde{\boldsymbol{h}}^{(0)}) - \delta\tilde{\boldsymbol{c}} \tag{16}$$

and

$$\delta c_{\alpha\gamma}(r) = g^{(0)}_{\alpha\gamma}(r)\{\exp[H_{\alpha\gamma}(r)-\beta u^{(1)}_{\alpha\gamma}(r)]-1\} - H_{\alpha\gamma}(r). \tag{17}$$

From Eqs. 13 and 15, we obtain

$$H_{\alpha\gamma}(r) = \beta u^{(1)}_{\alpha\gamma}(r) + \ln\frac{g_{\alpha\gamma}(r)}{g^{(0)}_{\alpha\gamma}(r)}. \tag{18}$$

For polar fluids, $h_{\alpha\gamma}(r)$ decays as r^{-6} at large r.[5,6] Thus, the following asymptotic forms of $H_{\alpha\gamma}(r)$ and $\delta c_{\alpha\gamma}(r)$ at large separations are derived from Eqs. 15 and 18,

$$H_{\alpha\gamma}(r) \sim \beta u^{(1)}_{\alpha\gamma}(r), \text{ and } \delta c_{\alpha\gamma}(r) \sim -\beta u^{(1)}_{\alpha\gamma}(r).$$

Since $u^{(1)}_{\alpha\gamma}(r)$ is the long-ranged Coulomb potential, serious truncation errors can arise when these functions are numerically integrated over a finite range. Thus, we define a new short-ranged function $H^{\mathrm{s}}_{\alpha\gamma}(r)$ and $\delta c^{\mathrm{s}}_{\alpha\gamma}(r)$ as follows,

$$H^{\mathrm{s}}_{\alpha\gamma}(r) = H_{\alpha\gamma}(r) - H^{\mathrm{L}}_{\alpha\gamma}(r) \tag{19}$$

and

$$\delta c^{\mathrm{s}}_{\alpha\gamma}(r) = \delta c_{\alpha\gamma}(r) + H^{\mathrm{L}}_{\alpha\gamma}(r), \tag{20}$$

where

$$H^{\mathrm{L}}_{\alpha\gamma}(r) = \frac{\beta q_{\alpha}q_{\gamma}}{4\pi\varepsilon_0 r}(1-\mathrm{e}^{-ar}) \tag{21}$$

and a is a disposable parameter chosen so as to make the function $\Psi^{\mathrm{s}}_{\alpha\gamma}(r)$, defined below, negligibly small at the termination of the finite range of r. By the use of new functions $H^{\mathrm{s}}_{\alpha\gamma}(r)$ and $\delta c^{\mathrm{s}}_{\alpha\gamma}(r)$, Eqs. 16 and

17 can be written as

$$\tilde{\boldsymbol{H}}^{\mathrm{S}} = (\tilde{\boldsymbol{\omega}}+\rho\tilde{\boldsymbol{h}}^{(0)})\{\boldsymbol{1}-\rho(\delta\tilde{\boldsymbol{c}}^{\mathrm{S}}-\tilde{\boldsymbol{H}}^{\mathrm{L}})(\tilde{\boldsymbol{\omega}}+\rho\tilde{\boldsymbol{h}}^{(0)})\}^{-1} \times (\delta\tilde{\boldsymbol{c}}^{\mathrm{S}}-\tilde{\boldsymbol{H}}^{\mathrm{L}})(\tilde{\boldsymbol{\omega}}+\rho\tilde{\boldsymbol{h}}^{(0)}) - \delta\tilde{\boldsymbol{c}}^{\mathrm{S}} \tag{22}$$

and

$$\delta c^{\mathrm{S}}_{\alpha\gamma}(r) = g^{(0)}_{\alpha\gamma}\{\exp\,[H^{\mathrm{S}}_{\alpha\gamma}(r)-\Psi^{\mathrm{S}}_{\alpha\gamma}(r)]-1\}-H^{\mathrm{S}}_{\alpha\gamma}(r), \tag{23}$$

where

$$\Psi^{\mathrm{S}}_{\alpha\gamma}(r) = \frac{\beta q_\alpha q_\gamma}{4\pi\varepsilon_0 r}\mathrm{e}^{-ar}$$

and

$$\tilde{H}^{\mathrm{L}}_{\alpha\gamma}(k) = \frac{\beta q_\alpha q_\gamma a^2}{\varepsilon_0 k^2(k^2+a^2)}.$$

