

Theoretical Study on the Dynamic Properties of Compressed Water and Water-Hydrophobic Solute Mixtures

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The dynamic properties, including shear viscosity, self-diffusion coefficient, dielectric relaxation time and single-molecular reorientational relaxation time, of neat compressed water and model water-hydrophobic solute mixtures are calculated theoretically from the intermolecular interaction potentials. The reference interaction-site model integral equation theory is used to obtain the equilibrium structure of the liquid, which in turn is used as the input of the numerical calculation by the mode-coupling theory for molecular liquids based on the interaction-site model. For neat compressed water, the theory reproduced the increase in the molecular mobility with applying pressure qualitatively. The reorientational mobility is more enhanced by pressure than the translational one, which is in harmony with experiments. The retardation of the motion of water in the aqueous solution of hydrophobic solutes is also obtained by the theory. In a model system in which the electrostatic interaction between the solute and solvent is continuously varied, the mobility of solvent water has a maximum as the function of the hydrophobicity of the solute. This theoretical trend is in harmony with the transition from positive, via negative, to hydrophobic hydration regimes experimentally observed.

1. Introduction

Water is the most abundant liquid on earth. Owing to its importance in various fields including engineering and biology, its thermodynamic, dynamic and structural properties have been investigated under various conditions.

The structure of liquid water under the ambient condition is distinguished from other molecular liquids by the tetrahedral hydrogen-bonding network structure. In addition to the microscopic structure, liquid water also exhibits thermodynamic and dynamic properties distinct from other molecular liquids, which have been ascribed to the tetrahedral network structure.

In this work, we shall focus on two dynamic properties of water and aqueous solutions that are peculiar to the aqueous systems. One is the molecular mobility of neat compressed water. The molecular mobility of many molecular liquids is the decreasing function of pressure, which is in harmony with our intuition that molecules are less mobile in a more crowded condition. On the other hand, the mobility of water is known to increase

with pressure around the atmospheric pressure [1,2]. This enhancement of the mobility has long been ascribed to the destruction of the tetrahedral network structure.

The second property we consider here is the mobility of water in the solutions of hydrophobic solutes. It has long been known that the dissolution of hydrophobic molecules, such as hydrocarbons and rare gases, makes the mobility of water lower [3]. Since the interaction between water and hydrophobic molecules is considered weaker than that between water molecules, the suppression of the mobility of solvent water by the hydrophobic solutes contradicts with our naïve consideration that the stronger intermolecular interaction makes the molecular mobility lower. The mobility of water in solutions of hydrophobic solutes therefore requires special considerations, and it has been ascribed to the formation of hydrophobic hydration shell that resembles the structure of crystalline hydrates.

The theoretical method we employed here is the mode-coupling theory for molecular liquids based on the interaction-site model. This theory is developed by Chong and Hirata [4,5], and recently

modified by Yamaguchi and Hirata to improve the description of reorientational motion [6]. It requires the site-site static structure factor as an input data, and calculates the dynamic extension of the site-site structure factor, which in turn is related to various dynamic properties. Since the theory relates the static structure to the dynamic properties, we believe it is suitable for the study of hydrogen-bonding systems where the relationship between the structure and the dynamics is important.

2. Model

Three systems are investigated in this work. The first one is the neat compressed water. The temperature and the density are varied from 273 to 373K and from 0.9 to 1.2 g/cm³, respectively.

The second system is the mixture of water and Lennard-Jones (LJ) molecule. The LJ molecule is considered as a model of hydrophobic solutes. The LJ parameters and the mass of the solute are set equal to the LJ parameters of the oxygen atom and the total mass of water, respectively. The temperature of the system is 298K, and the total number density is kept to that of neat water at the ambient condition.

The third system is the aqueous solution of model solutes whose interaction strength is varied continuously. The model solute is a triatomic molecule whose geometry, inertia parameters and LJ parameters of sites are the same as those of water. The partial charges on the sites of the solute are scaled from that of water in order to alter the hydrophobicity of the solute. The temperature of the system is 298K, and the total number density is the same as that of ambient water. The molar fraction of the solute is kept 0.1.

