Statistical Mechanical Calculation of the Radial Distribution Function for a Water-like Fluid

Fumio Hirata
Research Institute of Applied Electricity, Hokkaido University, Sapporo 060

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The radial distribution function (RDF) for a *water-like system*, which has the fundamental characteristics of water, is calculated using the graph-theoretical technique developed by Andersen and Chandler. An interaction potential devised to simulate the hydrogen bond is regarded as a perturbation of the pair interaction between the two molecules of a reference system which consists of hard spheres each having a point dipole at each center. The effect of the hydrogen bond-like potential on the distribution of the molecules is shown explicitly. The results show a tetrahedral coordination similar to that in water. The resulting RDF has qualitatively reproduced the features observed in the experimental RDF curve for water.

Water possesses various anomalous physicochemical properties. It is believed that such properties are caused by an "ice-like" structure tetrahedrally-linked *via* hydrogen bonds.[1] The strongest evidence for the tetrahedral coordination is radial distribution function (RDF) obtained from X-ray diffraction and neutron scattering data.[2] The first peak in the RDF is narrow in comparison with that of simple fluids, and corresponds to the low local-density caused by the tetrahedral coordination of the molecules. Another feature in the RDF of water concerns the location of the second peak. The location is characteristic not of simple fluids but of ice. Molecular dynamics and Monte Carlo studies have reproduced the features of the RDF of water.[3]

If we confine ourselves to simple fluids, there are theoretical methods which satisfactorily reproduce the observed values without the aid of any assumptions concerning the arrangement of the molecules.[4] In the case of water, however, if we do not wish to use such assumptions, we are immediately faced with the trouble problem of how to treat strong orientational correlations between water molecules.

Ben-Naim has numerically solved the Percus-Yevick (PY) equation,[5] which has been generalized to involve angular coordinates, in order to obtain the RDF of water.[6a] They used a model potential that effectively accounts for some geometrical features of the hydrogen bond, favoring the tetrahedral orientation. This model potential has a Lennard-Jones (12,6) part and an angle-dependent part based on Bjerrum's four point-charge model of a water molecule. Ben-Naim has proposed another model for the effective pair potential of water. This is expressed by the superposition of the following three terms: a Lennard-Jones (12,6) potential, a dipole-dipole interaction, and a potential devised to act only along the four directions pointing to the vertices of a regular tetrahedron. The hydrogen bond is simulated by the third term. However, actual calculations were carried out only for the case of a two-dimensional system with no dipole-dipole interaction.[6b,7]

New graph-theoretical methods, which are based on the technique of topological reduction, have recently been developed,[4] and have been successfully applied to electrolyte solutions, and dipolar and molecular fluids.[8-14] On the basis of their previous work,[12] Chandler and Andersen have proposed computationally simple techniques for calculating the thermodynamic properties and pair distribution functions of molecular fluids in which the intermolecular interactions are highly angular dependent.[13] The technique is based on the idea that a molecule has several interaction sites, and that the total interaction between two molecules is the sum of the site-site interactions that depend only on the distances between the sites of the two molecules.

Here, an application of this technique to a model system, which we refer to as a "water-like system," is reported. The water-like system is the simplest model which maintains the fundamental features of water, and is distinguished from water by the simplifications described in the following section.

In section I, the model which was used throughout this study is described in detail. In section II, a brief summary is given of the theoretical methods employed and then the methods are extended to the model system. In section III, the procedure for applying the method described in section II to the model is given and the results of the calculation are shown. In the final section, some consideration is given to the results obtained.

I. Effective Pair Potential for a Water-like System

It is expected that the interaction energy between two real water molecules consists of several parts: (1)

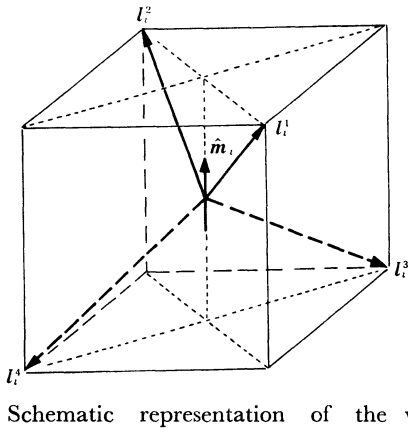


Fig. 1. Schematic representation of the water-like molecule. The molecule is a hard sphere which has a point dipole at its center and four interaction sites seated on the vertices of a regular tetrahedron. The positions of the four sites in a molecule are denoted by vectors starting from the center, $\boldsymbol{l}_i^1$, $\boldsymbol{l}_i^2$, $\boldsymbol{l}_i^3$, and $\boldsymbol{l}_i^4$. The sites at $\boldsymbol{l}_i^1$ and $\boldsymbol{l}_i^2$ correspond to hydrogen atoms of a water molecule and $\boldsymbol{l}_i^3$ and $\boldsymbol{l}_i^4$ to the lone pairs.

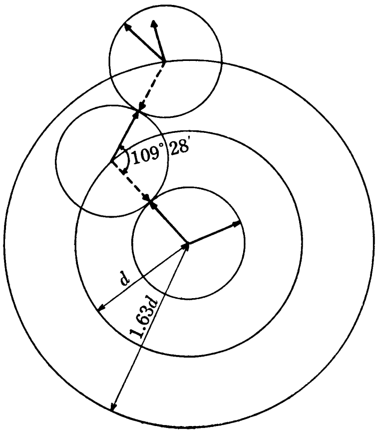


Fig. 2. A typical arrangement of a triplet of molecules in the crystal which consists of water-like molecules.

a steep repulsive part which plays a dominant role in the liquid state and a weak attraction at a short distance, (2) the dipole-dipole interaction at large distances, and (3) hydrogen bonding which is presumably of very short range and highly dependent on the orientation of the molecules. In place of a more realistic system, we consider a simplified model which maintains the fundamental characteristics of the real system. Imagine a hard sphere which has a point dipole at its center and four interaction sites situated on the surfaces of the sphere in the four tetrahedral directions from the center. Let unit vectors pointing to the four sites from the center of the i-th molecule be $\hat{\boldsymbol{l}}_i^\alpha$ (α; 1, 2, 3, 4). The vector giving a dipole orientation is denoted by $\hat{\boldsymbol{m}}_i$. The angles between $\hat{\boldsymbol{l}}_i$ and $\hat{\boldsymbol{m}}_i$ are denoted by χ_α, thus

$$\cos\chi_\alpha = (\hat{\boldsymbol{m}}_i \cdot \hat{\boldsymbol{l}}_i^\alpha), \qquad (\alpha = 1, \cdots, 4) \tag{1-1}$$

It is assumed that

$$\cos\chi_1 = \cos\chi_2 = \cos\chi,$$
and
$$\cos\chi_3 = \cos\chi_4 = -\cos\chi. \tag{1-2}$$