Equations 22 and 23 involve only short-ranged functions that can be numerically handled in the usual way. An iteration procedure is carried out for solving Eqs. 22 and 23 numerically. The iteration was started with the initial guess $H^{\mathrm{s}}_{\alpha\gamma}(r)=0$, and has been continued until the self consistency of

$$\left|\frac{H^{\mathrm{S}}_{\alpha\gamma}(r)_{\mathrm{out}}-H^{\mathrm{S}}_{\alpha\gamma}(r)_{\mathrm{in}}}{H^{\mathrm{S}}_{\alpha\gamma}(r)_{\mathrm{in}}}\right|<10^{-7} \tag{24}$$

is satisfied. The site-site radial distribution function is finally obtained as

$$g_{\alpha\gamma}(r) = g^{(0)}_{\alpha\gamma}(r)\exp\{H^{\mathrm{S}}_{\alpha\gamma}(r)-\Psi^{\mathrm{S}}_{\alpha\gamma}(r)\}. \tag{25}$$

The solution of Lowden's RISM computer program[18)] is used as a reference system site-site radial distribution function $g^{(0)}_{\alpha\gamma}(r)$.

Results and Discussion

A system considered is characterized by three parameters, that is, the reduced density $\rho^*=\rho d^3$, the reduced dipole moment $\mu^*=(\mu^2/4\pi\varepsilon_0 k_{\mathrm{B}}Td^3)^{1/2}$ and the reduced bond length $L^*=l/\sigma$. Here, $\mu=ql$ is the magnitude of the dipole moment of the molecules and d, the diameter of the hard sphere whose volume is the same as the molecule considered here, is defined by the following relations as

$$d^3 = \sigma^3\left(1+\frac{3L^*}{2}-\frac{L^{*3}}{2}\right). \tag{26}$$

Iteration procedures described above diverge when L^* is 0.2 or less.

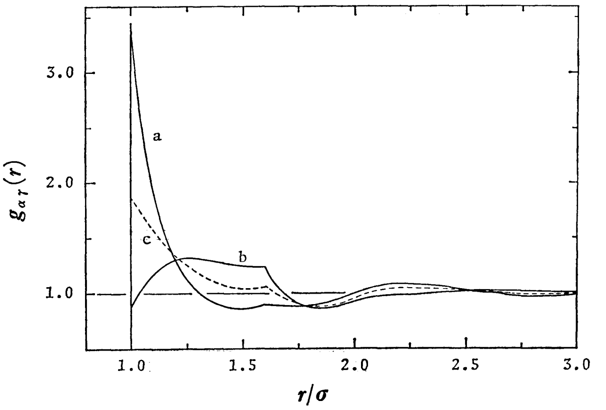

Fig. 2. The site-site radial distribution functions, $g_{\alpha\gamma}(r)$, for diatomic polar fluid at $\rho^*=0.8$, $\mu^{*2}=3.0$ and $L^*=0.6$. a; $g_{+-}(r)=g_{-+}(r)$, b; $g_{++}(r)=g_{--}(r)$, c; $g^{(0)}(r)$.

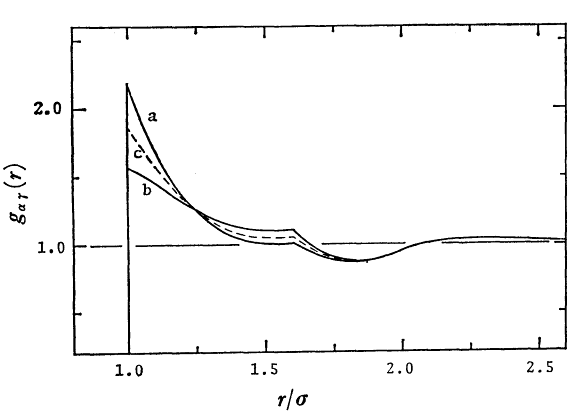

Fig. 3. Same as Fig. 2, except $\mu^{*2}=0.5$.

