July, 1978] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 51 (7), 1977—1981 (1978) 1977

Computation of the Correlation Functions for Fluids Composed of Diatomic Molecules by Means of the Method of Integral Equations

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(Received February 6, 1978)

Pair correlation functions and structure factors of molecular fluids were computed, based on the reference interaction site model (RISM) integral equation coupled with the Percus-Yevick (PY) and the hyper-netted chain (HNC) approximations. The system considered is a fluid of diatomic molecules consisting of two identical spheres of diameter σ with each center located at a distance L ($L<\sigma$). The total potential energy for the molecular fluid is assumed to be the sum of pair potentials of the Lennard-Jones type. It is shown that the pair correlation functions calculated are in agreement with results of molecular dynamics studies. The structure factors calculated by using two kinds of approximations (PY and HNC) are found to deviate from each other for small values of k (wave vector). Discussions are given on the behavior of the structure factors, $S(k)$. The rise of $S(k)$ at small k is ascribed to the effect of attractive forces between molecules.

It has become evident from studies on the properties of simple atomic fluids with use of the Percus-Yevick (PY) and the hyper-netted chain(HNC) equations that these equations are useful for fluids composed of spherical particles.[1)] In the case of fluids composed of nonspherical molecules, however, solving the equations is difficult since the interactions between molecules depend on the mutual orientation of molecules as well as on their positions. Chen and Steel[2)] applied the generalized PY equation to a system of diatomic molecules. In order to solve the equation, they transformed it into a set of coupled integral equations by expanding the correlation functions in a series of spherical harmonics. However, this treatment was laborious and not successful.

Chandler and Andersen[3)] proposed the embedded site and the reference interaction site models for fluids consisting of polyatomic molecules. In these models, the total interaction between molecules is expressed as a sum of site-site interactions depending only on the separation between sites. In the embedded site model, each molecule is regarded as a hard sphere with embedded sites. This model was applied to a system of water-like particles.[4)] In the reference interaction site model a molecule is composed of rigidly-connected hard spheres (the spheres within a molecule may overlap), where the centers of interaction sites are located at the centers of the spheres.

Lowden and Chandler[5,6)] solved the reference interaction site model (RISM) integral equation for molecular fluids in which each molecule interacts through the hard sphere site-site repulsive potentials only. Ladanyi and Chandler[7,8)] applied a topological reduction procedure to the new cluster expansion formula on the basis of the RISM theory, giving a relationship between the RISM equation for molecular fluids and the PY equation for simple atomic fluids. Hsu *et al.*[9)] calculated the correlation functions for systems of homonuclear diatomic molecules using the method of the associated RISM model and intermolecular site-site cluster functions. They treated the attractive potential as a perturbation.

Recently, Johnson[10)] has given a set of equations which are analogous to the RISM equation from the Ornstein-Zernike equation using Fourier-Wigner series. The equations using the PY approximation were applied to a system of molecules interacting through the Lennard-Jones site-site potential.

We have attempted to solve the RISM integral equation coupled with the PY and HNC approximations for the purpose of dealing with systems interacting through intermolecular site-site potentials without use of the perturbation technique. The results of our calculation are compared with those of molecular dynamics studies[11,12)] and other calculations.[9,10)]

Theory

Model. In the theory proposed by Chandler and Andersen,[3)] a molecule is assumed to have m interaction sites. The location of the αth site on jth molecule is denoted by $\boldsymbol{r}_j^\alpha=\boldsymbol{R}_j+\boldsymbol{l}_j^\alpha$. Here, $\boldsymbol{R}_j$ denotes the location of the center of the jth molecule. The vector $\boldsymbol{l}_j^\alpha$ depends on the orientation of the molecule as described by the Eulerian angles. We assume that the molecule as shown in Fig. 1 is rigid so that the magnitude of $\boldsymbol{l}_j^\alpha$ and of the angles between different $\boldsymbol{l}_j^\alpha$ vectors within the same molecule become constant. The total potential energy for the molecular fluid is assumed to be the sum of pair potentials, where the pair interaction between molecule 1 and 2 is given by

$$w(1,2)=\sum_{\alpha=1}^{m}\sum_{\gamma=1}^{m}w_{\alpha\gamma}(\boldsymbol{r}_1^\alpha-\boldsymbol{r}_2^\gamma). \tag{1}$$

