Site-site memory equation approach in study of density/pressure dependence of translational diffusion coefficient and rotational relaxation time of polar molecular solutions: acetonitrile in water, methanol in water, and methanol in acetonitrile

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We present results of theoretical study and numerical calculation of the dynamics of molecular liquids based on combination of the memory equation formalism and the reference interaction site model – RISM. Memory equations for the site-site intermediate scattering functions are studied in the mode-coupling approximation for the first order memory kernels, while equilibrium properties such as site-site static structure factors are deduced from RISM. The results include the temperature-density(pressure) dependence of translational diffusion coefficients $D$ and orientational relaxation times $\tau$ for acetonitrile in water, methanol in water and methanol in acetonitrile, all in the limit of infinite dilution. Calculations are performed over the range of temperatures and densities employing the SPC/E model for water and optimized site-site potentials for acetonitrile and methanol. The theory is able to reproduce qualitatively all main features of temperature and density dependences of $D$ and $\tau$ observed in real and computer experiments. In particular, a anomalous behavior, i.e. the increase in mobility with density, is observed for $D$ and $\tau$ of methanol in water, while acetonitrile in water and methanol in acetonitrile do not show deviations from the ordinary behavior. The variety exhibited by the different solute-solvent systems in the density dependence of the mobility is interpreted in terms of the two competing origins of friction, which interplay with each other as density increases: the collisional and dielectric frictions which, respectively, increase and decrease with increasing density.

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I. INTRODUCTION

The mobility of either polar molecules or small polyatomic ions in dense dipolar liquids exhibits some anomalies that have attracted considerable interest of scientists.\(^1,2,3,4,5,6,7,8,9,10,11,12,13,14,15\) In this paper we pay attention to the study of the so-called “anomalous pressure behavior” of polar binary molecular liquids by considering such popular models as methanol in water, acetonitrile in water and methanol in acetonitrile. In particular, we are interested in the density(pressure) dependence of translational diffusion coefficients and reorientation relaxation times of solutes. To begin with, we would like to say first few words about anomalies as they are.

The very primitive (classical, not quantum) picture of a molecular liquid could be the set of finite size structural particles – molecules – consisting of interacting sites, which are connected by chemical bonds. Positions of molecules as well as their orientations are not fixed in general and may vary randomly in time. The change may be achieved either by translational or rotational motion. Intuitively, it is then clear to understand that applying the external pressure for such system results in making the intermolecular distances shorter, which as the consequence will limit the molecular mobility. In this case one may expect a monotonous decrease with pressure for such quantities as translational or rotational diffusion coefficients. Limitation of the molecular mobility can also be discussed in terms of some other dynamical characteristics such as viscosity, dielectric relaxation, etc. This point of view has been confirmed experimentally for numerous liquids and solutions.\(^16\) At the same time, some molecular liquids do not obey strictly this abstraction and exhibit behavior which is different from the intuitive picture. Typical representatives of such molecular liquids are water and some aqueous solutions, whose mobility with pressure can be enhanced. The enhancement of the molecular (or ionic) mobility under pressure then has been identified as the anomalous one.

Historically, first attempts to explain dynamics of molecules in solutions were based on the use of the so-called continuum model for solvents.\(^20,21,22,23,24,25\) In this model the surrounding medium is regarded as a di-
electric continuum extending up to the surface of the particle. The particle itself is treated as a rigid sphere of finite size with some charge for ions or dipole moment for molecules. Dynamic behavior of the media are described by the Debye equation in terms of the frequency dependent dielectric susceptibility, and hydrodynamic effects are entirely neglected. The most important contribution of the theory was that it succeeded in extending the phenomenological approaches to consider the friction on a rotating dipole. When a dipole is surrounded by a dielectric continuum, it polarizes the medium. If the dipole rotates, the polarization should relax so that it adjusts itself to the electric field produced by the new orientation of the dipole. The relaxation process is associated with the energy dissipation which is identified as the dielectric friction. Later the theory was improved by obtaining velocity of fluid from linearized Navier-Stokes equation for a viscous incompressible fluid with boundary conditions of either perfect sticking or slipping at the surface of the particle.[26,27,28] Subsequently, there were many another suggestions on improvements of the theory, e.g. the enhanced “continuum mechanical framework” description has been given in series of works[29,30,31], where dissipation function is constructed by adding the electrical dissipation to the ordinary hydrodynamic one, etc. However, contrary to what was expected, the continuum model turned out to be unable to explain properly numerous contradictions of phenomenological laws with experimental data. One example is the failure of the Stokes-Einstein relation in explaining the dependence of mobility of ions in polar liquids on their size. In order to compromise the trouble it has been suggested to use the so-called “effective” radii of particles, or rewrite the relation so that it appears in the fractional exponent form.[32] Such kind of revisions had some effects, but there were also other difficulties which could not be resolved in principle. For instance, dielectric continuum theories cannot explain observed difference in mobility of anions and cations because the interaction between an ion and dielectric media does not depend on the sign of the ion charge. That is enough to realize that the insolvency of a conventional continuum model description can be overcome only by a microscopic formulation of the problem.

The microscopic, or statistical-mechanical, theory of molecular liquids is now on its rise, and the considerable progress has been achieved during last years both in the description of equilibrium and non-equilibrium properties.[33] It became possible due to the aptly used reference interaction site model – RISM,[34,35,36] and its modifications, or in the case of dynamics – due to appropriate unification of RISM and generalized Langevin equation (GLE) which is obtained in the Mori formalism.[37,38] The choice in favor of generalized Langevin equation is not accidental. For example, an alternative way of describing non-equilibrium processes can be based on the use of various types of kinetic equations which are derived from the BBGKY hierarchy.[39] However, when it is applied to systems with high density, there is an ambiguity in the construction of the collision integral. Also the linearization procedure for the collision integral cannot be justified by the same arguments which are used in the case of systems with low density.[40] In Mori formalism such questions do not appear. GLE describes the time evolution of several dynamic variables in concern as a function of the representative point in the phase space. All other variables which are not under explicit concern are projected onto the dynamic variables of interest with the help of a projection operator. The projection leads to an equation which looks similar to the phenomenological Langevin equation containing the frictional force proportional to the rate of change of the dynamic variables, and the random force, which are related to each other by the fluctuation-dissipation theorem. If one chooses as the dynamic variables the density and the conjugated current of sites or atoms of molecules in liquid, the theory gives a memory equation for the dynamic structure factor of atoms, which describes the time evolution of the site-site density pair correlation functions.[41] Initial values, i.e. site-site static structure factors and direct correlation functions which are necessary to solve this integro-differential equation, are obtained from the RISM or one of its generalizations.

