

Effect of water polyamorphism on the molecular vibrations of glycerol in its glassy aqueous solutions

Yoshiharu Suzuki^{a)} and Osamu Mishima

Research Center for Advanced Measurement and Characterization, National Institute for Materials Science (NIMS), Namiki 1-1, Tsukuba, Ibaraki 305-0044, Japan

(Received 27 April 2016; accepted 23 June 2016; published online 12 July 2016)

A glassy dilute glycerol-water solution undergoes a mutual polyamorphic transition relating to the transition between high- and low-density amorphous ices of solvent water. The polyamorphic transition behavior depends on the glycerol concentration, indicating that the glycerol affects the water polyamorphism. Here, we used the glassy dilute glycerol-water solution of the solute molar fraction of 0.07 and examined the effect of the polyamorphic change in solvent water on the molecular vibrations of glycerol via Raman spectroscopy. It is found that the molecular vibration of glycerol in high-density liquid like solvent water is different from that in the low-density liquid like solvent water and that the change in the molecular vibration of glycerol is synchronized with the polyamorphic transition of solvent water. The dynamical change of the solute molecule relates to the polyamorphic state of solvent water. This result suggests that the polyamorphic fluctuation of water structure emanated from the presumed liquid-liquid critical point plays an important role for the function of aqueous solution under an ambient condition such as the conformational stability of solute, the functional expression of solute, and so on. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4955318>]

I. INTRODUCTION

Water, one of the most familiar materials in our life, has many mysterious properties, such as the density maximum at 277 K.¹ One of new clues to understand the anomalous behaviors of low-temperature liquid water is the liquid-liquid critical point (LLCP) hypothesis of water that two liquid waters, low- and high-density liquids (LDL and HDL, respectively), exist at low temperatures and a liquid-liquid critical point, LLCP, relating to the two waters exists.¹⁻³ Computer simulation studies using the ST2 and TIP4P/2005 water potential models³⁻⁸ predict the existence of two liquid waters and the existence of LLCP. However, it may be impossible to examine the two liquid waters directly by experiment, much less to probe with the location of LLCP, because of the rapid crystallization of liquid water in the region named the no-man's land, that is, between the homogeneous nucleation temperature of liquid water, T_H , and the crystallization temperature of amorphous ice, T_X .^{1,2} At the present stage, there is no decisive experimental evidence that proves the LLCP hypothesis. We perceive, however, that many accumulative experimental results for the supercooled liquid water near the T_H and for the two amorphous ices, low- and high-density amorphous ices (LDA and HDA, respectively), are consistent with the LLCP hypothesis. We will verify the validity of the LLCP hypothesis while referring the experimental results in the past as shown in the following paragraphs.

When the LLCP hypothesis has been proposed by Poole *et al.*,³ two experimental findings, the existence of two kinds

of amorphous ices with different densities (LDA and HDA)⁹ and the first-order-like transition between LDA and HDA,¹⁰⁻¹² have been provided as its experimental evidence, where LDA and HDA are thought to correspond to the glassy states of LDL and HDL, respectively. However, there have been two important concerns for the experiments of amorphous ices performed under a non-equilibrium condition: (i) Do the two amorphous ices relate thermodynamically to liquid water at high temperatures? (ii) Is the transition between LDA and HDA really first order?

In order to wipe out the concern of (i), various experiments of amorphous ices have been carried out. The structural analysis of amorphous ices by the x-ray diffraction,^{9,13,14} the neutron diffraction,¹⁵⁻¹⁸ and the Raman spectroscopic¹⁹⁻²¹ studies shows that LDA and HDA form the disorder molecular configurations which are similar to the molecular configurations of ice I_h and those of liquid water, respectively. Finney *et al.*¹⁸ have asserted from the comparisons between the O-O intermolecular partial radial distribution functions of LDA, HDA, ice I_h , and liquid water that there exists no long-range order structure both in LDA and in HDA and that LDA and HDA are not the state of nano-crystalline ices. Furthermore, the tendency of the changes in the sound velocity,²² the shear modulus,²² and the thermal conductivity²³ for LDA with the pressure change is contrary to the tendency for HDA. These experimental results indicate that HDA and LDA are distinct amorphous ices. The existence of the very high-density amorphous ice, VHDA, is proposed,²⁴ but it is likely the sub-states of HDA because the volume of HDA shows no sign of sharp discontinuity at least up to 1.5 GPa.¹²

On the other hand, the thermodynamical relation between the amorphous ices and the liquid water at high temperatures has been proved by the direct vitrification by the cooling of