Figure 1 shows a schematic picture of such a model particle. The interaction energy between two such molecules may be expressed as the superposition ot three terms:

$$u(i,j) = u_d(R) + u_{DD}(i,j) + u_{HB}(i,j), \tag{1-3}$$

where i and j denote the positions and the orientations of molecules i and j, respectively, and R is the distance between the centers of the two molecules. In particular, let i represent $\boldsymbol{R}_i$ (the position of the center of the i-th molecule) and $\boldsymbol{\Omega}_i$ (the Euler angle required to specify the orientation of the i-th molecule). The position of the α-site on the i-th molecule is denoted by $\boldsymbol{r}_i^\alpha = \boldsymbol{R}_i + \boldsymbol{l}_i^\alpha$. The molecules are assumed to be rigid. Thus, $\boldsymbol{l}_i^\alpha$ depends only on $\boldsymbol{\Omega}_i$. The magnitudes of all $\boldsymbol{l}_i^\alpha$ (α=1, 2,3,4) are identical and are represented by l. $u_d(R)$ and $u_{DD}(i,j)$ are defined as

$$\begin{aligned} u_d(R) &= \infty, \qquad R<d, \\ &= 0, \qquad R>d, \end{aligned} \tag{1-4}$$

and

$$u_{DD}(i,j) = (-m^2/R^3)D(i,j), \tag{1-5}$$

where

$$D(i,j) = 3(\hat{\boldsymbol{m}}_i \cdot \hat{\boldsymbol{R}})(\hat{\boldsymbol{m}}_j \cdot \hat{\boldsymbol{R}}) - (\hat{\boldsymbol{m}}_i \cdot \hat{\boldsymbol{m}}_j),$$

d is the hard-sphere diameter and $\hat{\boldsymbol{R}}$ the unit vector along the relative position $\boldsymbol{R} = \boldsymbol{R}_i - \boldsymbol{R}_j$. The $u_{HB}(i,j)$ is a sum of site-site interactions of the two molecules, and thus the hydrogen bonding is simulated by

$$u_{HB}(i,j) = \sum_\alpha^4 \sum_\gamma^4 u_{\alpha\gamma}(|\boldsymbol{r}_i^\alpha - \boldsymbol{r}_j^\gamma|). \tag{1-6}$$

It is assumed that the site located at $\boldsymbol{l}_i^1$ is identical with that at $\boldsymbol{l}_i^2$ in kind and is different from those at $\boldsymbol{l}_i^3$ and $\boldsymbol{l}_i^4$, which are of the same kind. The sites at $\boldsymbol{l}_i^1$ and $\boldsymbol{l}_i^2$ correspond to the hydrogen atoms of a water molecule and those at $\boldsymbol{l}_i^3$ and $\boldsymbol{l}_i^4$ to lone pairs. A site on one molecule is assumed to interact with a site on another molecule only if the two sites differ in kind. A square-well potential is chosen as the interaction potential, such that

$$\begin{aligned} u_{\alpha\gamma}(|\boldsymbol{r}_i^\alpha - \boldsymbol{r}_j^\gamma|) &= -\varepsilon_H, \qquad 0<|\boldsymbol{r}_i^\alpha - \boldsymbol{r}_j^\gamma|<b, \\ &= 0, \qquad b<|\boldsymbol{r}_i^\alpha - \boldsymbol{r}_j^\gamma|, \end{aligned} \tag{1-7}$$

where ε_H and b are parameters which represent the depth and the width of the hydrogen-bond potential. These circumstances correspond to the fact that the hydrogen bond in water occurs only if a hydrogen atom of one molecule encounters a lone pair of another molecule.

The model potential just described is similar to that of Ben-Naim but is apparently distinguishable from the latter in the details of the short-range and the hydrogen bond parts.[7)]

II. Application of Graph-Theoretical Techniques to the Water-like System

Outline of the Andersen-Chandler Theory. In this section, the graph-theoretical technique of Andersen and Chandler is applied to the model described in the preceding section. The technique is outlined here.[12)]

An interaction potential between two molecules is expressed as a superposition of two parts, a reference part $u_0(1,2)$ and a perturbation $u_1(1,2)$:

$$u(1,2) = u_0(1,2) + u_1(1,2). \tag{2-1}$$

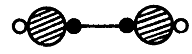
Let $h_0(1,2)$ be the total correlation function[4)] of the reference system which depends only upon $u_0(1,2)$. Functions $F_0(1,2)$ and $\Phi(1,2)$, which are referred to as the "*reference system hypervertex*"[8b,12)] and the "*perturbation bond*,"[12)] respectively, are defined as:

$$F_0(1,2) = \rho\delta(1,2) + \rho^2 h_0(1,2), \tag{2-2}$$

$$\Phi(1,2) = -\beta u_1(1,2), \tag{2-3}$$

where $\beta = 1/kT$, k is the Boltzmann constant and $\delta(1,2)$ the Dirac delta function. The sum of an infinite series is defined by convolution integrals of functions F_0 and Φ, whose first few terms are represented with the aid of diagrams:

$$C(1,2) = \sum_{n=1}^\infty C^{(n)}(1,2),$$
$$C^{(1)}(1,2) = \int F_0(1,3)\Phi(3,4)F_0(4,2)\mathrm{d}(3)\mathrm{d}(4) \tag{2-4}$$

=  , and

$$C^{(2)}(1,2) = \int F_0(1,3)\Phi(3,4)F_0(4,5)\Phi(5,6) \times F_0(6,2)\mathrm{d}(3)\mathrm{d}(4)\mathrm{d}(5)\mathrm{d}(6)$$

$$=$$  ,

where the large circles with two small circles tangent to their circumferences represent F_0 and the lines with small circles at both ends denote Φ. $C^{(n)}(1,2)$ and $C(1,2)$ are called a "*generalized chain*" with n perturbation bonds and a "*renormalized potential*," respectively. Andersen and Chandler have shown that the pair distribution function is approximately expressed by the equation:[12)]

$$\rho^2 g(1,2) = \rho^2 g_0(1,2)\exp C(1,2), \tag{2-5}$$

where $\rho^2 g_0(1,2)$ is the pair distribution function of the reference system and

$$g_0(1,2) = h_0(1,2) + 1. \tag{2-6}$$

Thus, our problem is reduced to the evaluation of the renormalized potential $C(1,2)$, if we know $h_0(1,2)$ in advance.

Application of Graph-Theoretical Techniques to the Water-like System. Here a representation for the pair distribution function of the water-like system is presented using the graph-theoretical technique above outlined. The procedure follows the method presented by Chandler and Andersen.[13)]

The first two terms of Eq. 1-3 are regarded as the reference potential and the last term as the perturbation. Thus,

$$u_0(1,2) = u_d(R) + u_{DD}(1,2), \tag{2-7}$$

$$u_1(1,2) = u_{HB}(1,2). \tag{2-8}$$

Many studies have been devoted to applying the graph-theoretical and integral equation techniques of the theory of classical fluids to the problem of the dielectric constant or the pair distribution function of a system possessing the pair interaction described by Eq. 2-7. Recent progress in such studies involves an analytical solution of the MSM equation[15)] and treatments based on the γ-ordering technique.[8,10,11)] These studies can be employed to postulate the form of the total correlation function of our reference system. It has been proven that the renormalized potential (Eq. 2-4) for such a system reduces to only the sum of convolution integrals of the perturbation bonds, $-\beta u_{DD}(1,2)$.[16)] The convolution intergrals can be evaluated to explicitly represent the renormalized potential:[10)]

$$C_{DD}(1,2) = \frac{\beta m^2}{(1+2y)(1-y)} \times \left\{\frac{1}{R^3}D(1,2) + \frac{8\pi y}{3}\delta(R)\Delta(1,2)\right\} \tag{2-9}$$

where $y = 4\pi\beta m^2\rho/9$ and $\Delta(1,2) = (\hat{m}_1 \cdot \hat{m}_2)$.