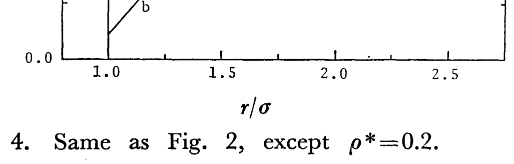

Fig. 4. Same as Fig. 2, except $\rho^*=0.2$.

Distribution Functions. Figures 2—5 show the site-site radial distribution functions calculated according to the procedures described in the preceding section. All of $g_{\alpha\gamma}(r)$ shown in these figures have cusps at $r/\sigma=1+L^*$. These cusps are characteristic of fluids composed of diatomic molecules with a hard core repulsion. For the system with continuous potentials, these cusps are rounded off.[4)] It is noted that all the curves of $g_{++}(r)$ and $g_{+-}(r)$ in Figs. 2—5 are nearly symmetrical with respect to the curve of $g^{(0)}(r)$, and have oscillatory structure around the curve of $g^{(0)}(r)$. These behaviors are explained as follows: Let the center of the + atom of one molecule fix the origin. Then, if the + atom of the other molecule exist at $r\simeq\sigma$, the − atom of its molecule necessarily exist at $r\simeq\sigma+l$. Thus, because of the decrease of the value of $g_{++}(r)$ at $r\simeq\sigma$ due to the electrostatic repulsion in comparison with the value of $g^{(0)}(r)$, the value of $g_{+-}(r)$ decrease at $r\simeq\sigma+l$. Similar effects will cause the behaviors described above.

A large deviation of $g_{\alpha\gamma}(r)$ from $g^{(0)}(r)$ are shown at $\rho^*=0.8$, $\mu^{*2}=3.0$ and $L^*=0.6$ (Fig. 2). The deviation at $\rho^*=0.8$, $\mu^{*2}=0.5$ and $L^*=0.6$ (Fig. 3) are smaller than that shown in Fig. 2 and $g_{\alpha\gamma}(r)$ almost agree with $g^{(0)}(r)$ at $r>2\sigma$. It is shown in Fig. 4 that $g^{(0)}(r)$ at $\rho^*=0.2$, $\mu^{*2}=3.0$ and $L^*=0.6$ is nearly equal to one, on the other hand the deviations of $g_{\alpha\gamma}(r)$ from $g^{(0)}(r)$ are similar to those shown in Fig. 2. Figure 5 shows $g_{\alpha\gamma}(r)$ at $\rho^*=0.6$, $\mu^{*2}=1.0$ and $L^*=0.3$. The shapes of curves are considerably dif-

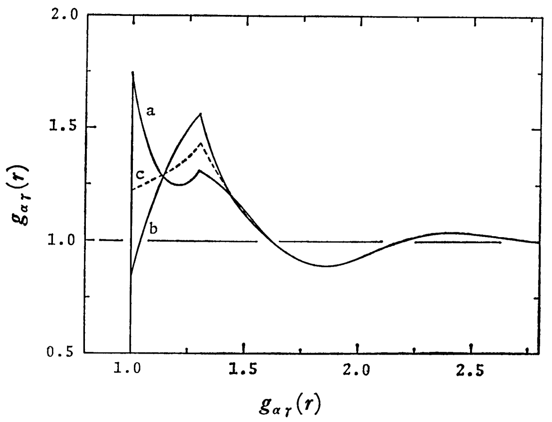

Fig. 5. The site-site radial distribution functions, $g_{\alpha\gamma}(r)$, for diatomic polar fluid at $\rho^*=0.6$, $\mu^{*2}=1.0$ and $L^*=0.3$. a; $g_{+-}(r)=g_{-+}(r)$, b; $g_{++}(r)=g_{--}(r)$, c; $g^{(0)}(r)$.

ferent from those at $L^*=0.6$. This difference is due to the difference of the shape of $g^{(0)}(r)$. On the other hand, the deviation of $g_{\alpha\gamma}(r)$ from $g^{(0)}(r)$ is similar to that at $L^*=0.6$.