^{a)} Author to whom correspondence should be addressed. Electronic mail: suzuki.yoshiharu@nims.go.jp

liquid water. That is, LDA and HDA are directly prepared by the hyper-quenching of the μm -size liquid water droplet at 1 atm²⁵ and by the rapid-cooling of the small amount of liquid water under pressure,^{26,27} respectively. Although the detailed comparison between the HDA made by compression of ice I_h and the HDA made by rapid-cooling of high-pressure liquid water is necessary, this indicates that LDA and HDA correspond to glassy waters. In addition, the thermodynamical relation between HDA and liquid water is supported by the continuity between the pressure-induced melting curve of ice I_h and the pressure-induced amorphization curve of ice I_h .²⁸

The experiments of the softening of amorphous ices by heating^{29–31} suggest that the amorphous ice becomes liquid at high temperatures. In particular, the existence of two liquid waters is supported strongly by the difference in the onset temperature of glass-to-viscous liquid transitions, T_g , between LDA and HDA.²⁹ These experimental results suggest that LDA and HDA are different glassy waters relating to two different kinds of liquid water. At the present stage, this conclusion has the support of many experimental researchers. Although the viscous liquid state slightly above T_g has been confirmed,²⁹ the liquid-liquid transition (LLT) of pure water has not been observed directly yet. However, the LLT in water-rich solution system relating closely to the LLT of pure water has been observed.^{32,33} This LLT of dilute glycerol aqueous solution in Ref. 32 is essentially different from the LLT reported by Murata and Tanaka.³⁴ The transition observed by Murata and Tanaka may relate to the crystallization of solution.^{32,35,36}

Next we will consider the concern of (ii) whether the true nature of LDA-HDA transition is the first order or not. So far, the discontinuous behavior of LDA-HDA transition has been observed in many experiments.^{10–12,22,23} However, this concern remains because the transition occurs in the non-equilibrium conditions. We think that this concern may be removed by the experimental fact that only two states of LDA and HDA, not their intermedium state, coexist during the LDA-HDA transition.^{37–40} Actually, the coexistence of HDA and LDA at the transition from HDA to LDA during decompression⁴⁰ and at the transition from HDA to LDA during heating at ambient pressure^{37–39} has been observed. Moreover, the coexistence of LDA and HDA at the LDA-HDA transition during compression and decompression has been confirmed using a diamond anvil cell.⁴¹ Therefore, the nature of LDA-HDA transition is likely first order, although there are some opposite views^{42,43} and one cannot draw the clear conclusion as to the nature of HDA-LDA transition.^{44,45}

We presume from these experimental facts about glassy waters that the LLT exists and that a terminal point of the LLT, that is a LLCPP, exists somewhere in the no-man's land, though the existence of LLCPP is not axiomatic in general.⁴⁶ The existences of LLT and LLCPP have been implied in some experiments performed by Mishima and Stanley.^{47,48} Mishima and Stanley have measured the melting curves of some high-pressure crystalline ices (ice III, IV, and so on) in the no-man's land and have found a discontinuity of the slope of melting curves of ice IV.⁴⁷ This indicates that the state of liquid water changes drastically, in short that the LLT line exists. The existence of LLT in the confined water system has also been reported.⁴⁹ Moreover, the melting curve

of ice III continues smoothly to the temperatures lower than T_H , indicating that the ice III melting curve does not intersect with the LLT line.⁴⁸ The slope of the ice III melting curve also indicates that LDL exists slightly below T_H and this is supported by other recent experiments.^{50–53} The behavior of these melting curves suggests that the LLCPP locates in the positive-pressure region and in the region between the melting curves of ice III and IV. On the other hand, the existence of LLCPP is suggested also from the measurement of pressure-volume-temperature, P - V - T , surface of supercooled liquid water above T_H .⁵⁴ The location of LLCPP estimated from these experimental data is 0.02–0.05 GPa and 221–225 K.^{54,55} Mishima has mentioned that there is a minimum in the thermal expansion coefficient above 200 MPa confirming the previous experimental result.⁵⁶ This is consistent with the existence of LLCPP.^{54,57} Additionally, there is a large hysteresis of the pressure-induced LDA-HDA transition at, or slightly above, their T_g .⁵⁸ This measured P - V - T surface of the supercooled liquid water agrees qualitatively with the ST2-potential volume surface of the ST2-potential simulation.⁵⁹

The dynamic crossover of liquid water has been observed around 220 K in the confined water system,^{60,61} and the maximum in heat capacity of the confined water around 220 K⁶² has been detected. The dynamic behavior of the confined water is conjectured to be the fragile-strong crossover of bulk water,⁶³ and the heat behavior is inferred to be caused by the polyamorphic fluctuation of two liquid waters emanated from LLCPP. These seem to be consistent with the LLCPP hypothesis of bulk water though the polyamorphic property of the confined water might be different from that of bulk water.