In all the calculations, we employed the enhanced simple point charge (SPC/E) model for water. The LJ core of 0.7 Å diameter is put on the hydrogen atom, in order to avoid the undesired divergence of the solution of integral equation.

3. Theoretical Methods

The site-site static structure factor is calculated by the RISM integral equation theory [7]. The HNC closure is employed for the first series of calculations, neat compressed water. For the second and third systems, the PLHNC closure is used to improve the convergence in the calculation on mixtures. No correction for the static dielectric constant is performed in all the calculations.

The site-site dynamic structure factor is obtained by the time-integration of the generalized Langevin equation for the site density of molecular liquids. The memory function is calculated from the site-site dynamic structure factor in a self-consistent way, and the correction for the reorientational part of the memory function proposed by Yamaguchi and Hirata is applied [6]. The mode-coupling approximation for the memory function is used for the whole time course of the memory function.

The dynamic properties of the liquids are evaluated from the site-site dynamic structure factor. A mode-coupling expression is used for shear viscosity [8]. The dielectric relaxation spectrum is described by the charge-density time correlation function [9]. The self-diffusion coefficient and the reorientational relaxation time are evaluated from the long wave vector limit of the self-part of the site-site dynamic structure factor.

4. Results and Discussions

4.1. Neat Compressed Water Figure 1 shows the theoretical results on the shear viscosity, dielectric relaxation time, self-diffusion coefficient and single-molecular reorientational relaxation time of the dipole moment.

At the lowest temperature investigated, 273K, the increase in the mobility is observed between 0.9 ~1.0 g/cm³ in all the dynamic properties. This anomalous behavior becomes weaker with increasing temperature, which is in qualitative agreement with experiments.

The translational and reorientational mobilities respond to the pressure in a different way. The anomalous increase in the mobility with pressure is not observed in the translational mobility as the shear viscosity and self-diffusion coefficient. On the other hand, the anomaly in the reorientation is stronger than the translational one, and it persists up to 373K, the highest temperature studied in this work. Experimentally, the increase in the reorientational mobility is observed also in the subcritical water around 200°C [10]. The stronger anomaly in the reorientational mobility suggests that the reorientational mode plays an essential role in the increase in the mobility with pressure. The theoretical analysis shows that the electrostatic friction on the dielectric mode, induced by the number-density fluctuation, is the reason for the anomalous behavior [11], which explains the stronger anomaly in the reorientational mobility.

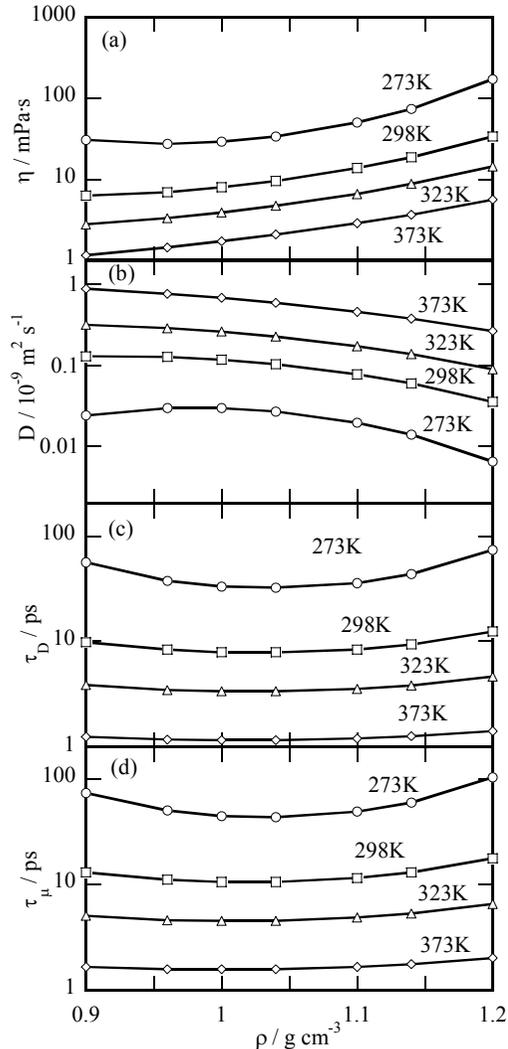


Fig. 1. The theoretical values of the transport coefficients and reorientational relaxation times of water as functions of density for various temperatures indicated in the figures. (a) Shear viscosity, η , (b) translational diffusion coefficient, D , (c) dielectric relaxation time, τ_D , (d) rank-1 reorientational relaxation times of the dipole moment, τ_μ .