The pair interaction between α site of a molecule and γ site of another molecule is expressed as

$$w_{\alpha\gamma}(r)=4\varepsilon\left\{\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right\}. \tag{2}$$

Reference Interaction Site Model Equation.[3)] The pair correlation function considered is the intermolecular site-site radial distribution function defined as

$$g_{\alpha\gamma}(r)=\rho^{-2}\langle\sum_{i=1}^{N}\sum_{\substack{j=1\\(i\neq j)}}^{N}\delta(\boldsymbol{r}_i^\alpha)\delta(\boldsymbol{r}_j^\gamma-\boldsymbol{r})\rangle, \tag{3}$$

where the bracket $\langle\cdots\rangle$ denotes an ensemble average, $\rho=\langle N/V\rangle$ the average density, and $\delta(\boldsymbol{r})$ the Dirac delta function. The structure of molecular fluid is given by the $g_{\alpha\gamma}(r)$ function where $4\pi r^2\rho g_{\alpha\gamma}(r)$ is a probability distribution for finding a site γ associated with one molecule at a distance r from an origin when a site α (in another molecule) is located at the origin.

The total correlation function is

$$h_{\alpha\gamma}(r) = g_{\alpha\gamma}(r) - 1, \tag{4}$$

which is a functional of site-site cluster functions, $f_{\alpha\gamma}(r)$ and intramolecular pair distribution functions, $s_{\alpha\gamma}(r)$. These quantities are defined as

$$f_{\alpha\gamma}(r) = \exp\{-\beta w_{\alpha\gamma}(r)\} - 1, \tag{5}$$

where β^{-1} is Boltzmann's constant times temperature and

$$\begin{aligned} s_{\alpha\gamma}(r) &= (1-\delta_{\alpha\gamma})\rho^{-1}\langle\sum_{i=1}^{N}\delta(\boldsymbol{r}_i^\alpha)\delta(\boldsymbol{r}_i^\gamma-\boldsymbol{r})\rangle, \\ &= (1-\delta_{\alpha\gamma})(4\pi L_{\alpha\gamma})^{-1}\delta(r-L_{\alpha\gamma}). \end{aligned} \tag{6}$$

The second equality in Eq. 6 holds for rigid molecules only, where the distance between site α and γ within the same molecule is a constant $L_{\alpha\gamma}$.

The site-site total correlation function $h_{\alpha\gamma}(r)$ and the site-site direct correlation function $c_{\alpha\gamma}(r)$ are related by an Ornstein-Zernike type equation:

$$\hat{\boldsymbol{h}}(\boldsymbol{k}) = \hat{\boldsymbol{\omega}}(\boldsymbol{k})\hat{\boldsymbol{c}}(\boldsymbol{k})[\boldsymbol{1}-\rho\hat{\boldsymbol{\omega}}(\boldsymbol{k})\hat{\boldsymbol{c}}(\boldsymbol{k})]^{-1}\hat{\boldsymbol{\omega}}(\boldsymbol{k}), \tag{7}$$

where $\hat{\boldsymbol{h}}(\boldsymbol{k})$, $\hat{\boldsymbol{c}}(\boldsymbol{k})$, and $\hat{\boldsymbol{\omega}}(\boldsymbol{k})$ denote matrices with elements $\hat{h}_{\alpha\gamma}(k)$, $\hat{c}_{\alpha\gamma}(k)$, and $\hat{\omega}_{\alpha\gamma}(k)$,