Structure Factors. The structure factor is expressed in terms of site-site correlation functions as follows,[11)]

$$S(k)=(\sum_{\alpha} b_{\alpha})^{-2}\sum_{\alpha}\sum_{\gamma} b_{\alpha}b_{\gamma}\{\tilde{\omega}_{\alpha\gamma}(k)+\rho\tilde{h}_{\alpha\gamma}(k)\}$$
$$=\frac{(b_+^2+b_-^2)\{1+\tilde{h}_{++}(k)\}+2b_+b_-\{\tilde{\omega}_{+-}(k)+\tilde{h}_{+-}(k)\}}{(b_++b_-)^2}, \tag{27}$$

where we use the relations $h_{++}(r)=h_{--}(r)$ and $h_{+-}(r)=h_{-+}(r)$ in the second equality and b_{α} denote the coherent scattering amplitude for an atoms of type α. Figures 6 and 7 show the structure factors calculated under the assumptions of $b_+=b_-$ and $b_+=10b_-$, respectively. The structure factor at $b_+=b_-$ is nearly equal to that of reference system except at small k. This result arises from the fact that the deviation of $g_{++}(r)$ from $g^{(0)}(r)$ cancells that of $g_{+-}(r)$. Because of the decrease of these cancellations, $S(k)$ at $b_+=10b_-$ fairly deviate from $S^{(0)}(k)$. The values of $S(k)$ increase in small range of $k\sigma$ in comparison with $S^{(0)}(k)$. The behavior of the structure factors at small k seems to be due to the contribution of averaged attractive potentials.[4,19)]

Thermodynamic Quantities. The total internal energy U and the isothermal compressibility κ_T are expressed in terms of the site-site pair correlation functions as follows,

$$\frac{U}{Nk_BT}=\frac{\rho}{2k_BT}\sum_{\alpha}\sum_{\gamma}\int \mathrm{d}\boldsymbol{r}u_{\alpha\gamma}(r)g_{\alpha\gamma}(r), \tag{28}$$

and

$$\rho k_BT\kappa_T=S(0)=1+\rho\tilde{h}_{\alpha\gamma}(0), \tag{29}$$

where N is the number of molecules. Figures 8 and 9 show the internal energy and the isothermal compressibility at $L^*=0.6$, respectively. The L^* dependence of the internal energy and the isothermal compressibility are also shown in Figs. 10 and 11, respectively. In Fig. 10, the values at $L^*=0$ are those

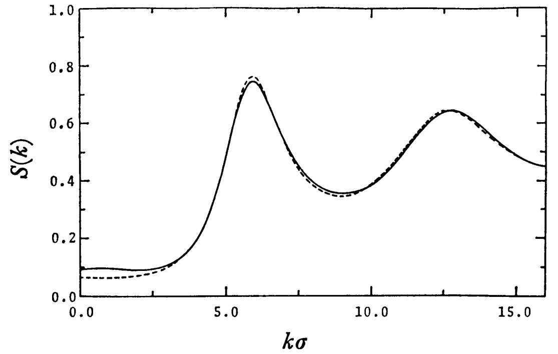

Fig. 6. The structure factor, $S(k)$, for diatomic polar fluids at $\rho^*=0.8$, $\mu^{*2}=3.0$, $L^*=0.6$ and $b_+=b_-$. ——: The structure factor for diatomic polar fluid, ----: the structure factor for the reference system.

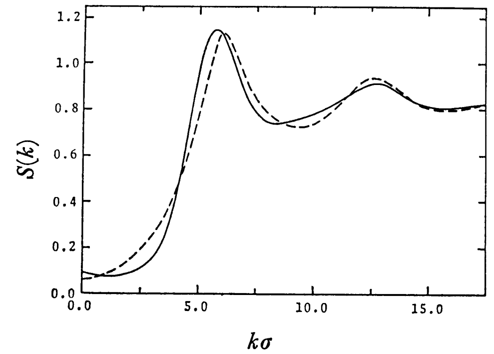

Fig. 7. Same as Fig. 6, except $b_+=10b_-$.