Practically, to prove the existence of LLCPP by any experiment is impossible because of the crystallization⁴⁶ and, therefore, the LLCPP should be a “virtual” or “metastable” point.⁶⁴ All the experimental results as shown above are the indirect evidences for the LLCPP hypothesis. However, they are consistent with the LLCPP hypothesis and support strongly the existence of the “virtual” LLCPP. There are no definitively negative experimental data of the LLCPP hypothesis. On the assumption of the existence of the LLCPP, therefore, we believe that it is worth to discuss about the effect of the LLCPP on the aqueous solution.

Now, assuming that the LLCPP exists, it will be important to understand the effects of polyamorphic fluctuation between LDL-like and HDL-like water structures emanated from the LLCPP on the structure and function of aqueous solutions. However, the effects are unclear. Previously, we have studied the glassy dilute aqueous solutions from a viewpoint of water polyamorphism^{32,58,65,66} and have shown that the polyamorphic transition behavior of the solution depends on the solute concentration and the solute component.^{32,58,65} Recently, we have reported that the polyamorphic transition of glassy dilute glycerol-water solutions under high pressure³² relates closely to the LDA-HDA transition of pure water. This transition is supported by recent experiment and simulation.^{67,68} Moreover, the reversible polyamorphic transition of the glycerol-water solution has been highly reproduced by the repeated pressure changes, indicating that the glycerol molecules disperse homogeneously both in the LDA- and HDA-like bulk waters. Considering that both

LDA- and HDA-like waters are probably good solvents for glycerol, the glycerol-water solution becomes one of the most suitable solution systems for examining the difference between the effect of HDA-like solvent water on the solute and the effect of LDA-like solvent water. In this study, we prepared the glassy dilute glycerol-water solution and examined the effect of the polyamorphic transition of solvent water on the molecular vibrations of glycerol molecule using Raman spectroscopy.

II. SAMPLE PREPARATION AND EXPERIMENTAL METHOD

A. Preparation of glassy sample

The glycerol-water solution of the solute molar fraction of 0.07 mf was prepared by mixing glycerol and H₂O or D₂O. We used the bulk sample. It was not the emulsified sample which has been used in the measurements of polyamorphic transition under pressure in the previous study.³² The glycerol and D₂O were purchased from Wako Chemical Co. Ltd. H₂O was purified by Direct-Q (Millipore Co.). D₂O instead of H₂O was used in order to avoid the overlapping of the OH-stretching bands of H₂O appearing in the 3000-3800 cm⁻¹ region with the OH-stretching bands of glycerol in the Raman spectroscopic study. In addition, in order to check an effect of the hydrogen/deuterium exchange between glycerol and D₂O, we performed the measurements for the glycerol-H₂O system using the same experimental method performed for the glycerol-D₂O system.

About 1.5 ml of solution sample was sealed in an indium container, compressed to 0.3 GPa at room temperature by using a piston-cylinder apparatus with a temperature controller, and cooled to 77 K at a cooling rate of ~40 K/min. Next, the pressure was decreased from 0.3 GPa to 1 atm at 77 K and then the sample was recovered at 77 K at 1 atm. The recovered sample was transparent. We verified that there were no crystalline peaks in its Raman spectra. Therefore, we identified that the recovered sample was a homogeneous glass. The glassy sample was mounted firmly in the indium holder designed for a cryostat. The thermal contact between the sample and the indium holder was good. The sample holder was placed in the cryostat (Iwatani Industrial Gases Corp.) with a temperature controller with a window for Raman spectroscopic measurement.