A crucial development of the theory is rather conceptual, not mathematical, in the sense that it has provided a new concept to view dynamics of a molecule in solution, which is quite different from the model traditionally exploited in the field. The new model regards the molecular motion in liquid as a correlated translational motion of atoms: if two atoms in a diatomic molecule are moving in the same direction, then the molecule as a whole is making translational motion, while the molecule should be rotating if its atoms are moving in opposite directions. This view differs from the traditionally developed rotational-translational model which is based on the use of angular coordinates.[42,43,44,45,46] Another important issue of RISM-based theories, which should be mentioned here, is that they pioneered in explaining the observed difference in the behavior of anions and cations in solution. Both equilibrium[47] and non-equilibrium[48] systems were studied, and now we know that these differences should be attributed to dissimilarities of the microscopic structure of solvent surrounding the ion.

The new theory of dynamic processes in molecular liquids has been under development in last decade in works by Hirata and Chong,[49,50] and get its extension in studies by Hirata, Yamaguchi and others,[51,52,53,54,55,56,57,58,59,60] Particularly, theoretical description of pressure dependence of the molecular motion of liquid water and transport properties of ionic liquids were subjects for investigation in recent papers by Yamaguchi et al.[35,56]. In present manuscript we continue this line and report our latest study which is the pressure and temperature dependence of dynamics of polar molecules in solution. The manuscript is organized as follows. In subsection IIA, we write down equations of motion, which are memory equations, for site-site intermediate scattering functions,
and give relations for translational diffusion coefficient and reorientation correlation time in terms of these functions. In subsection 1.1 we deal with equilibrium properties of the system which we obtain using DRISM with hypernetted chain (HNC) type of the closure. In order to solve a memory equation one needs to set the model for memory kernels. This question is discussed in some detail in subsection 1.1. More attention is paid to the so-called mode-coupling approximation, which is used to study dynamical behavior of the system in the long-time scale. We apply our formalism to investigate some realistic systems such as acetonitrile in water, methanol in water and methanol in acetonitrile. Set up for these models and details of numerical procedures in the computational part of this work are briefly explained in section 1.2. Obtained results and remedies are discussed in section 1.3 and conclusions are given in section 1.4.

II. THEORY

A. Memory equations for site-site intermediate scattering functions

Time-correlation functions are convenient tools for describing properties of many-body systems and can directly be associated with experimental observables. A general theoretical scheme for calculation of time-correlation functions is provided by the Mori approach, which where they are phrased in terms of memory function equations. Hereafter we will follow the formalism by Hirata and Chomaz, which is the judicious unification of the theory of dynamical processes in simple liquids based on the Mori approach, and reference interaction site model for molecular liquids. In this formalism “slow” variables of the system are partial number densities and longitudinal current densities. Then, of practical interest are elements of the matrix of the site-site intermediate scattering functions $\mathbf{F}(k; t)$ and the matrix of their self-parts $\mathbf{F}_s(k; t)$ defined by

\begin{align}
F^{\alpha\gamma}(k; t) &= \frac{1}{N} \langle \rho^{\alpha\gamma}(k; 0) \rho^{\gamma}(k; t) \rangle, \\
F_s^{\alpha\gamma}(k; t) &= \frac{1}{N} \langle \rho^{\alpha\gamma}(k; 0) \rho^{\gamma}(k; t) \rangle_s,
\end{align}

where $N$ is the total number of particles, $\rho^{\alpha}(k; t)$ is the site $\alpha$ number density in reciprocal space, $k$ is the wave-vector, $k = |k|$, $t$ is time, $*$ means complex conjugation, angular brackets denote appropriate statistical average (e.g., canonical Gibbs ensemble average), and suffix “s” stands for “self” and means the correlations between two sites in a same molecule. In the present paper, we consider the limit of infinite dilution, the limit that the solute concentration vanishes. One has two types of memory equations for the solvent subsystem and one for the solute subsystem (indicated by the superscript “s”) which are:

\begin{align}
\mathbf{F}(k; t) &= -\langle \omega_k^2 \rangle \mathbf{F}(k; t) - \int_0^t d\tau \mathbf{K}(k; \tau) \mathbf{F}(k; t - \tau), \\
\mathbf{F}_s(k; t) &= -\langle \omega_k^2 \rangle_s \mathbf{F}_s(k; t) - \int_0^t d\tau \mathbf{K}_s(k; \tau) \mathbf{F}_s(k; t - \tau), \\
\mathbf{F}_s^{u}(k; t) &= -\langle \omega_k^2 \rangle_s^{u} \mathbf{F}_s^{u}(k; t) - \int_0^t d\tau \mathbf{K}_s^{u}(k; \tau) \mathbf{F}_s^{u}(k; t - \tau).
\end{align}