$$\begin{aligned} \hat{h}_{\alpha\gamma}(k) &= \int \mathrm{d}\boldsymbol{r}\, h_{\alpha\gamma}(r)\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\boldsymbol{r}}, \\ \hat{c}_{\alpha\gamma}(k) &= \int \mathrm{d}\boldsymbol{r}\, c_{\alpha\gamma}(r)\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\boldsymbol{r}}, \\ \hat{\omega}_{\alpha\gamma}(k) &= \int \mathrm{d}\boldsymbol{r}\, \omega_{\alpha\gamma}(r)\mathrm{e}^{-\mathrm{i}\boldsymbol{k}\boldsymbol{r}}, \end{aligned} \tag{8}$$

respectively. The $\omega_{\alpha\gamma}(r)$ is defined as

$$\omega_{\alpha\gamma}(r) = \delta_{\alpha\gamma}\delta(r) + s_{\alpha\gamma}(r). \tag{9}$$

PY and HNC Approximations. The RISM integral equation can be solved when the site-site direct correlation function $c_{\alpha\gamma}(r)$ is expressed in terms of the site-site total correlation function $h_{\alpha\gamma}(r)$.[3] According to Chandler[8] the $c_{\alpha\gamma}(r)$ on the RISM integral equation is expressed as

$$c_{\alpha\gamma}(r) = y_{\alpha\gamma}(r)f_{\alpha\gamma}(r), \tag{10}$$

where $y_{\alpha\gamma}(r)$ is

$$y_{\alpha\gamma}(r) = \exp\{\beta\omega_{\alpha\gamma}(r)\}g_{\alpha\gamma}(r). \tag{11}$$

He refers to Eq. 10 as a "PY like approximation." We propose here the application of a "HNC like approximation" defined as

$$c_{\alpha\gamma}(r) = h_{\alpha\gamma}(r) - \ln y_{\alpha\gamma}(r), \tag{12}$$

which is similar to the HNC approximation for simple atomic fluids.[13] A set of coupled non-linear integral equations is formed by combining Eq. 7 with the closure Eq. 10 or Eq. 12.

Computational Procedure

Computational Method. For a fluid composed of homonuclear diatomic molecules such as shown in Fig. 1, we have $h_{\alpha\gamma}(r)=h_{11}(r)$ and $c_{\alpha\gamma}(r)=c_{11}(r)$ for all (α,γ). The RISM integral equation (Ref. 5, Eq. 2.7) is

$$\hat{h}_{11}(k) = \{1+\hat{\omega}_{12}(k)\}^2\hat{c}_{11}(k)/[1-2\rho\{1+\hat{\omega}_{12}(k)\}\hat{c}_{11}(k)], \tag{13a}$$

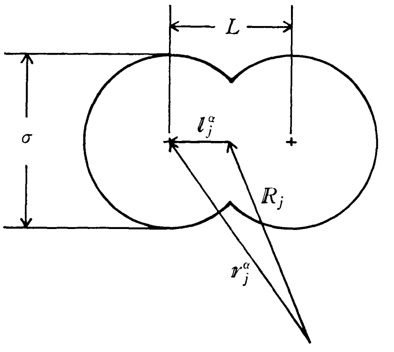

Fig. 1. The shape of RISM molecule.

$$\hat{\omega}_{12}(k) = (kL_{12})^{-1}\sin(kL_{12}), \tag{13b}$$

$$c_{11}(r) = y_{11}(r)f_{11}(r), \quad \text{(PY)} \tag{13c}$$

$$= h_{11}(r) - \ln y_{11}(r). \quad \text{(HNC)} \tag{13d}$$

An iteration procedure is carried out for solving Eqs. 13 numerically, the method of fast Fourier transformation (FFT) being used for the calculation.[14] The function $h_{11}(r)$ is discontinuous at $r=\sigma$ but the function $\gamma(r)=h_{11}(r)-c_{11}(r)$ is a continuous function of r.[5] With use of $\gamma(r)$, Eqs. 13a—d are written as

$$\rho\gamma(r) = \rho(2\pi)^{-3}\int \mathrm{d}\boldsymbol{k}\left[\frac{\{1+\hat{\omega}_{12}(k)\}^2}{1-2\rho\{1+\hat{\omega}_{12}(k)\}\hat{c}_{11}(k)}-1\right]\hat{c}_{11}(k)\mathrm{e}^{\mathrm{i}\boldsymbol{k}\boldsymbol{r}} \tag{14}$$