It is assumed that the total correlation function of the present reference system can be represented by the superposition of two terms,

$$h_0(1,2) = h_d(R) + C_{DD}(1,2), \tag{2-10}$$

where $h_d(R)$ is the total correlation function of the hard-sphere fluid. The right-hand side of Eq. 2-10 coincides with the MSM approximation if the PY approximation is used for $h_d(R)$[5,17)] and C_{DD} (1,2) equals zero for $R<d$.[12,16)] Using Eqs. 1-6, 2-3, 2-8, and 2-10 the perturbation bond and the reference system hypervertex for the water-like system are, respectively, defined as:

$$\Phi_{\alpha\gamma}(1,2) = -\beta u_{\alpha\gamma}(|\boldsymbol{r}_1^\alpha - \boldsymbol{r}_2^\gamma|), \tag{2-11}$$

and

$$F_0(1,2) = (\rho/\Omega)\delta(\boldsymbol{R}_1 - \boldsymbol{R}_2)\delta(\boldsymbol{\Omega}_1 - \boldsymbol{\Omega}_2) + (\rho/\Omega)^2 h_0(1,2). \tag{2-12}$$

The generalized chain with n perturbation bonds is given by

$$C_{WL}^{(n)}(1,2) = (\rho/\Omega)^{-2}\int \mathrm{d}(3)\mathrm{d}(4)\cdots\mathrm{d}(2n+2) \times \sum_{\alpha,\gamma}\cdots\sum_{\eta,\nu} F_0(1,3)\Phi_{\alpha\gamma}(3,4)F_0(4,5)\cdots \times \Phi_{\eta\nu}(2n+1,2n+2)F_0(2n+2,2). \tag{2-13}$$

The simple case of $n=2$ is investigated in some detail.

$$C_{WL}^{(2)}(1,2) = (\rho/\Omega)^{-2}\int \mathrm{d}(3)\cdots\mathrm{d}(6) \times \sum_{\alpha,\gamma}\sum_{\eta,\nu} F_0(1,3)\Phi_{\alpha\gamma}(3,4)F_0(4,5) \times \Phi_{\eta\nu}(5,6)F_0(6,2). \tag{2-14}$$

We assume that the Fourier transform of $\Phi_{\alpha\gamma}(1,2)$ is $\Phi_{\alpha\gamma}(k)$ and hence,

$$\Phi_{\alpha\gamma}(1,2) = (2\pi)^{-3}\int \mathrm{d}\boldsymbol{k}\tilde{\Phi}_{\alpha\gamma}(k)\exp[i\boldsymbol{k}\cdot(\boldsymbol{r}_1^\alpha - \boldsymbol{r}_2^\gamma)]. \tag{2-15}$$

By inserting Eq. 2-15 into Eq. 2-14, we obtain

$$C_{WL}^{(2)}(1,2) = (\rho/\Omega)^{-2}(2\pi)^{-6}\int \mathrm{d}(3)\cdots\mathrm{d}(6)\int \mathrm{d}\boldsymbol{k}_1\mathrm{d}\boldsymbol{k}_2 \times \sum_{\alpha,\gamma}\sum_{\eta,\nu}\tilde{\Phi}_{\alpha\gamma}(k_1)\tilde{\Phi}_{\eta\nu}(k_2) \times F_0(1,3)F_0(4,5)F_0(6,2) \times \exp[i\boldsymbol{k}_1\cdot(\boldsymbol{r}_3^\alpha - \boldsymbol{r}_4^\gamma) + i\boldsymbol{k}_2\cdot(\boldsymbol{r}_5^\eta - \boldsymbol{r}_6^\nu)]. \tag{2-16}$$

Integrals over the configurations of molecules 4 and 5 are carried out, giving

$$(2\pi)^{-3}\int \mathrm{d}(4)\mathrm{d}(5)F_0(4,5)\exp[-i(\boldsymbol{k}\cdot\boldsymbol{r}_4^\alpha + \boldsymbol{k}'\cdot\boldsymbol{r}_5^\gamma)] = \delta(\boldsymbol{k}+\boldsymbol{k}')\Gamma_{\alpha\gamma}(k) \tag{2-17}$$

$\Gamma_{\alpha\gamma}(k)$ is the sum of two terms, $\Gamma^{h}_{\alpha\gamma}(k)$ and $\Gamma^{c}_{\alpha\gamma}(k)$ as follows,

$$\Gamma_{\alpha\gamma}(k) = \Gamma^{h}_{\alpha\gamma}(k) + \Gamma^{c}_{\alpha\gamma}(k). \tag{2-18}$$

$\Gamma^{h}_{\alpha\gamma}(k)$ and $\Gamma^{c}_{\alpha\gamma}(k)$ are given by

$$\Gamma^{h}_{\alpha\gamma}(k) = \rho\omega_{\alpha\gamma}(k) + \rho^2 z_\alpha(k)z_\gamma(-k)\tilde{h}_d(k) \tag{2-19}$$

and

$$\Gamma^{c}_{\alpha\gamma}(k) = \frac{\beta m^2}{(1+2y)(1-y)}\left(\frac{\rho}{\Omega}\right)^2 \times \int \mathrm{d}\boldsymbol{\Omega}_i\mathrm{d}\boldsymbol{\Omega}_j\tilde{C}'_{DD}(i,j)\exp[-i\boldsymbol{k}\cdot(\boldsymbol{l}_i^\alpha - \boldsymbol{l}_j^\gamma)], \tag{2-20}$$

where

$$\omega_{\alpha\gamma}(k) = \frac{\sin(k|\boldsymbol{l}_i^\alpha - \boldsymbol{l}_i^\gamma|)}{k|\boldsymbol{l}_i^\alpha - \boldsymbol{l}_i^\gamma|}, \tag{2-21}$$

$$z_\alpha(k) = \frac{\sin(kl^\alpha)}{kl^\alpha}, \tag{2-22}$$

$$\tilde{C}'_{\mathrm{DD}}(i,j) = -\frac{4\pi}{3}\tilde{\boldsymbol{D}}(i,j) + \frac{8}{3}\pi y\tilde{\boldsymbol{\Delta}}(i,j), \tag{2-23}$$

$$\tilde{\boldsymbol{D}}(i,j) = 3(\hat{\boldsymbol{m}}_i\cdot\hat{\boldsymbol{k}})(\hat{\boldsymbol{m}}_j\cdot\hat{\boldsymbol{k}}) - (\hat{\boldsymbol{m}}_i\cdot\hat{\boldsymbol{m}}_j), \tag{2-24}$$