In these equations, dot over the quantity means its time derivative, and the memory function matrices, denoted as $\mathbf{K}(k; t), \mathbf{K}_s(k; t)$ and $\mathbf{K}_s^{u}(k; t)$, describe the friction on the motion of interaction sites and are subject for definition later. Quantities $\langle \omega_k^2 \rangle$, $\langle \omega_k^2 \rangle_s$ and $\langle \omega_k^2 \rangle_s^{u}$ are normalized second order frequency matrices given by

\begin{align}
\langle \omega_k^2 \rangle &= k^2 \mathbf{J}_s(k) \mathbf{S}^{-1}(k), \\
\langle \omega_k^2 \rangle_s &= k^2 \mathbf{J}_s(k) \mathbf{S}^{-1}_s(k), \\
\langle \omega_k^2 \rangle_s^{u} &= k^2 \mathbf{J}_s^u(k) \mathbf{S}^{-1}_s^{u}(k),
\end{align}

where $\mathbf{S}(k) \equiv \mathbf{F}(k; t = 0), \mathbf{S}_s(k) \equiv \mathbf{F}_s(k; t = 0)$ and $\mathbf{S}_s^{u}(k) \equiv \mathbf{F}_s^{u}(k; t = 0)$ are matrices of static site-site structure factors and their self parts, respectively, while $\mathbf{J}_s(k)$ is the matrix of static longitudinal site-current correlation functions, i.e.

\begin{equation}
|J_{\alpha}(k)|^{\alpha\gamma} = \frac{1}{N} \sum_{i,j} \langle v_{i,z}^{\alpha} v_{j,z}^{\gamma} e^{-ik \cdot (r_i^0 - r_j^0)} \rangle,
\end{equation}

where subscripts $i, j$ refer to molecules, $r_i^0 \equiv r_i(0)$ is the initial position of site $\alpha$, and $v_{i,z}^{\alpha} \equiv v_{i,z}^{\alpha}(0)$ is longitudinal component of the initial velocity of site $\alpha$. The analytical expression for arbitrary shape of the molecule has been given recently by Yamaguchi et al. and reads

\begin{equation}
|J_{\alpha}(k)|^{\alpha\gamma} = \frac{k_B T}{M} j_0(kl^{\alpha\gamma}) + \frac{k_B T}{3} \left[j_0(kl^{\alpha\gamma}) + j_2(kl^{\alpha\gamma}) \right] \\
\times [\delta \gamma]^{\alpha} \cdot \left[ \text{Tr} \mathbf{I}^{-1} \mathbf{I}^{-1} \right] \cdot \delta \gamma
- \frac{k_B T}{(\ell^{\alpha\gamma})^2} j_2(kl^{\alpha\gamma}) \left[ [\delta \alpha] \times [\delta \gamma] \right]^{\alpha} \cdot \left[ \mathbf{I}^{-1} \cdot [\delta \alpha] \times [\delta \gamma] \right],
\end{equation}

where $k_B$ is the Boltzmann constant, $T$ is thermodynamic temperature, $M$ is the total mass of the molecule, $\ell^{\alpha\gamma}$ is the distance between sites, $[\delta \alpha]$ is the vector pointed from the center of mass to the site $\alpha$, $\mathbf{I}$ is tensor of inertia moments of the molecule, $\mathbf{I}$ is the diagonal unit matrix; finally, $j_0$ and $j_2$ are spherical Bessel functions of the first kind. Definition for $J_{\alpha}^{u}(k)$ is similar to the one given by equation (2.3a) with the difference that summation runs over the solute molecule only.
Expressions for static site-site structure factors and memory kernels are discussed separately in sections III and IV, respectively. Here we show how quantities of our interest in this paper, which are solute’s translational diffusion coefficient $D$ and rank-1 reorientation correlation time $\tau_{R1}$, are related with $F_2^\gamma(k; t)$. The diffusion coefficient can be expressed in terms of the site-site velocity autocorrelation function, while the relaxation time is integrated rank-1 reorientation autocorrelation function. Both of them are described in terms of the $F_2^\gamma(k; t)$.

Following the derivation procedure presented in Ref. [61], the translational diffusion coefficient $D$ is obtained as

$$D = \frac{1}{3} \int_0^\infty dt \; Z^{\alpha\gamma}(t)$$

$$= \frac{1}{3} \int_0^\infty dt \; \left[ \frac{1}{N} \sum_i \langle \vec{v}_i^\alpha(0) \cdot \vec{v}_i^\gamma(t) \rangle_s \right]$$

$$= - \lim_{t \to \infty} \int_0^t dt' \lim_{k \to 0} \frac{1}{k^2} \sum_{\alpha\gamma} F_2^\alpha(\vec{k}; \tau) |^{\alpha\gamma}, \quad (2.6)$$

where $Z^{\alpha\gamma}(t)$ is the site-site velocity autocorrelation function with sites $\alpha$ and $\gamma$ belonging to the same molecule.

The rank-1 reorientation autocorrelation function $C_\mu(t)$ is defined by

$$C_\mu(t) = \frac{\sum_i \langle \vec{\mu}_i(0) \cdot \vec{\mu}_i(t) \rangle}{\sum_i \langle |\vec{\mu}_i|^2 \rangle}, \quad (2.7)$$

where $\vec{\mu}_i(t)$ is a vector fixed on the molecule $i$. In our case it is the dipole moment and therefore can be described by the linear combination of site coordinates as

$$\vec{\mu}_i(t) = \sum_\alpha z_\alpha \vec{r}_\alpha(t) \quad (2.8)$$

with $z_\alpha$ being site partial charges. Since the molecule is considered to be the neutral one, partial charges satisfy the condition of electro-neutrality $\sum_\alpha z_\alpha = 0$, and make definition of $\vec{\mu}_i(t)$ invariant under the transformation of translation of the laboratory reference frame. Putting equation (2.8) into equation (2.7) and using properties of time-correlation functions, one arrives at

$$C_\mu(t) = \frac{\sum_i \sum_\alpha \sum_\gamma z_\alpha z_\gamma \langle \vec{r}_i^\alpha(0) \vec{r}_i^\gamma(t) \rangle}{\sum_j \langle |\vec{\mu}_j|^2 \rangle}, \quad (2.9a)$$

$$\dot{C}_\mu(t) = - \frac{N \sum_\alpha \sum_\gamma z_\alpha z_\gamma Z^{\alpha\gamma}(t)}{\sum_j \langle |\vec{\mu}_j|^2 \rangle}. \quad (2.9b)$$

Hence, the time development of both $Z^{\alpha\gamma}(t)$ and $C_\mu(t)$ is governed by the memory equation for the self-part of the site-site intermediate scattering function $F_2^\gamma(k; t)$.