and

$$\gamma(r) = y_{11}(r) - 1, \quad \text{(PY)} \tag{15a}$$

$$= \ln y_{11}(r), \quad \text{(HNC)} \tag{15b}$$

respectively. The iteraction procedure is carried out by means of Eqs. 14 and 15. The values of $\hat{c}_{11}(k)$ given by Lowden and Chandler[5] for the hard sphere intermolecular site-site interactions are taken as initial ones. The iteration has been continued until the self-consistency of

$$\left|\frac{y_{11}^{\mathrm{out}}(r)-y_{11}^{\mathrm{in}}(r)}{y_{11}^{\mathrm{in}}(r)}\right| < 10^{-7} \tag{16}$$

is satisfied.

Structure Factor. Neutron scattering experiments determine the molecular structure factor, $S(k)$, which is defined as

$$S(k) = (\sum_{\alpha=1}^{m} b_\alpha)^{-2}\sum_{\alpha,\gamma}^{m} b_\alpha b_\gamma\langle N^{-1}\sum_{i,j}^{N}\exp\{i\boldsymbol{k}\cdot(\boldsymbol{r}_i^\alpha-\boldsymbol{r}_j^\gamma)\}\rangle. \tag{17}$$

In the calculation of $S(k)$ it is assumed that the interaction sites are located on the nuclei so that $\boldsymbol{r}_j^\alpha$ is the location of αth nucleus in the jth molecule. The coherent neutron scattering amplitude for a nucleus of type α is denoted by b_α. By performing the ensemble average in Eq. 17, the structure factor can be expressed in terms of site-site pair correlation functions:[6]

$$S(k) = (\sum_{\alpha=1}^{m} b_\alpha)^{-2}\sum_{\alpha,\gamma}^{m} b_\alpha b_\gamma\{\hat{\omega}_{\alpha\gamma}(k)+\rho\hat{h}_{\alpha\gamma}(k)\}, \tag{18}$$

$$= \frac{1}{2}\{1+\hat{\omega}_{12}(k)\} + \rho\hat{h}_{11}(k). \tag{19}$$

The equality in Eq. 19 holds for fluids composed of homonuclear diatomic molecules. If the intermolecular structure of a fluid is completely random (the ideal gas limit), the structure factor becomes

$$S_{\mathrm{ideal}}(k) = (\sum_{\alpha=1}^{m} b_\alpha)^{-2} \sum_{\alpha,\gamma}^{m} b_\alpha b_\gamma \hat{\omega}_{\alpha\gamma}(k). \tag{20}$$

Molecular Parameters. We have carried out the calculation according to the procedure described above for liquid nitrogen. Barojas *et al.*[12] and Cheung and Powles[15] made a computer simulation for the homonuclear diatomic molecular liquid by means of a molecular dynamics method using the same potential as in the present paper. The parameters corresponding to liquid nitrogen are

$$L_{12} = |l^1 - l^2| = 1.100\,\mathrm{A},$$

$$\sigma = 3.341\,\mathrm{A},$$

$$\varepsilon/k = 44\,\mathrm{K},$$

and

$$L^* = L_{12}/\sigma = 0.3,$$

where k is Boltzmann's constant. When these parameters are used, the values $\rho^* = \rho\sigma^3$ and $T^* = kT/\varepsilon$ at the triple point are 0.6964 and 1.437, respectively, and those at the critical point are $\rho^* = 0.246$ and $T^* = 2.86$. For the sake of comparison we have made a calculation of $S(k)$ for the same values of parameters. The values $\rho^* = 0.6964$, $T^* = 1.61$ used correspond to $T = 71$ K, $\rho = 0.868$ g/cm^3 for liquid nitrogen.[11]