$$\tilde{\boldsymbol{\Delta}}(i,j) = (\hat{\boldsymbol{m}}_i\cdot\hat{\boldsymbol{m}}_j), \tag{2-25}$$

and $\hat{\boldsymbol{k}}$ is the unit vector pointing in the direction of $\boldsymbol{k}$. Substituting Eq. 2-17 into Eq. 2-16 and integrating over $\boldsymbol{k}'$, we have

$$C^{(2)}_{\mathrm{WL}}(1,2) = (\rho/\Omega)^{-2}(2\pi)^{-3}\int \mathrm{d}(3)\mathrm{d}(6)\int \mathrm{d}\boldsymbol{k}\sum_{\alpha,\gamma}\sum_{\eta,\nu}\tilde{\Phi}_{\alpha\gamma}(k)\Gamma_{\gamma\eta}(k)\tilde{\Phi}_{\eta\nu}(k)F_0(1,3)F_0(6,2)\exp[i\boldsymbol{k}\cdot(\boldsymbol{r}^{\alpha}_3+\boldsymbol{r}^{\nu}_6)]. \tag{2-26}$$

The integrals of Eq. 2-26 over the configurations of molecules 3 and 6 lead to

$$\begin{aligned} C^{(2)}_{\mathrm{WL}}(1,2) = {} & (2\pi)^{-3}\int \mathrm{d}\boldsymbol{k}\sum_{\alpha,\gamma}\sum_{\eta,\nu}\tilde{\Phi}_{\alpha\gamma}(k)\Gamma_{\gamma\eta}(k)\tilde{\Phi}_{\eta\nu}(k)\exp[i\boldsymbol{k}\cdot(\boldsymbol{r}^{\alpha}_1-\boldsymbol{r}^{\nu}_2)][1+\rho\{z_{\alpha}(k)\tilde{h}_{\mathrm{d}}(k) \\ & + \Omega^{-1}\int \mathrm{d}\boldsymbol{\Omega}_3\tilde{C}_{\mathrm{DD}}(1,3)\exp(i\boldsymbol{k}\cdot\boldsymbol{l}^{\alpha}_3)\}\exp(-i\boldsymbol{k}\cdot\boldsymbol{l}^{\alpha}_1)] \\ & \times [1+\rho\{z_{\nu}(-k)\tilde{h}_{\mathrm{d}}(k)+\Omega^{-1}\int \mathrm{d}\boldsymbol{\Omega}_6 C_{\mathrm{DD}}(6,2)\exp(-i\boldsymbol{k}\cdot\boldsymbol{l}^{\nu}_6)\}\exp(i\boldsymbol{k}\cdot\boldsymbol{l}^{\nu}_2)] \end{aligned} \tag{2-27}$$

The generalized chain with n perturbation bonds is analyzed in the same way. The result is

$$\begin{aligned} C^{(n)}_{\mathrm{WL}}(1,2) = {} & (2\pi)^{-3}\int \mathrm{d}\boldsymbol{k}\sum_{\alpha,\nu}\{\tilde{\boldsymbol{\Phi}}(k)[\boldsymbol{\Gamma}(k)\tilde{\boldsymbol{\Phi}}(k)]^{n-1}\}_{\alpha,\nu}\exp[i\boldsymbol{k}\cdot(\boldsymbol{r}^{\alpha}_1-\boldsymbol{r}^{\nu}_2)] \\ & \times [1+\rho\{z_{\alpha}(k)\tilde{h}_{\mathrm{d}}(k)+\Omega^{-1}\int \mathrm{d}\boldsymbol{\Omega}_3\tilde{C}_{\mathrm{DD}}(1,3)\exp(i\boldsymbol{k}\cdot\boldsymbol{l}^{\alpha}_3)\}\exp(-i\boldsymbol{k}\cdot\boldsymbol{l}^{\alpha}_1)] \\ & \times [1+\rho\{z_{\nu}(-k)\tilde{h}_{\mathrm{d}}(k)+\Omega^{-1}\int \mathrm{d}\boldsymbol{\Omega}_6\tilde{C}_{\mathrm{DD}}(6,2)\exp(-i\boldsymbol{k}\cdot\boldsymbol{l}^{\nu}_6)\}\exp(i\boldsymbol{k}\cdot\boldsymbol{l}_2)], \end{aligned} \tag{2-28}$$

where $\boldsymbol{\Phi}(k)$ and $\boldsymbol{\Gamma}(k)$ are 4×4 matrices with elements $\tilde{\Phi}_{\alpha\gamma}(k)$ and $\Gamma_{\alpha\gamma}(k)$, respectively. The renormalized potential is given by the sum over the entire generalized chain ($n\geq1$):

$$\begin{aligned} C_{\mathrm{WL}}(1,2) = \sum_{n=1}^{\infty} C^{(n)}_{\mathrm{WL}}(1,2) = {} & \sum_{\alpha,\nu}(2\pi)^{-3}\int \mathrm{d}\boldsymbol{k}\{\tilde{\boldsymbol{\Phi}}(k)[\boldsymbol{1}-\boldsymbol{\Gamma}(k)\tilde{\boldsymbol{\Phi}}(k)]^{-1}\}_{,\nu}\exp[i\boldsymbol{k}\cdot(\boldsymbol{r}^{\alpha}_1-\boldsymbol{r}^{\nu}_2)] \\ & \times [1+\rho\{z_{\alpha}(k)\tilde{h}_{\mathrm{d}}(k)+\Omega^{-1}\int \mathrm{d}\boldsymbol{\Omega}_3\tilde{C}_{\mathrm{DD}}(1,3)\exp(i\boldsymbol{k}\cdot\boldsymbol{l}^{\alpha}_3)\}\exp(-i\boldsymbol{k}\cdot\boldsymbol{l}^{\alpha}_1)] \\ & \times [1+\rho\{z_{\nu}(-k)\tilde{h}_{\mathrm{d}}(k) + \Omega^{-1}\int \mathrm{d}\boldsymbol{\Omega}_6\tilde{C}_{\mathrm{DD}}(6,2)\exp(-i\boldsymbol{k}\cdot\boldsymbol{l}^{\nu}_6)\}\exp(i\boldsymbol{k}\cdot\boldsymbol{l}^{\nu}_2)], \end{aligned} \tag{2-29}$$

where $\boldsymbol{1}$ is the 4×4 identity matrix. Remembering Eq. 2-5, we have the representation for the pair distribution function of the water-like fluid, thus

$$g_{\mathrm{WL}}(1,2) = g_0(1,2)\exp C_{\mathrm{WL}}(1,2), \tag{2-30}$$

or in its linearized version,

$$g_{\mathrm{WL}}(1,2) = g_0(1,2)\{1+C_{\mathrm{WL}}(1,2)\}. \tag{2-31}$$

The radial distribution function is obtained by integrating Eq. 2-31 over the orientations of molecules 1 and 2. Remembering Eq. 2-10 and taking account of the fact that