Although the theory reproduces the increase in mobility with pressure qualitatively well, the agreement of the absolute values of the mobility with experimental ones are rather dissatisfactory. The shear viscosity is about one order of magnitude larger than experiments, and the self-diffusion coefficient is smaller than experiments by the same degree. Although the rank-1 reorientational

relaxation time of water is not determined by experiments, the theoretical reorientational relaxation time is several times longer than that from computer simulations. The agreement of the dielectric relaxation time with experimental ones is good compared with other three quantities. It is however the cancellation of errors, because the RISM/HNC theory underestimates the static dielectric constant by the factor of four, which makes the dielectric relaxation time shorter.

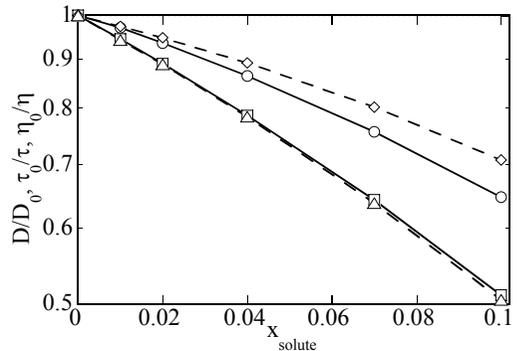


Fig.2. The relative mobility of the solvent water as the functions of the molar fraction of the Lennard-Jones model solutes, x_{solute} . Circle: D/D_0 , square: $\tau_{\mu,0}/\tau_{\mu}$, triangle: $\tau_{D,0}/\tau_D$, diamond: η_0/η . The symbols with suffixes '0' represent the values of neat ambient water. The squares and the triangles are almost overlapped with each other. Note that the longitudinal axis is plotted in a log scale.

4.2. Hydrophobic Solute Figure 2 demonstrates the change in the mobility of water with the addition of the model hydrophobic solutes. The concentration dependence of four quantities plotted there indicates that the motion of water is suppressed by the hydrophobic solute, in harmony with various experiments and computer simulations. The decrease in the reorientational mobility with the addition of hydrophobic solutes is larger than that of translational one, as is the case of the increase in the mobility of neat water with decreasing pressure. It suggests that the reorientational mode is important also in the dynamics of hydrophobic hydration, and there can be some relationship between the microscopic mechanisms of the dynamics of neat compressed water and hydrophobic hydration [12].

Figure 3 exhibits the mobility of solvent water of the solution of model solutes whose hydrophobicity is varied continuously. The larger value of the

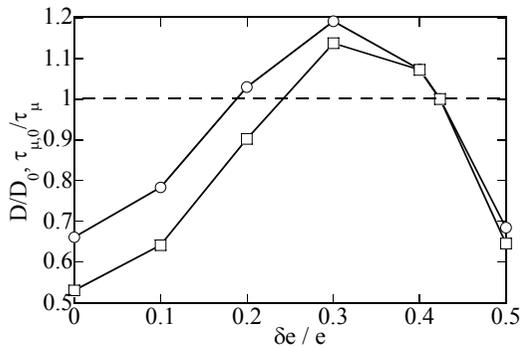


Fig.3. The relative mobility of the aqueous solution of the model water-like solutes as the functions of the partial charges of the hydrogen atom of the solute, Δe . Circles and squares stand for D/D_0 and $\tau_{m,0}/\tau_m$, and diamonds do η_0/η , where "0" indicates the value of the neat ambient water.

partial charge on the hydrogen atom, Δe , means that the solute is more hydrophilic. Since the solute and solvent is the same except for partial charges, the value of $\Delta e=0.4238e$ indicates the neat ambient water. On the other hand, $\Delta e=0$ is almost the same as the second system, because the LJ core of hydrogen of water is embedded in that of the oxygen.