In this work we restrict our consideration to reorientation relaxation processes of the rank-1 only and hereafter will not use the subscript R1 in notations. For the (rank-1) reorientation relaxation time we use definition [61]

$$\tau = \int_0^\infty dt \; C_\mu(t). \quad (2.10)$$

B. Equilibrium properties of molecular liquids via RISM/DRISM

Initial values of intermediate scattering functions, that we need to solve memory equations (2.2), can be obtained using the RISM theory [41]. It predicts static structure of molecular fluids via the calculation of site-site pair correlation functions. This method has been extensively used and proved to be the powerful tool in the microscopic description of equilibrium quantities of the system [61]. In this paper, we employ the DRISM version of the theory [64] instead of the standard RISM/HNC theory. The DRISM theory incorporates a bridge function which is determined to reproduce the dielectric constant of solvent in phenomenological fashion. The use of the DRISM theory is known to improve the dielectric loss spectrum of solvent quantitatively, although it does not change the essential conclusion of the study with respect to the pressure dependence of the dynamics of solute in solvent [62].

C. Mode-Coupling approximation for memory kernels

It makes sense to talk about translational diffusion coefficient and reorientation relaxation time only when dynamics of the system is considered in the long-time limit, i.e. when the time scale is large enough for fast relaxation processes to be completed. Memory kernel of the memory equation in that case is usually constructed by the so-called mode-coupling approximation [63]. In works by Chong et al. [64, 65], the conventional mode-coupling theory has been extended to the case of molecular liquids based on the interaction-site model. In particular, mode-coupling expressions for memory function matrices, which we will denote as $K_{\mu\mu}(k, t)$ and $K_{\alpha\mu\mu}(k, t)$, were obtained as bilinear combinations of site-site intermediate scattering functions or their self parts as
\[
\left[ J_L^{-1}(k) \cdot K_{MC}(k, t) \right]^{\alpha \gamma} = \frac{\rho}{(2\pi)^3} \int dq \left\{ q^2 \left[ \mathbf{c}(q) \cdot \mathbf{F}(q, t) \cdot \mathbf{c}(q) \right]^{\alpha \gamma} F^{\alpha \gamma}(|k - q|, t) - q_3 (k - q_3) \left[ \mathbf{c}(q) \cdot \mathbf{F}(q, t) \right]^{\alpha \gamma} \right\}, \\
\left[ J_L^{-1}(k) \cdot K_{s,MC}(k, t) \right]^{\alpha \gamma} = \frac{\rho}{(2\pi)^3} \int dq q_3^2 \left[ \mathbf{c}(q) \cdot \mathbf{F}(q, t) \cdot \mathbf{c}(q) \right]^{\alpha \gamma} F_s^{\alpha \gamma}(|k - q|, t),
\]  

(2.11a, 2.11b)

Here for simplicity the wave-vector \( k \) has been taken to be parallel to \( z \)-axis. It has been shown, however, that the proposed expressions for memory functions underestimate friction in orientational motions.\(^{54}\) According to the recipe by Yamaguchi and Hirata\(^{54}\), memory functions for the self-part should be given by the linear combination of corresponding mode-coupling memory functions as

\[
\left[ K_s(k, t) \cdot J_L(k) \right]^{\alpha \gamma} = \sum_{m_{1,2,3} = \{x,y,z\}} \left\langle u_{z m_1}^{(i)} Z_{m_1 m_2}^{\alpha \mu} Z_{m_2 m_3}^{\nu \gamma} u_{m_3}^{(i)} \mathbf{c}^k (r_i - r_j + r_k) \right\rangle \left[ J_L^{-1}(k) \cdot K_{s,MC}(k, t) \right]^{\mu \nu}, 
\]

(2.12)

where \( u_{z m_1} \) stands for the unitary matrix that describes rotation between molecular and space-fixed reference frames of the molecule \( i \), while \( Z_{m_1 m_2}^{\alpha \gamma} \) denotes orientation-dependent site-site velocity correlation matrix in the molecular coordinate system and is given by

\[
Z_{m_1 m_2}^{\alpha \gamma} = \frac{k_B T}{M} \delta_{m_1, m_2} + k_B T [\mathbf{e}_{m_1} \times \delta \mathbf{r}]^T \cdot [\mathbf{e}_{m_2} \times \delta \mathbf{r}]^\gamma. 
\]

(2.13)

Here \( \mathbf{e}_{m_1} \) is the unit vector in the \( m_1 \) direction. The collective part of the memory function (neglecting the orientational correlation between different molecules) is obtained as\(^{54}\)

\[
K(k, t) = K_{MC}(k, t) + K_s(k, t) - K_{s,MC}(k, t).
\]

(2.14)

In the case of solute corresponding quantities are given by relations

\[
\left[ J_L^{-1}(k) \cdot K_s^{\nu}(k, t) \right]^{\alpha \gamma} = \frac{\rho}{(2\pi)^3} \int dq q_3^2 \left[ \mathbf{c}^{\alpha \nu}(q) \cdot \mathbf{F}^{\nu}(q, t) \cdot \mathbf{c}^{\alpha \nu}(q) \right]^{\alpha \gamma} F_s^{\alpha \gamma}(|k - q|, t), \\
\left[ K_s^{\nu}(k, t) \cdot J_L^{\nu}(k) \right]^{\alpha \gamma} = \sum_{m_{1,2,3} = \{x,y,z\}} \left\langle u_{z m_1}^{(i)} Z_{m_1 m_2}^{\alpha \mu} Z_{m_2 m_3}^{\nu \gamma} u_{m_3}^{(i)} \mathbf{c}^k (r_i - r_j + r_k) \right\rangle \left[ J_L^{-1}(k) \cdot K_{s,MC}^{\nu}(k, t) \right]^{\mu \nu}.
\]

(2.15, 2.16)

Here, superscript “\( s \)” is used to indicate the solvent subsystem, and intermediate scattering functions \( F^{\nu}(k, t) \) are those obtained in the process of solving of memory equations \( (2.10) \) and \( (2.12) \) with mode-coupling expressions for memory kernels deduced from equations \( (2.14) \) and \( (2.16) \), respectively.