$$\Omega^{-2}\int C_{\mathrm{DD}}(1,2)\mathrm{d}\boldsymbol{\Omega}_1\mathrm{d}\boldsymbol{\Omega}_2 = 0,$$

we get

$$\begin{aligned} g_{\mathrm{WL}}(R) &= \Omega^{-2}\int g_{\mathrm{WL}}(1,2)\mathrm{d}\boldsymbol{\Omega}_1\mathrm{d}\boldsymbol{\Omega}_2 \\ &= \{1+C_{\mathrm{WL}}(R)\}g_{\mathrm{d}}(R) + C_{\mathrm{WL}}{*}C_{\mathrm{DD}}, \end{aligned} \tag{2-32}$$

where $g_{\mathrm{d}}(R)$ is the RDF for the hard-sphere fluid and $C_{\mathrm{WL}}(R)$ and $C_{\mathrm{WL}}{*}C_{\mathrm{DD}}$ are defined by

$$C_{\mathrm{WL}}(R) = \Omega^{-2}\int C_{\mathrm{WL}}(1,2)\mathrm{d}\boldsymbol{\Omega}_1\mathrm{d}\boldsymbol{\Omega}_2 \tag{2-33}$$

and

$$C_{\mathrm{WL}}{*}C_{\mathrm{DD}} = \Omega^{-2}\int C_{\mathrm{WL}}(1,2)C_{\mathrm{DD}}(1,2)\mathrm{d}\boldsymbol{\Omega}_1\mathrm{d}\boldsymbol{\Omega}_2. \tag{2-34}$$

III. Computational Procedures and Results

After some manipulation, we obtain a more tractable equation for $C_{\mathrm{WL}}(R)$ from Eqs. 2-29 and 2-33:

$$\begin{aligned} C_{\mathrm{WL}}(R) = {} & (2\pi)^{-2}\int_0^{\infty}\mathrm{d}k\frac{2k\sin(kR)}{R}[z(k)(1+\rho\tilde{h}_{\mathrm{d}}(k))]^2 \\ & \times \sum_{\alpha,\nu}\{\tilde{\boldsymbol{\Phi}}(k)[\boldsymbol{1}-\boldsymbol{\Gamma}(k)\tilde{\boldsymbol{\Phi}}(k)]^{-1}\}_{\alpha,\nu}, \end{aligned} \tag{3-1}$$

where $z(k)=\sin(kl)/kl$. The integral in Eq. 2-20 must be carried out to obtain the elements of $\boldsymbol{\Gamma}(k)$. It can be performed by a suitable choice of Euler angles to give

$$\Gamma^{\mathrm{c}}_{\alpha\gamma}(R) = \frac{-6y\rho}{(1+2y)}\cos\chi_{\alpha}\cos\chi_{\gamma}\left\{\frac{\cos(kl)}{kl}-\frac{\sin(kl)}{(kl)^2}\right\}^2. \tag{3-2}$$

The details of calculations leading to Eq. 3-2 are given in the appendix. The equation for $C_{\mathrm{WL}}{*}C_{\mathrm{DD}}$ is obtained from Eqs. 2-9, 2-29, and 2-34 after some tedious calculations and the result is

$$\begin{aligned} C_{\mathrm{WL}}{*}C_{\mathrm{DD}} = {} & \frac{(2\pi)^{-2}\beta m^2}{(1+2y)^3(1-y)}\left\{\frac{2}{R^2}+\frac{8\pi y}{3}\delta(R)\right\} \\ & \times \int_0^{\infty}\mathrm{d}k k^2\left\{\frac{\cos(kl)}{(kl)}-\frac{\cos(kl)}{(kl)^2}\right\}^2 \\ & \times \left\{\frac{2\sin(kR)}{kR}+\frac{4\cos(kR)}{(kR)^2}+\frac{4\sin(kR)}{(kR)^3}\right\} \\ & \times \sum_{\alpha,\nu}\cos\chi_{\alpha}\cos\chi_{\nu}\{\tilde{\boldsymbol{\Phi}}(k)[\boldsymbol{1}-\boldsymbol{\Gamma}(k)\tilde{\boldsymbol{\Phi}}(k)]^{-1}\}_{\alpha,\nu}. \end{aligned} \tag{3-3}$$

It is necessary to obtain explicit forms of the summations in Eqs. 3-1 and 3-3. Combining Eqs. 2-18, 1-2, and 3-2, we obtain the explicit form of $\boldsymbol{\Gamma}(k)$:

$$\boldsymbol{\Gamma}(k) = \begin{pmatrix} \Gamma'_- & \Gamma_- & \Gamma_+ & \Gamma_+ \\ \Gamma_- & \Gamma'_- & \Gamma_+ & \Gamma_+ \\ \Gamma_+ & \Gamma_+ & \Gamma'_- & \Gamma_- \\ \Gamma_+ & \Gamma_+ & \Gamma_- & \Gamma'_- \end{pmatrix}, \tag{3-4}$$

where Γ_-, Γ'_- and Γ_+ are

$$\Gamma_- = \Gamma_\mathrm{h} - \Gamma_\mathrm{c}, \tag{3-5}$$

$$\Gamma'_- = \Gamma'_\mathrm{h} - \Gamma_\mathrm{c}, \tag{3-6}$$

and

$$\Gamma_+ = \Gamma_\mathrm{h} + \Gamma_\mathrm{c}, \tag{3-7}$$

and

$$\Gamma_\mathrm{h} = \rho\omega(k) + \rho^2 z(k)^2 \tilde{h}_\mathrm{d}(k), \tag{3-8}$$

$$\Gamma'_\mathrm{h} = \rho + \rho^2 z(k)^2 \tilde{h}_\mathrm{d}(k), \tag{3-9}$$

and

$$\Gamma_\mathrm{c} = -\frac{6y\rho}{(1+2y)}\cos^2\chi\left\{\frac{\cos(kl)}{kl} - \frac{\sin(kl)}{(kl)^2}\right\}^2. \tag{3-10}$$

Taking into account the characteristics of the site-site interactions described in the section I, we have

$$\tilde{\boldsymbol{\Phi}}(k) = \tilde{\Phi}(k)\begin{pmatrix} 0 & 0 & 1 & 1 \\ 0 & 0 & 1 & 1 \\ 1 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 \end{pmatrix}, \tag{3-11}$$

where $\tilde{\Phi}(k)$ is given by

$$\tilde{\Phi}(k) = -4\pi\beta\varepsilon_\mathrm{H}\left\{\frac{b\cos(kb)}{k^2} - \frac{\sin(kb)}{k^3}\right\}. \tag{3-12}$$