Results and Discussions

Correlation Functions. Figures 2—5 show the site-site radial distribution functions calculated according to the procedure described in the preceding section. The $g_{11}(r)$ calculated are compared with the results of other theories[9,10] as well as those of molecular dynamics[11,12] in Figs. 2—4. The agreement between these results is satisfactory on the whole. The site-site pair correlation curve obtained from the RISM equation for the system with hard sphere site-site interactions is known to have two cusps appearing at $r^* = (r/\sigma) = 1$ and $r^* = 1 + L^*$.[5] For the system with the Lennard-ones site-site potential, these cusps are supposed to be rounded off with a shoulder appearing instead at $r^* = 1 + L^*$. If one site is σ away from a site at the origin, then another site of the same molecule is located between σ and $\sigma + L_{12}$ from the site at the origin resulting in appearance of a shoulder at $r^* = 1 + L^*$. This feature distinguishes the structure of molecular fluids from

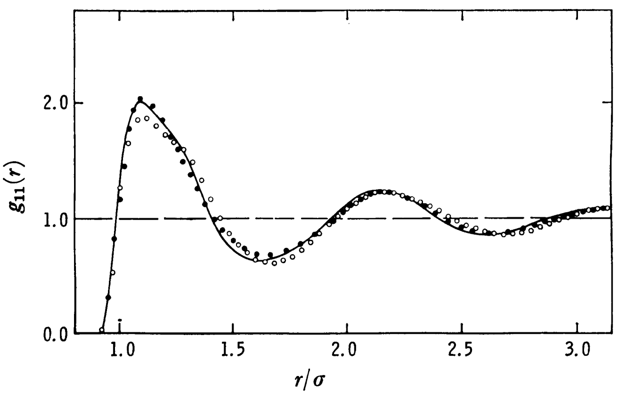

Fig. 2. Site-site radial distribution function, $g_{11}(r)$, for homonuclear diatomic fluids at $\rho^* = 0.6964$ and $T^* = 1.61$.
○: The molecular dynamics results of Ref. 11, ●: the calculated results of Ref. 10, ——: this work.

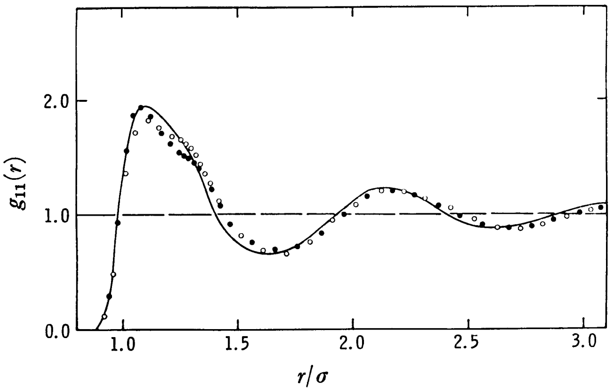

Fig. 3. Site-site radial distribution function, $g_{11}(r)$, for homonuclear diatomic fluids at $\rho^* = 0.6964$ and $T^* = 1.83$.
○: The molecular dynamics results of Ref. 12, ●: the calculated results of Ref. 9, ——: this work.

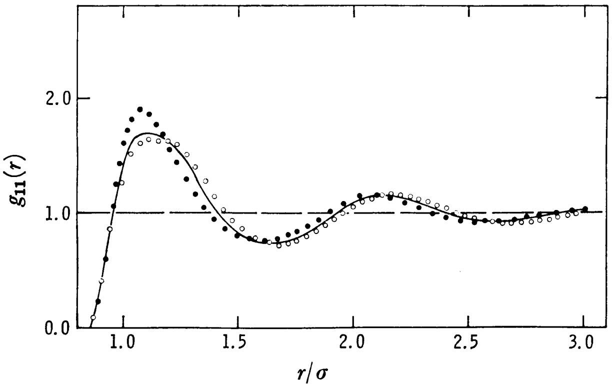

Fig. 4. Site-site radial distribution function, $g_{11}(r)$, for homonuclear diatomic fluids at $\rho^* = 0.696$ and $T^* = 4.03$.
○: The molecular dynamics results of Ref. 12, ●: the calculated results of Ref. 10, ——: this work.