### III. SETUP OF MODELS AND NUMERICAL PROCEDURES

We performed explicit calculations for several popular systems, namely, acetonitrile (CH\(_3\)CN) in water, methanol (CH\(_3\)OH) in water and methanol in acetonitrile, all in the case of infinite dilution. As for the structure and the intermolecular potential of water we employed a model of the extended simple point charge (SPC/E)\(^{68}\). We also put the Lennard-Jones (LJ) core on the hydrogen atoms in order to avoid the undesired divergence of the solution of the RISM integral equation. The LJ parameters of the hydrogen atom, the depth of the well and the diameter, were chosen to be 0.046 kcal/mol and 0.7 Å, respectively.

In acetonitrile and methanol the methyl group was considered to be a single interaction site (Me) located on the methyl carbon atom. Consequently, all chemical compounds consist of three sites which interact through the pair potential\(^{69,70}\)

\[
\phi(r_i^{\alpha \gamma}) = 4\epsilon_{\alpha \gamma} \left( \sigma_{\alpha \gamma} \right)^{12} \left( \frac{r_i^{\alpha \gamma}}{r_i^{\alpha \gamma}} \right)^6 + \frac{\sigma_{\alpha \gamma}}{r_i^{\alpha \gamma}},
\]

(3.1)
i.e., LJ plus Coulomb. Here \( r_i^{\alpha \gamma} = (r_i^{\alpha} - r_i^{\gamma}) \); parameters \( \epsilon_{\alpha \gamma} \) and \( \sigma_{\alpha \gamma} \) are LJ well-depths and LJ diameters defined as \( \epsilon_{\alpha \gamma} = \sqrt{\epsilon_{\alpha} \epsilon_{\gamma}} \) and \( \sigma_{\alpha \gamma} = (\sigma_{\alpha} + \sigma_{\gamma})/2 \), respectively, with \( \sigma_{\alpha} \) being the LJ diameter of a single site. Point charges for acetonitrile were chosen to reproduce electrostatic potential obtained in \textit{ab initio} calculations\(^{92}\). Numerical values of masses of sites, parameters of the site-site interaction potential \( 6.1 \) and cartesian coordi-
nates of sites are specified in Table I. Information about bond length can be deduced from cartesian coordinates of sites \((x, y, z)\).

**TABLE I:** Masses of sites \(m_\alpha\), parameters of the site-site interaction potential \((\varepsilon_\alpha, \sigma_\alpha)\) and cartesian coordinates of sites for water, acetonitrile and methanol. All values of \(\varepsilon_\alpha\) are multiplied by the factor \(10^{14}\), \(\alpha\) stands for “atomic units”.

| \(m_\alpha\) (u.a.) | \(z_\alpha\) | \(\varepsilon_\alpha\) (erg/mole) | \(\sigma_\alpha\) (\(\AA\)) | \(x\) (\(\AA\)) | \(y\) (\(\AA\)) | \(z\) (\(\AA\)) |
|-----------------|--------|------------------|--------|--------|--------|--------|
| O               | 16.0   | -0.8476          | 3.16   | 1.084  | 0      | 0      |
| H               | 1.008  | 0.4238           | 0.7    | 0.3196 | 0      | 0.8165 |
|                 | 1.008  | 0.4238           | 0.7    | 0.3196 | 0      | -0.8165|
| Me              | 15.024 | 0.269            | 3.6    | 2.64   | 0      | 0      |
| C               | 12.0   | 0.129            | 3.4    | 0.6878 | 0      | 0      |
| N               | 14.0   | -0.398           | 3.3    | 0.6878 | 0      | 0      |
| Me              | 15.024 | 0.265            | 3.74   | 1.4525 | -1.4246|
| O               | 16.0   | -0.7             | 3.03   | 1.1943 | 0      | 0      |
| H               | 1.008  | 0.435            | 1.0    | 0.3196 | 0.3004 |
|                 |        |                  |        | 0.8961 |

In calculations for acetonitrile or methanol in water the temperature of the system was varied from 258.15 to 373.15 K, and the density of water from 0.9 to 1.2 g/cm\(^3\); for the case of methanol in acetonitrile the temperature of the system was varied from 293.15 to 323.15 K, and the density of acetonitrile from 0.6726 to 0.815 g/cm\(^3\). Connection of the water parameters with thermodynamic pressure is shown in Table II (except for the metastable regions where we do not have reliable data).