The inverse matrix which appears in Eqs. 3-1 and 3-3 can easily be calculated thanks to the high symmetry of matrices $\boldsymbol{\Gamma}(k)$ and $\tilde{\boldsymbol{\Phi}}(k)$, and as a result we obtain

$$\sum_{\alpha,\nu}\{\tilde{\boldsymbol{\Phi}}(k)[\mathbf{1}-\boldsymbol{\Gamma}(k)\tilde{\boldsymbol{\Phi}}(k)]^{-1}\}_{\alpha,\nu} = \frac{8\tilde{\Phi}(k)}{1-2\tilde{\Phi}(k)\{3\Gamma_\mathrm{h}(k)+\Gamma'_\mathrm{h}(k)\}}, \tag{3-13}$$

and

$$\sum_{\alpha,\nu}\cos\chi_\alpha\cos\chi_\nu\{\tilde{\boldsymbol{\Phi}}(k)[\mathbf{1}-\boldsymbol{\Gamma}(k)\tilde{\boldsymbol{\Phi}}(k)]^{-1}\}_{\alpha,\nu} = \frac{-8\tilde{\Phi}(k)\cos^2\chi}{1-2\tilde{\Phi}(k)\{\Gamma_\mathrm{h}(k)-\Gamma'_\mathrm{h}(k)+4\Gamma_\mathrm{c}(k)\}}. \tag{3-14}$$

The correlation function obtained on the basis of the PY approximation is used as the total correlation function of the hard-sphere system, h_d, and its Fourier transform is expressed as

$$\tilde{h}_\mathrm{d}(k) = \frac{\tilde{C}_\mathrm{PY}(k)}{1-\tilde{C}_\mathrm{PY}(k)}, \tag{3-15}$$

where $\tilde{C}_\mathrm{PY}(k)$ is the Fourier transform of the direct correlation function of the hard-sphere fluid, which is the Wertheim solution to the PY equation.[5,17] Although $h_\mathrm{d}(R)$, and hence $g_\mathrm{d}(R)$, are obtained from the Fourier transform of $\tilde{h}_\mathrm{d}(k)$, the numerical calculation is performed in practice with the aid of a function,

$$\tilde{\gamma}(k) = \tilde{h}_\mathrm{d}(k) - \tilde{C}_\mathrm{PY}(k), \tag{3-16}$$

because $h_\mathrm{d}(R)$ and its derivatives are discontinuous at $R=d$.[18] All the integrals over k are performed numerically on the basis of the Simpson rule. The accuracy of the calculations has been checked against the exact values of $g_\mathrm{d}(R)$ given by Throop and Bearman.[19] The results for $C_\mathrm{WL}(R)$ are shown in Figs. 3—5 and those for $g_\mathrm{WL}(R)$ in Figs. 6 and 7. $C_\mathrm{WL}{*}C_\mathrm{DD}$ is not shown explicitly, since its contribution is very small compared with that of $C_\mathrm{WL}(R)$. It should be noted that $C_\mathrm{WL}(R)$ represents the effect of the hydrogen bonds on the molecular distribution.

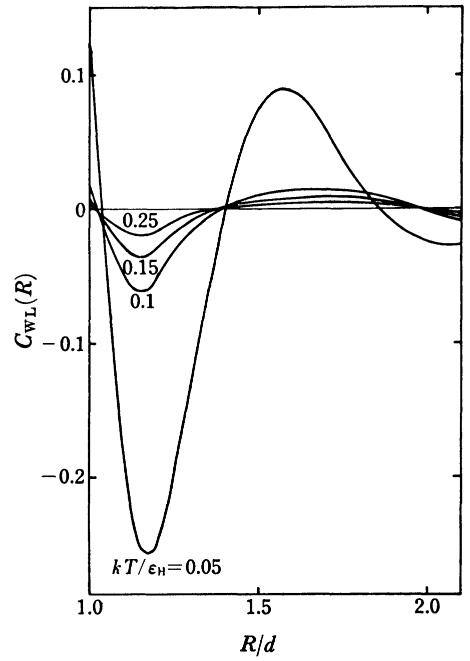


Fig. 3. The functions $C_\mathrm{WL}(R)$ for $b=0.2d$, $\rho d^3=0.6$, $kT/\varepsilon_\mathrm{H}=0.05$, 0.1, 0.15, and 0.25. It represents the effect of the hydrogen bonds.

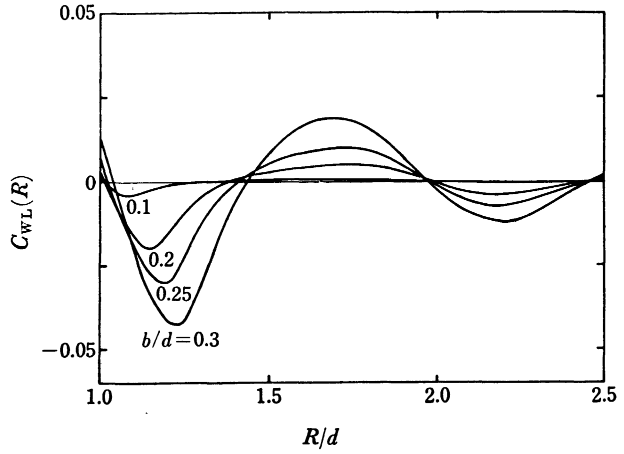


Fig. 4. The functions $C_\mathrm{WL}(R)$ for $\rho d^3=0.6$, $kT/\varepsilon_\mathrm{H}=0.25$, $b=0.3d$, $0.25d$, $0.2d$, and $0.1d$.

IV. Discussion

We imagine a crystal consisting of water-like molecules, which has a tetrahedral structure similar to ice. A typical arrangement for a triplet of molecules in the crystal is depicted in Fig. 2. If the model potential described in section I favors such an arrangement, it is expected that the following two effects on the molec-

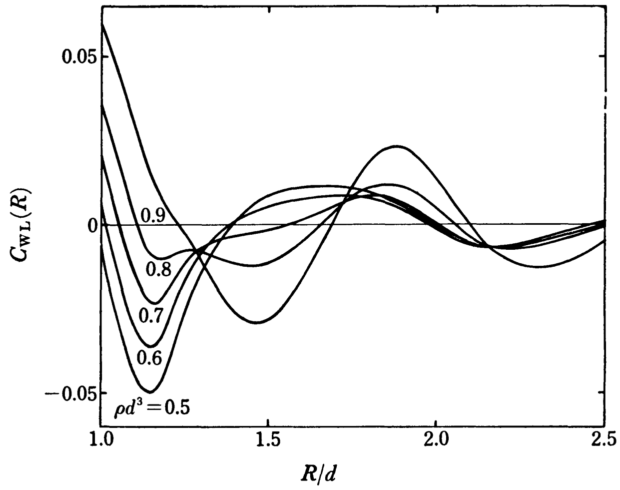


Fig. 5. The functions $C_{\rm WL}(R)$ for $kT/\varepsilon_{\rm H}=0.15$, $b=0.2d$, $\rho\, l^3=0.5$, 0.6, 0.7, 0.8, and 0.9.