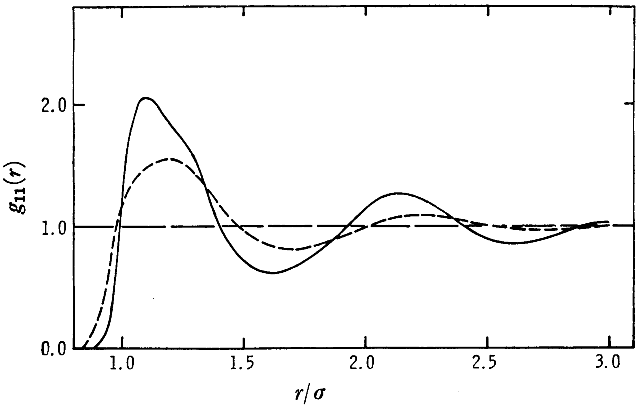

Fig. 5. Site-site radial distribution function, $g_{11}(r)$, for homonuclear diatomic fluids, ——: at $\rho^* = 0.6964$ and $T^* = 1.46$, ----: at $\rho^* = 0.55$ and $T^* = 4.03$.

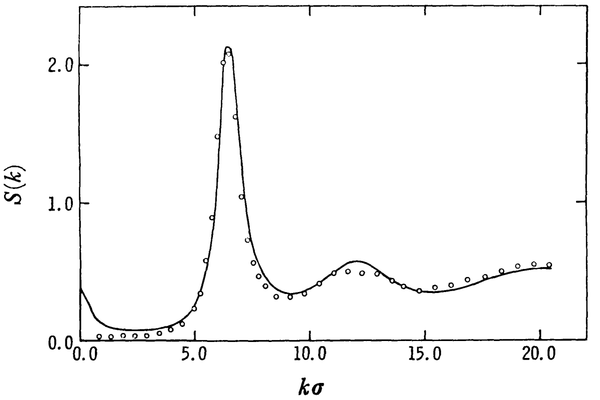

Fig. 6. Structure factor, $S(k)$, for homonuclear diatomic fluids at $\rho^*=0.6964$ and $T^*=1.61$.
○: The molecular dynamics results of Ref. 11, ——: this work.

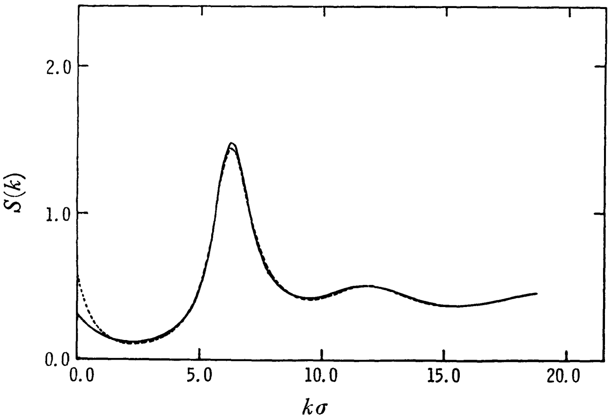

Fig. 7. Comparison of the structure factor, $S(k)$, calculated by using PY and HNC approximations at $\rho^*=0.60$ and $T^*=3.14$.
——: PY approximation, ----: HNC approximation.

that of simple atomic fluids. The $g_{11}(r)$ obtained by Johnson[10] (Fig. 2) has no shoulder which is in sharp contrast to the result of our calculation as well as that of molecular dynamics.[11] The curve of Johnson deviates on the whole from the result of molecular dynamics[12] at higher temperatures (Fig. 4), while our curve is in a fairly good agreement. The shoulder disappears at higher temperatures, the $g_{11}(r)$ becoming similar to the radial distribution function for the fluid composed of spherical particles with the Lennard-Jones potential, as shown in Fig. 5.