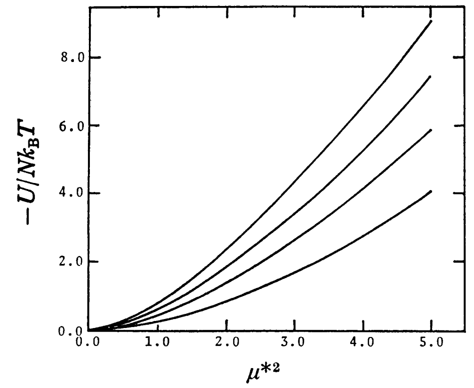

Fig. 8. The internal energy for diatomic polar fluids at $L^*=0.6$.
From top to bottom, the curves are for $\rho^*=0.8$, 0.6, 0.4, and 0.2, respectively.

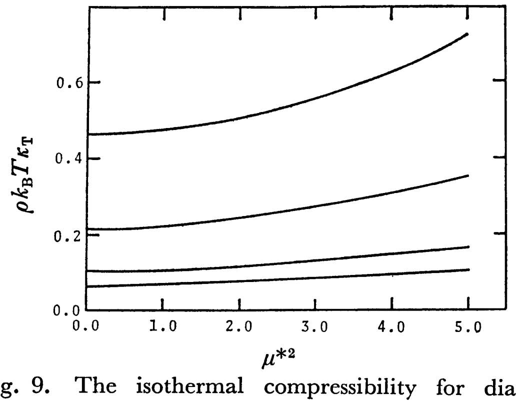

Fig. 9. The isothermal compressibility for diatomic polar fluids at $L^*=0.6$. From top to bottom, the curves are for $\rho^*=0.2$, 0.4, 0.6, and 0.8, respectively.

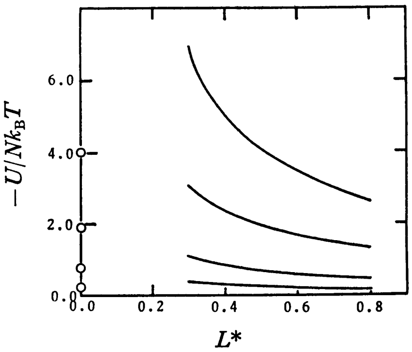

Fig. 10. The L^* dependence of the internal energy for diatomic polar fluids. From top to bottom, the curves and circles are for $(\rho^*, \mu^{*2})=(0.6, 3.0)$, $(0.2, 3.0)$, $(0.6, 1.0)$, and $(0.2, 1.0)$, respectively.
○: LHNC results for dipolar hard sphere fluids, —: this work.

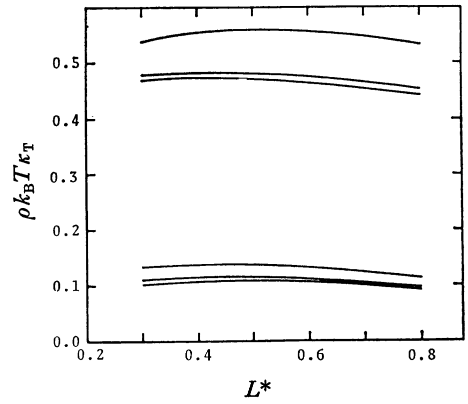

Fig. 11. The L^* dependence of the isothermal compressibility for diatomic polar fluids. From top to bottom, the curves are for $(\rho^*, \mu^{*2})=(0.2, 3.0)$, $(0.2, 1.0)$, $(0.2, 0.0)$, $(0.6, 3.0)$, $(0.6, 1.0)$, and $(0.6, 0.0)$, respectively.

of fluids composed of dipolar hard spheres at the same reduced density and dipole moment calculated by the LHNC integral equations.[20] All the values of Patey *et al.* are nearly equal to those at $L^*=0.5$. It is shown in Figs. 10 and 11 that the values of $\rho k_BT\kappa_T$ are nearly constant with respect to the values of L^*, in sharp contrast to the case of the internal energy which has a large L^* dependence.

In this paper, we have proposed the RHNC like integral equations of RISM-1 type for polyatomic molecular fluids, and applied the equation to diatomic polar fluids. This calculation made from the first principles gives some new informations with respect to the structure and properties of diatomic polar fluids.

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