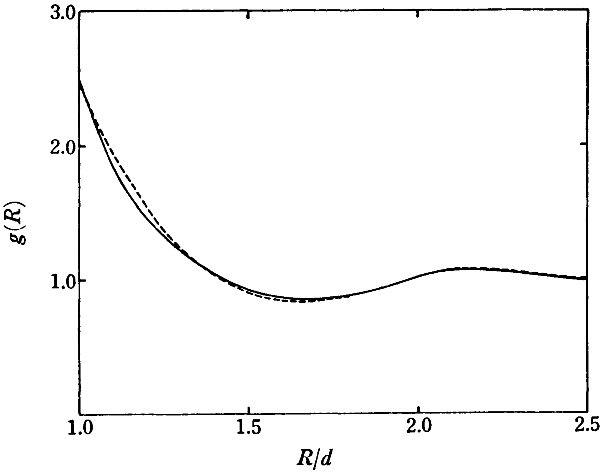


Fig. 6. The calculated RDF for the water-like fluid (solid line) at $\rho d^3=0.6$, $kT/\varepsilon_{\rm H}=0.1$, and $b=0.2d$, compared with one for the hard-sphere fluid (dashed line).

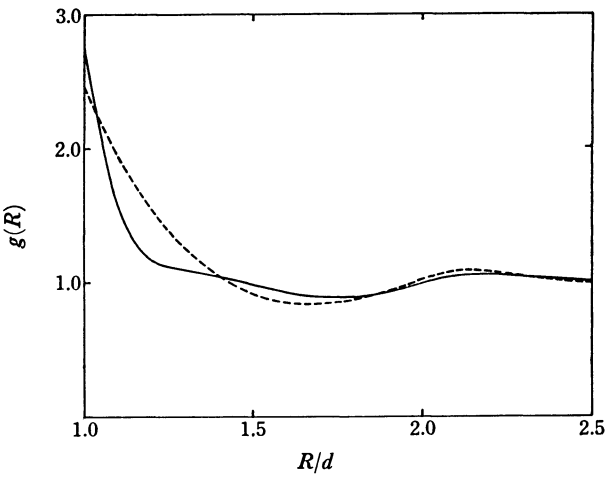


Fig. 7. The calculated RDF for the water-like fluid (solid line) at $\rho d^3=0.6$, $kT/\varepsilon_{\rm H}=0.05$, and $b=0.2d$, compared with one for the hard-sphere fluid (dashed line).

ular distribution of the reference system are produced: a decrease in the density of the first coordination shell and an increase in the density in the neighborhood of a position $1.63d$ distant from the central molecule. The behavior of $C_{\rm WL}(R)$ in Fig. 3 is consistent with this expectation. The negative value of $C_{\rm WL}(R)$ at short distances is due to the former effect and the positive values in the neighborhood of $R=1.6d$ to the latter. It should be noted that there is a peak in the neighborhood of $R=1.6d$. It is also reasonable that the features become more prominent as the depth of the square-well potential, $\varepsilon_{\rm H}$, increases. All the curves with various values of $kT/\varepsilon_{\rm H}$ given in Fig. 3 are observed to have a nearly common point of intersection with the abscissa. This is supposed to be primarily due to the maintenance of the magnitude of b as a constant through all the calculations. This is determined easily from Fig. 4, where several $C_{\rm WL}(R)$ curves with different values of b are depicted. An evident shift in the location of the intersection is observed. The manner in which the $C_{\rm WL}(R)$ curves change with density is shown in Fig. 5. Appreciable differences are observed between the curves for high and low densities. It appears that the trend of forming a tetrahedral geometry is dominant at low densities and that it weakens with increasing density. On the basis of rapid increase of the first peak, the behavior of $C_{\rm WL}(R)$ at higher densities appears to indicate that the square-well potential serves as a central attractive force rather than as a non-central force leading to the tetrahedral geometry. The increase in density would have two results: an enhancement of the role of repulsive force in the determination of the molecular distribution and an increase in the probability of sites on one molecule encountering those on another molecule. The former effect prevents the hydrogen bonds from forming a tetrahedral geometry, and the latter produces a strong attraction between the two molecules.

The results for the RDF are shown in Figs. 6 and 7. A narrowing of the first peak similar to that observed for the RDF of water[2,7] is found, and this feature increases as the magnitude of $\varepsilon_{\rm H}$ increases. Although characteristics of the second peak for the RDF of water do not appear in the present calculation, this peak does appear to grow. This is noticeable in spite of the use of overestimated values of $\varepsilon_{\rm H}$.

The coordination number is to be obtained from the first peak of the RDF curve using the equation,

$$n_{\rm CN} = \rho\int_0^{R_{\rm m}} g(R)4\pi R^2{\rm d}R. \qquad (4\text{-}1)$$

It should be noted that the values of $n_{\rm CN}$ depend on the choice of $R_{\rm m}$. The most reasonable choice of $R_{\rm m}$ would be the location of the first minimum in the RDF. However, this choice cannot be adopted in the present case since no minimum corresponding to the first minimum in the RDF of water is found. Therefore, it is only possible to give the coordination number obtained for a rather arbitrary value of $R_{\rm m}$. The coordination number is about 6.2 when $R_{\rm m}$ equals $1.4d$ which corresponds to the point of intersection of the $C_{\rm WL}(R)$ curve with the abscissa.[20] It should be noted that a similar arbitrariness in the choice of $R_{\rm m}$ is also found in the report of Ben-Naim.[6a)]

It is hoped that the application of the method proposed here to water and ionic solutions will be reported in future publications. There are several possibilities for improving the model and the mathematical formalism. It is not too difficult to replace the hard-sphere potential with the Lennard-Jones (12,6) potential. Systematic ways of performing such a replacement have been given.[21)] Moreover, the present rough representation of $h_0(1,2)$, Eq. 2-10, could be replaced by a more elaborate representation. More fundamental improvements concern the graph-theoretical treatment. A possible improvement could be achieved by taking account of the graphs ignored in this study. However, it would be rather promising to employ the optimization procedure proposed by Andersen and Chandler.[12)]

It is interesting to apply this method to the problems of ion-water interactions. The orientational effect due to ion-dipole interactions is different in charater from that due to the hydrogen bonds. It is possible that the ion-dipole interaction exerts a torque on the molecule, which prevents the molecule from hydrogen-bonding. If this is true, the contribution of ion-dipole interactions to the molecular distribution should be opposite to the effect of the hydrogen bonds. It is expected, therefore, that the RDF for a water-like system under the influence of an electrostatic field due to ions approaches that for a simple fluid. This would provide an explanation of the so-called "*structure-breaking effect*" of ions.[22–24)]

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Appendix: the Derivation of Eq. 3-2