As is clearly seen in Fig. 3, the mobility of water has a maximum as the function of the hydrophobicity of the solute. The hydrophobic solute makes the water less mobile, as is shown in Fig. 2. On the other extreme, the strong solute-solvent interaction also lowers the mobility of water. An interesting point is that the solute enhances the motion of water in the intermediate case.

The existence of the maximum in the mobility of solvent water as the function of the solute-solvent interaction strength has been found in electrolytic solutions. The increase in the water mobility with the hydrophilicity of the solute is also found in various aqueous solutions of organic compounds. The small ions as Li^+ and Na^+ restrict the motion of solvated water, called "positive hydration". The ions as K^+ and hydrophilic neutral molecules slightly enhance the motion of water, called "negative hydration". The larger ions as tetraalkylammonium ones and hydrophobic molecules suppress the mobility of water, which is ascribed to the hydrophobic hydration [13]. According to this nomenclature, we can name the regions of $\Delta e < 0.2e$, $0.2e < \Delta e < 0.4238e$ and $\Delta e > 0.4238e$ as the hydrophobic, negative and positive hydrations, respectively.

5. Conclusions

The generalized Langevin / mode-coupling theory for molecular liquids based on the interaction-site model is applied to the neat compressed water and aqueous solutions of model hydrophobic solutes. The theory succeeded in reproducing the increase in the mobility of water with increasing pressure, and also the decrease in mobility by the hydrophobic solutes. In addition, a maximum is found in the mobility of water in solution as the function of the hydrophobicity of the solute, which resembles the transition from positive, via negative, to hydrophobic hydration regimes experimentally observed for aqueous electrolytic solutions. The success of the theory in reproducing the characteristic properties of water and aqueous solutions indicates that the present theory can be a basis to clarify the molecular mechanisms of the dynamic properties of aqueous systems, which are described in our previous papers [11,12], and also discussed in the conference.

References and Notes

- [1] D. Eisenberg and W. J. Kauzmann, *The Structure and Properties of Water* (Clarendon Press, London, 1969). and references therein.
- [2] K. Tödheide, in *Water: A Comprehensive Treatise*, Vol. 1, ed. F. Franks (Plenum Press, New York, 1972), Chap.13.
- [3] M. D. Zeidler, in *Water: A Comprehensive Treatise*, Vol. 2, ed. F. Franks (Plenum Press, New York, 1972), Chap.12.
- [4] S.-H. Chong and F. Hirata, *Phys. Rev. E*, **58**, 6188 (1998).
- [5] S.-H. Chong and W. Götze, *Phys. Rev. E*, **64**, 011503 (2001).
- [6] T. Yamaguchi and F. Hirata, *J. Chem. Phys.*, **117**, 2216 (2002).
- [7] F. Hirata, *Molecular Theory of Solvation* (Kluwer, Dordrecht, 2003).
- [8] T. Yamaguchi and F. Hirata, *J. Chem. Phys.* **115**, 9340 (2001).
- [9] F. O. Raineri, Y. Zhou, H. L. Friedman, and G. Stell, *Chem. Phys.*, **152**, 201 (1991).
- [10] J. Jonas, T. de Fries, and D. J. Wilbur, *J. Chem. Phys.*, **65**, 582 (1976).
- [11] T. Yamaguchi, S.-H. Chong, and F. Hirata, *J. Chem. Phys.*, **119**, 1021 (2003).
- [12] T. Yamaguchi, T. Matsuoka, and S. Koda, *J. Chem. Phys.*, **120**, 7590 (2004).
- [13] H. G. Hertz, in *Water: Comprehensive Treatise*, Vol. 3, ed. F. Franks (Plenum Press, New York, 1972), Chap.7.