**TABLE II:** Density-pressure correspondence for water\(^{23}\) given for temperatures \(T_1 = 273.15\) K, \(T_2 = 298.15\) K and \(T_3 = 373.15\) K.

| Density (g/cm\(^3\)) | Number density (\(\AA^{-3}\)) | Pressure at \(T_1\) (MPa) | Pressure at \(T_2\) (MPa) | Pressure at \(T_3\) (MPa) |
|----------------------|-----------------------------|--------------------------|--------------------------|--------------------------|
| 0.900                | 0.63098                     | -                         | -                         | -                         |
| 1.000                | 0.63334                     | 0.4085                   | 6.6914                   | 100.6450                 |
| 1.025                | 0.63426                     | 52.6119                  | 66.3549                  | 173.0629                 |
| 1.050                | 0.63510                     | 111.7871                 | 133.7116                 | 255.2558                 |
| 1.075                | 0.63593                     | 179.4861                 | 209.9492                 | 347.8493                 |
| 1.100                | 0.63676                     | 257.2009                 | 296.1955                 | 451.5134                 |
| 1.125                | 0.63760                     | 346.1457                 | 393.4575                 | 566.9920                 |
| 1.200                | 0.64011                     | 689.0266                 | 760.7554                 | 993.3837                 |

Temperature/density dependent dielectric constant \(\varepsilon\) for water used in numerical calculations has been evaluated as a physical solution of an empirical nonlinear equation presented in Ref. \(^{22}\)

\[
\varepsilon = \frac{1}{2} \left(1 + \frac{1}{\varepsilon_0} \right) = \frac{1}{v} \left(17 + \frac{9.32 \cdot 10^4 \left(1 + \frac{153}{v^2 T} \right)}{(1 - 3/v^2 T)} \right),
\]

where \(v\) is a molar volume in units of \(\text{cm}^3/\text{mol}\), and \(T\) is thermodynamic temperature in K. This equation was also used in such temperature/density points where no experimental values exist. Density and dielectric constant for acetonitrile at different temperatures are indicated in Table III.

**TABLE III:** Density and dielectric constant for acetonitrile as functions of temperature: experimental data used in our computation. Temperature is in K, and density is in g/cm\(^3\).

| \(T\) (K) | \(\rho\) (g/cm\(^3\)) | \(\varepsilon\) |
|----------|-----------------|---------------|
| 293.15   | 0.782           | 38.8          |
| 295.05   | 0.776           | 37.5^b        |
| 298.15   | 0.771^a         | 36.7^a        |
| 303.15   | 0.765^b         | 35.9^a        |
| 308.15   | 0.760^a         | 35.3^a        |
| 313.15   | 0.754^b         | 33.5^f        |

^aRef. \(^{74}\)^ bRef. \(^{72}\) ^cRef. \(^{73}\) ^dRef. \(^{74}\) ^eRef. \(^{75}\) Extrapolated.

From the memory equation / mode-coupling theory and the DRISM/HNC integral equation theory, the diffusion coefficients and the reorientation relaxation times of solute molecules in solution can be obtained based solely on the information about molecular shapes, inertia parameters, intermolecular interaction potentials, temperature and density. First, we calculate the site-site static structure factor by solving the DRISM equation using the intermolecular interaction, molecular shape, temperature and density. In order to improve the convergence of the DRISM calculation, we use the method of the modified direct inversion in an iterative space (MDIIS) proposed by Kovalenko et al.\(^{23}\) From the static site-site structure factor, we calculate the site-site intermediate scattering function using the site-site memory equation with the mode-coupling approximation for the memory kernels. The memory equation is time-integrated numerically. Time-development of correlation functions in the \(k \to 0\) limit is treated separately by the analytical limiting procedure of theoretical expressions. In the numerical procedure, the reciprocal space is linearly discretized as \(k = (n + \frac{1}{2})\Delta k\), where \(n\) is an integer from 0 to \(N_k - 1\). Values of \(\Delta k\) and \(N_k\) are 0.061 \(\text{Å}^{-1}\) and \(2^9 = 512\), respectively. The choice for \(N_k\) as the power of two is coming as the requirement of the subroutine for the fast Fourier transform, which is used in DRISM / MDIIS. The diffusion coefficient \(D\) is calculated from the asymptotic slope of the time dependence of the mean square displacement, and the orientational relaxation time \(\tau\) is deduced from the rotational autocorrelation function.

**IV. RESULTS AND DISCUSSIONS**

A. Equilibrium properties: static structure

Since the discovery of anomalous behavior of the molecular mobility with pressure it has been attributed to the hydrogen bonding properties of the system. The idea is that the hydrogen bonds or hydrogen bonding network are distorted upon compression, so that the dissolved molecule is actually having fewer hydrogen bonds at higher pressure, thus making it easier to move and rotate. The extensive test of this idea has been the objective of many researches. In particular, the time evolution of the formation and rupture of hydrogen bonds turns...
out to be a popular quantity to be examined in studies based on the computer simulation (see, e.g., Ref. 79 and references therein). In order to circumvent the problem, a number of alternative definitions of hydrogen bonds was suggested on top of the traditional one based either on geometric and/or energetic criteria, though none of them is conclusive. The definition of hydrogen bond in the theoretical study based on the integral equation is somewhat ambiguous as well. However, it is a quite general observation for such liquids like water and alcohol that a pair of atoms having small size and/or large charges with opposite sign makes a well-defined first peak in the pair correlation function: for example, hydrogen and oxygen in water and alcohol. Especially, in order for making a hydrogen bond, one of the pair of atoms should be as small as a hydrogen atom. Since those liquids are known to make a hydrogen bond between the pair of atoms, the well-defined peak has been assigned to a “hydrogen bond”. The hydrogen bond between a pair of atoms induces a “liquid structure” which is specific to molecules consisting the fluid, which in turn produces peculiar peaks in the pair correlation function at particular distances. For example, in the case of water, the hydrogen bond peak appears at $\sim 1.8 \text{ Å}$ in the O-H correlation function, which induces a new peak in the O-O correlation function around $\sim 4.5 \text{ Å}$. The O-O distance is peculiar to the ice-like tetrahedral coordination. Therefore, the peak at $\sim 4.5 \text{ Å}$ is regarded as a “finger print” of the hydrogen bond network existing in liquid water.

Alcohol also makes a hydrogen bond between a pair of the molecules, but does not make a three dimensional network, which is distinct from water. Instead, it makes zigzag chains of hydrogen bonds. It is because one of the four hydrogen-bonding sites is replaced by an alkyl group which is too large to form the bond. In the case of neat acetonitrile, there is no indication for making hydrogen bonds between a pair of the molecules. It is understood...
from its molecular constituents, i.e., it does not have a small atom as a possible hydrogen-bonding site. Therefore, the structure of the liquid or the pair correlation function is determined essentially by the repulsive interactions and the molecular geometry.