Let $\boldsymbol{k}$ be the z-axis, then Eq. 2-23 becomes:

$$\begin{aligned}\tilde{C}'_{\mathrm{DD}}(i,j) &= -\frac{4\pi}{3}\tilde{\boldsymbol{D}}(i,j) + \frac{8\pi}{3}y\tilde{\boldsymbol{\Delta}}(i,j)\\ &= \frac{8}{3}\pi(y-1)\cos\theta_{ik}\cos\theta_{jk}\\ &\quad + \frac{4}{3}\pi(1+2y)\cos(\phi_i-\phi_j),\end{aligned} \tag{A-1}$$

where θ_{ik} and ϕ_i are the polar and the azimuthal angles of the unit vector $\hat{\boldsymbol{m}}_i$ of the i-th molecule, respectively, and θ_{jk} and ϕ_j are those of the j-th molecule. Eq. 2-20 can, therefore, be rewritten as

$$\begin{aligned}\Gamma^{c}_{\alpha\gamma}(k) &= -\frac{8\pi\beta m^2\rho^2}{3(1+2y)}\frac{1}{\Omega^2}\int \mathrm{d}\boldsymbol{\Omega}_i\cdot\mathrm{d}\boldsymbol{\Omega}_j\\ &\quad\times\exp[-i\boldsymbol{k}\cdot(\boldsymbol{l}_i^\alpha-\boldsymbol{l}_j^\gamma)]\cos\theta_{ik}\cos\theta_{jk}\\ &\quad+\frac{4\pi\beta m^2\rho^2}{3(1-y)}\frac{1}{\Omega^2}\int \mathrm{d}\boldsymbol{\Omega}_i\cdot\mathrm{d}\boldsymbol{\Omega}_j\\ &\quad\times\exp[-i\boldsymbol{k}\cdot(\boldsymbol{l}_i^\alpha-\boldsymbol{l}_j^\gamma)]\cos(\phi_i-\phi_j).\end{aligned} \tag{A-2}$$

The integrals can be broken up into factors each of which is an integral over $\boldsymbol{\Omega}_i$ or $\boldsymbol{\Omega}_j$. As an example, we investigate in some detail the integral, involving the i-th molecule and the α site.

Let us first take the Cartesian-coordinate system, x′y′z′, fixed to the i-th molecule, whose origin coincides with the center of the molecule and the z′-axis points in the direction of the α site of the molecule. The Cartesian coordinates of the unit vector of the dipole, $\hat{\boldsymbol{m}}_i$, in the coordinate system are denoted by $m_{x'}$, $m_{y'}$ and $m_{z'}$. Then, this coordinate system is rotated to a new coordinate system, xyz, whose z axis coincides with $\boldsymbol{k}$. The orientation of the xyz system relative to the x′y′z′ system can be specified by the Euler angles θ, ϕ and ψ. Thus, the components of $\hat{\boldsymbol{m}}_i$ in the new xyz system are given by the linear transformation:[25)]

$$\begin{bmatrix} m_x\\ m_y\\ m_z\end{bmatrix} = \begin{bmatrix} \cos\psi\cos\phi-\cos\theta\sin\phi\sin\psi & \cos\psi\sin\phi+\sin\theta\cos\phi\sin\psi & \sin\psi\sin\theta\\ -\sin\psi\cos\phi-\cos\theta\sin\phi\cos\psi & -\sin\psi\sin\phi+\cos\theta\cos\phi\sin\psi & \cos\psi\sin\theta\\ \sin\theta\sin\phi & -\sin\theta\cos\phi & \cos\theta\end{bmatrix}\begin{bmatrix} m_{x'}\\ m_{y'}\\ m_{z'}\end{bmatrix} \tag{A-3}$$

The components of $\hat{\boldsymbol{m}}_i$ are also represented by the polar coordinate system whose polar axis coincides with $\boldsymbol{k}$:

$$m_x = \sin\theta_{ik}\cos\phi_i,\quad m_y = \sin\theta_{ik}\sin\phi_i,\quad m_z = \cos\theta_{ik}. \tag{A-4}$$

From Eqs. A-3 and A-4, we obtain

$$\left.\begin{aligned}\cos\theta_{ik} &= m_{x'}\sin\theta\sin\phi - m_{y'}\sin\theta\cos\phi + m_{z'}\cos\theta,\\ \cos\phi_i &= \{m_{x'}(\cos\psi\cos\phi-\cos\theta\sin\phi\sin\psi) + m_{y'}(\cos\psi\sin\phi+\sin\theta\cos\phi\sin\psi) + m_{z'}\sin\psi\sin\theta\}/\sin\theta_{ik}\\ \sin\phi_i &= \{m_{x'}(-\sin\psi\cos\phi-\cos\theta\sin\phi\cos\psi) + m_{y'}(-\sin\psi\sin\phi+\cos\theta\cos\phi\cos\psi) + m_{z'}\cos\psi\sin\theta\}/\sin\theta_{ik}.\end{aligned}\right\} \tag{A-5}$$

Thus, the integral over $\boldsymbol{\Omega}_i$ can be performed using Eq. A-5.

$$\begin{aligned}\frac{1}{\Omega}\int \mathrm{d}\boldsymbol{\Omega}_i\exp(-i\boldsymbol{k}\cdot\boldsymbol{l}_i^\alpha)\cos\theta_{ik} &= \frac{1}{8\pi^2}\int_0^\pi \mathrm{d}\theta\sin\theta\int_0^{2\pi}\mathrm{d}\phi\int_0^{2\pi}\mathrm{d}\psi\exp(-ikl\cos\theta)\{m_{x'}\sin\theta\sin\phi-m_{y'}\sin\theta\cos\phi+m_{z'}\cos\theta\}\\ &= \frac{m_{z'}}{2}\int_0^\pi \mathrm{d}\theta\sin\theta\cos\theta\exp(-ikl\cos\theta) = im_{z'}\left\{\frac{\cos(kl)}{kl}-\frac{\sin(kl)}{(kl)^2}\right\} = i\cos\chi_\alpha\left\{\frac{\cos(kl)}{kl}-\frac{\sin(kl)}{(kl)^2}\right\}.\end{aligned} \tag{A-6}$$

The last equation results since the angle between vectors $\boldsymbol{l}_i^\alpha$ and $\hat{\boldsymbol{m}}_i$ is χ_α. By similar manipulations, we obtain

$$\frac{1}{\Omega}\int \mathrm{d}\boldsymbol{\Omega}\exp(i\boldsymbol{k}\cdot\boldsymbol{l}_j^\gamma)\cos\theta_{jk} = \frac{\cos\chi_\gamma}{i}\left\{\frac{\cos(kl)}{kl}-\frac{\sin(kl)}{(kl)^2}\right\}. \tag{A-7}$$

Therefore, the first intergal in Eq. A-2 is

$$\frac{1}{\Omega^2}\int \mathrm{d}\boldsymbol{\Omega}_i\cdot\mathrm{d}\boldsymbol{\Omega}_j\exp[-i\boldsymbol{k}\cdot(\boldsymbol{l}_i^\alpha-\boldsymbol{l}_j^\gamma)]\cos\theta_{ik}\cos\theta_{jk} = \cos\chi_\alpha\cos\chi_\gamma\left\{\frac{\cos(kl)}{kl}-\frac{\sin(kl)}{(kl)^2}\right\}^2. \tag{A-8}$$

It may be proved in the same way that the second integral vanishes. Using the relation, $y=4\pi\beta m^2\rho/9$, one obtains

$$\Gamma^{c}_{\alpha\gamma}(k) = \frac{-6y\rho}{1+2y}\cos\chi_{\alpha}\cos\chi_{\gamma}\left\{\frac{\cos(kl)}{kl}-\frac{\sin(kl)}{(kl)^2}\right\}^2. \quad \text{(A-9)}$$

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