Structure Factors. The structure factor calculated is compared with the results of molecular dynamics[11] in Fig. 6. Agreement is satisfactory except for small values of k. Figure 7 shows the structure factors calculated using the PY and HNC approximations, some difference appearing at small values of k. The difference appears also in structure factors calculated by use of the PY and HNC approximations for simple atomic fluids.[16] The structure factors we obtained for different temperatures at a fixed density are given in Fig. 8. The values of $S(k)$ increase in the small range of $k\sigma$ ($k\sigma<\pi$).[17] This has never been found in the results calculated by the method of a perturbation technique using blip function.[9] The behavior of the structure factors at small values of k seems to be due to the contribution of attractive potentials. In fact, at higher temperatures, the behavior of $S(k)$ becomes similar to that of $S(k)$ for the case of the hard sphere potential.

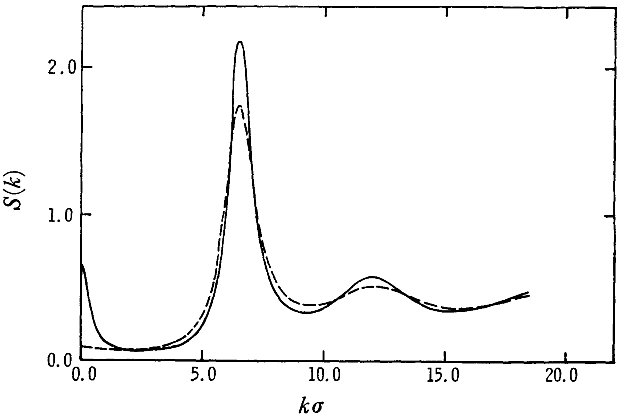

Fig. 8. Structure factor, $S(k)$, for homonuclear diatomic fluids.
——: At $\rho^*=0.6964$ and $T^*=1.51$, ----: at $\rho^*=0.6964$ and $T^*=3.14$.

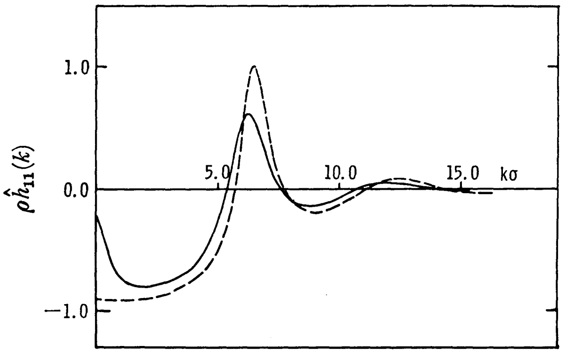

Fig. 9. Comparison of $\rho\hat{h}_{11}(k)$ between two different state.
——: At $\rho^*=0.55$ and $T^*=3.14$, ----: at $\rho^*=0.6964$ and $T^*=3.14$.

Weeks *et al.*[18] pointed out that the behavior of $\rho\hat{h}(k)$ is dominated by repulsive forces, and effect of the attractive forces is primarily manifested in the small wave vector portion as shown in Fig. 9. At lower densities, the contribution of the attractive forces becomes dominant at small values of k. On the other hand, at higher densities this contribution disappears and becomes similar to the behavior of $\rho\hat{h}(k)$ for the fluids consisting of hard sphere particles.

Concluding Remarks

The RISM integral equation coupled with the PY and HNC approximations has been applied to fluids consisting of homonuclear diatomic molecules interacting through the Lennard-Jones site-site potentials. Computation procedure and results are summarized as follows: (1) the RISM integral equation coupled with the PY and HNC approximations can be solved numerically by means of a method of an iteration procedure with a fast Fourier transformation (FFT), (2) the site-site pair correlation function, $g_{11}(r)$, and structure factor, $S(k)$, are in agreement with the results of molecular dynamics, (3) the shoulder in $g_{11}(r)$ appears at $r^*=1+L^*$, which is considered to be characteristic of $g_{11}(r)$ for molecular fluids, not being present in $g(r)$ for simple atomic fluids, and (4) the behavior of $S(k)$ at small values of k is ascribed to the attractive part of potentials, the effect becoming more evident as compared with the results of the perturbation method.

The authers are much indebted to Dr. Yoshio Tago, Fujitsu Inc. Ltd., for preparation of the computer program used in the present paper.

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