The pressure or density dependence of the liquid structure is determined essentially by the interplay between the repulsive interaction and the hydrogen bonding, which interfere each other through the intramolecular constraints or molecular geometry. Increasing pressure will make repulsive interactions more dominant, which will weaken the hydrogen bond by distorting the favorable arrangement between the two molecules. The pair correlation functions on pressure or density should reflect the interplay mentioned above. Increasing pressure or density will result in reduction in all the indications of hydrogen bonding and of the consequent liquid structure, and will make the steric or packing effect more dominant.

Fig. 2 shows the site-site RDF for neat methanol in water. There are two possible hydrogen bond sites in methanol, O and H, which make hydrogen bonds, respectively with H and O of water molecules. The O(water)-H(methanol) RDF, Fig. 2b), has the hydrogen bond peak at the position where that in neat water appears. The peak height and resolution are less compared to the case in neat water, implying the hydrogen bond is somewhat weaker. The density dependence of the peak shows similar behavior with that in neat water, indicating that the hydrogen bond is weakened due to the steric distortion caused by pressure. The O(methanol)-H(water) RDF, Fig. 2c), has the hydrogen bond peak at \( \sim 1.5 \) Å, which is much shorter than that in the O(water)-H(methanol) RDF. The peak is even more sharply defined than that in neat water, implying that the hydro-
B. Dynamical properties: diffusion coefficient and reorientation relaxation time

Fig. 5 shows the density(pressure) dependence of the normalized translational diffusion coefficient $D/D_0$ for investigated solutes at various temperatures. Here $D_0$ is the translational diffusion coefficient of the solute at the ambient density for the solvent, which is $\rho = 0.997047$ g/cm$^3$ for water in cases a), b), and $\rho = 0.782$ g/cm$^3$ for acetonitrile in the case c), respectively. Fig. 5(a) shows that for sufficiently low temperature the diffusion coefficient of methanol in water first increases with density(pressure), and then begins to decrease. A relatively flat maximum is observed for the density slightly smaller than that at the ambient condition. The increase in the diffusion coefficient with increasing density (or pressure) can not be explained by the phenomenological theory such as the Stokes-Einstein law. In that reason, such behavior is often stated “anomalous”. This is the first to realize such anomalous pressure dependence of the diffusion constant of a solute in water by means of the statistical mechanics theory. As can be seen in the figure, the anomalous density dependence is suppressed as temperature increases and turns into normal behavior, i.e., the diffusion constant decreases monotonously with density. At the ambient condition, the diffusion constant does not show any anomaly and is consistent with the one obtained from the molecular dynamics simulation, which is plotted in the figure with the filled triangles. Using the multi-parametric empirical equation of state for water we converted original data from “diffusion versus pressure” into “diffusion versus density”.

Similar features can be observed in the behavior of the diffusion coefficient of acetonitrile in water, Fig. 5(b). In this case, the increase of the diffusion coefficient at the lowest temperature is discernible, but very small as can be barely observed with the guide of the cubic spline curve. Behavior of the diffusion coefficient at higher temperatures, as in the case of methanol in water, does not show any anomaly. The behavior is in harmony with the results of the molecular dynamics simulation at the ambient condition, which is plotted in the figure with the filled squares. The experimental measurements of diffusion coefficients for acetonitrile in water and acetonitrile-D$_3$ (CD$_3$CN) in water, both at $T = 303$ K, reported by Nakahara et al. testify the same tendency in their density(pressure) dependence as those obtained from the theory.

The diffusion coefficient of methanol in acetonitrile are plotted in Fig. 5(c) as the function of density. The results show monotonous decrease of the diffusion coefficient in the entire range of densities and at all investigated temperatures.

Fig. 6 shows the density(pressure) dependence of the normalized reorientation relaxation time $\tau/\tau_0$ for investigated systems at the same temperatures as for normalized translational diffusion coefficient $D/D_0$. $\tau_0$ is the reorientation relaxation time of the solute at the ambient density for the solvent. Fig. 6(a) is a typical example of anomalous density(pressure) dependence of the reorientation relaxation time. It is clear to see that it first decreases with density(pressure) and then starts to increase. The anomalous behavior becomes weaker as temperature increases, and disappears at some point. Apparently, the anomaly persists through higher temperature than what is observed in the diffusion coefficient. The theoretical result is consistent again with that from the molecular dynamics simulation at the ambient condition in the sense that the both plots show a minimum, although the positions of the minimum are slightly different from each other.
In the case of acetonitrile in water, Fig. 6b), the normal behavior of the reorientation relaxation time is observed almost entirely except for the lowest temperature, where a shallow minimum is discernible. The relaxation time at the ambient temperature exhibits monotonic increase. The behavior is in qualitative accord with the results from molecular dynamics simulation for $T = 298$ K, lines connecting open symbols are cubic splines for the eye-guide.

Fig. 7 has the purpose to demonstrate the anomalous density(pressure) behavior of the reorientation relaxation time in terms of the reorientation time-correlation function $C_\mu(t)$. It has been found that at $T = 298.15$ K the curves for acetonitrile in water and methanol in acetonitrile move to the right as density increases, namely the relaxation time becomes longer when pressure is increased. On the other hand, for methanol in water it shifts first to the left, and then for higher densities(pressures) it starts to shift to the right. At the highest temperature $C_\mu(t)$ for methanol in water moves only to the right, but the

**FIG. 5:** Normalized translational diffusion coefficient $D/D_0$ for methanol in water a); acetonitrile in water b); and for methanol in acetonitrile c). □, ◇, ○ – theory, ■, ▲ – results of MD simulation for $T = 298$ K, lines connecting open symbols are cubic splines for the eye-guide.

**FIG. 6:** Normalized reorientation relaxation time $\tau/\tau_0$ for methanol in water a); acetonitrile in water b); and for methanol in acetonitrile c). □, ◇, ○ – theory, ■, ▲ – results of MD simulation for $T = 298$ K, lines connecting open symbols are cubic splines for the eye-guide.
FIG. 7: Reorientation correlation functions for methanol in water (left), acetonitrile in water (center) and methanol in acetonitrile (right) at $T = 298.15$ K and different values of density of the solvent. Arrows inside of each plot indicate direction(s) of the displacement for curves with the increase of density.

displacement is very small. Considering that the time-correlation function is related to the reorientation time by an integral, the behaviors in the time-correlation functions are consistent with those of the reorientation time as has been described above.

In our previous studies concerning the neat water, we have clarified the cause of anomalous dependence of the molecular dynamics on pressure, or the appearance of extrema in the pressure dependence. The anomalous behavior is caused by an interplay of two competing tendencies: the increasing mobility at the lower pressure and the suppression of the motion in the higher pressure. The suppression of the motion with increasing pressure is a normal behavior caused by increased molecular collisions, and the increase in the mobility is caused by the decrease in the dielectric relaxation time. The appearance of the extrema is attributed to the increasing dielectric motion at the lower pressure. The origin of the decrease in the dielectric relaxation time at the lower pressure is in the reduction of the electrostatic friction on the dielectric mode. Although the detailed analysis is presented in our previous paper, let us summarize it below. The dielectric mode describes the collective alignment of the polar molecules. When the inhomogeneity of the number density is present as is described in Fig. 8a), the alignment of the collective dipole moment induces the inhomogeneity of the charge density, which leads to the electrostatic friction on the dielectric mode. Increasing density or pressure will suppress the number density fluctuation, which in turn causes the reduction of the charge density fluctuation as is illustrated in Fig. 8b). The reduced charge density fluctuation in turn causes decrease in the electrostatic friction on the dielectric mode, or increase in the collective rotational motion. This is the rough picture with respect to the anomalous pressure dependence of the rotational dynamics in water, which is consistent with the analysis based on the mode coupling theory.
Now we turn to the single-particle motion in water. In the case of neat water, the translational and the rotational diffusion of a molecule respond to pressure differently, as is observed experimentally. The translational motion of a molecule couples with the high wave vector collective translational mode, which have inherent tendency to become slower as pressure increases. On the other hand, the coupling between the rotational motion of a molecule and high wave vector collective translational modes is weak, and the friction on the rotation of a molecule mainly comes from the coupling with the low wave vector charge density mode, which is usually referred to as the dielectric friction. The rotational motion of a molecule will induce a relaxation process of surrounding molecules in order to make themselves aligned to the electric field produced by the new orientation of the molecule in concern. The energy dissipation associated with the relaxation process is an origin of the friction on the rotational motion, or the dielectric friction. Slower the dielectric relaxation, greater the dielectric friction. The anomalous pressure dependence observed in the translational dynamics or the diffusion coefficient turns out to be the secondary effect induced by the anomaly in the rotational motion. The anomaly in the translational diffusion is therefore weaker than that in the rotational relaxation.

The solute-solvent systems considered in the present paper can be understood in a similar way as follows. Whether the anomalous behavior actually shows up or not also depends on the role of repulsive core in the rotational motion of solute, which gives rise to the collisional friction: a spherical molecule like water will be free from the collisional friction, while a rod-like molecule such as acetonitrile should have significant collision with solvent molecules upon rotation. The behavior exhibited in Fig. 1 is consistent with the physical picture drawn above. Figs. 2a) and 2b), which concern water as solvent, show anomalous density dependence of the rotational relaxation time, which disappears with increasing temperature. The methanol-in-water system exhibits more significant anomaly compared to the acetonitrile-in-water system. The anomalous behavior is attributed to the strong electrostatic interaction, so called “hydrogen bond”, among the solvent molecules and those between solute and solvent. The former causes the decrease in the dielectric relaxation time with pressure, and the latter brings about the coupling between the dielectric mode of the solvent and the rotation of the solute. The anomaly is largely suppressed for the acetonitrile-in-water system due to the enhanced significance of the repulsive core in the molecule. The methanol-in-acetonitrile system does not show any indication of the anomalous density dependence, although there is a hydrogen bond between solute and solvent as is indicated in Fig. 2b). The reason is because there is strong collisional friction on the collective reorientation of the solvent in this case, so that the dielectric relaxation becomes slower with pressure. The enhanced density or pressure just amplifies the significance of the repulsive core upon rotation and thereby of the collisional friction.

V. SUMMARY

In present paper we have calculated the density(pressure) dependence at various temperatures for the translational diffusion coefficients \( D \) and rank-1 reorientation relaxation times \( \tau \) for three solute-solvent systems at infinite dilution: acetonitrile and methanol in water, and methanol in acetonitrile. Calculations have been performed using the site-site memory equation with the mode-coupling approximation for memory kernels, and the DRISM theory for static properties.

The theory was able to reproduce qualitatively all main features of temperature and density dependences of \( D \) and \( \tau \) observed in real and computer experiments. In particular, anomalous behavior, i.e. the increase in mobility with density, is observed for \( D \) and \( \tau \) of methanol in water at the ambient condition, while acetonitrile in water and methanol in acetonitrile show the ordinary behavior, i.e. the monotonous decrease in mobility with increasing density. The variety exhibited by the different solute-solvent systems in the density dependence of the mobility was interpreted in terms of the two competing origins of friction, which interplay with each other as density increases: the collisional and dielectric frictions which, respectively, increase and decrease with increasing density. The cause of the dielectric friction is the inhomogeneity in the charge density of solvent, induced by the number density fluctuation due to the hydrogen bond. The suppression of the number density fluctuation and the consequential decrease in the charge density fluctuation are the physical origins of the anomalous density dependence of the molecular mobility in hydrogen-bonding systems.

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