B. Temperature protocols

In the previous study,³² we have confirmed the occurrence of the transition between low-density and high-density glassy glycerol aqueous solutions under pressure (Fig. 1(a)). This polyamorphic transition under pressure is reversible and has hysteresis. In addition, it depends on temperature; the transition pressure at which the high-density form transforms to the low-density form during decompression decreases with the decrease in temperature. We think, therefore, that the transition from high-density to low-density state induced by heating at ambient pressure as shown in Fig. 1(a) is equivalent to the decompression-induced polyamorphic transition. This

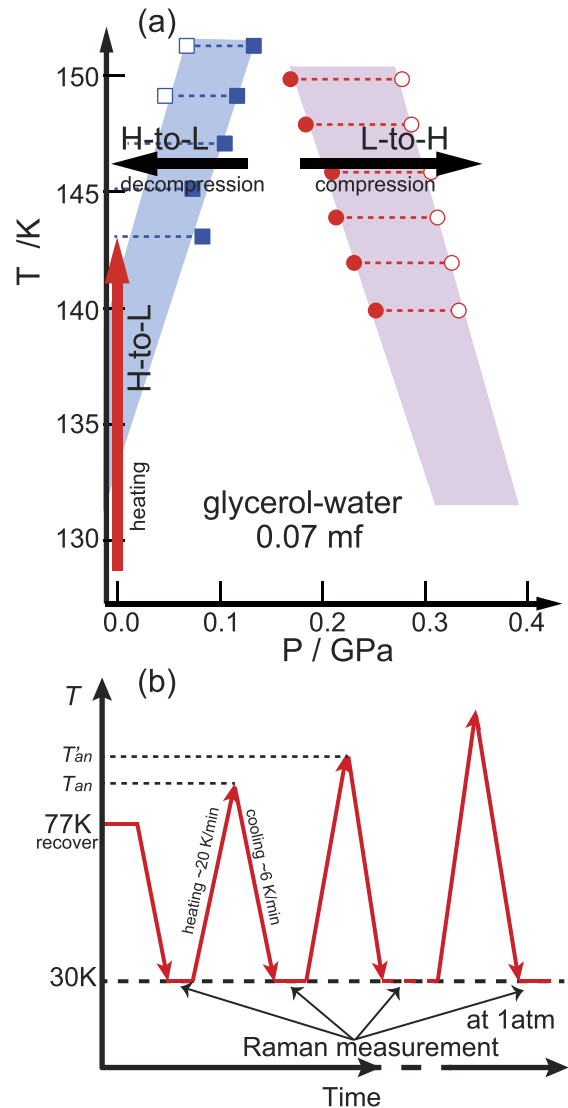


FIG. 1. P - T diagram of polyamorphic transition of glycerol-water system and temperature protocols for Raman spectroscopic measurement. (a) This is the P - T diagram for the 0.07 mf sample.³² The “H-to-L” region (blue) and “L-to-H” region (red) stand for the decompression-induced transition from high-density to low-density state and the compression induced transition from low-density to high-density state, respectively. The filled and open marks (circles and squares) stand for the onset and offset transition pressures, respectively. (b) The recovered sample is cooled down to ~30 K and the Raman spectroscopic measurement is performed at ~30 K. In order to freeze the state of sample at T_{an} , the sample is heated up to T_{an} at ~20 K/min. After the sample temperature reaches at T_{an} , the sample is cooled down to 30 K at ~6 K/min immediately and then the Raman spectrum is recorded at 30 K. Next, the sample is heated up to T'_{an} which is slightly higher than T_{an} , the sample is cooled down to 30 K immediately, and then the Raman spectrum of the sample in which the state at T'_{an} is frozen is recorded at 30 K. The set of “the heating up to T_{an} , the cooling down to 30 K, and the Raman measurement at 30 K” are repeated while increasing the T_{an} little by little.

heating-induced transition at ambient pressure is expected to occur in the temperature region between 130 and 140 K.

We transform the high-density glassy glycerol aqueous solution to low-density glassy solution by heating at the ambient pressure and examined the change in the state of solvent water and the change in the state of glycerol molecule using Raman spectroscopy. In order to examine the state of sample at a given temperature, T_{an} , by Raman spectroscopy,

the sample temperature was controlled as shown in Fig. 1(b). The sample was heated up to T_{an} , and as soon as the sample temperature reached at the T_{an} , the sample was cooled to 30 K rapidly and the state of sample at T_{an} was frozen. Subsequently the Raman spectra of the sample were recorded at 30 K. There are two advantages of Raman measurement at low temperature (~ 30 K); one is to avoid the temperature effects of molecular vibrations and another is to clarify a difference between the Raman profile of LDA-like solvent water and that of HDA-like solvent water because their Raman spectra become sharper at low temperature. Next, the sample was heated up to T'_{an} which was higher than T_{an} and the state of sample changed slightly. As soon as the sample temperature reaches to the T'_{an} , the sample is cooled to 30 K rapidly and then the Raman measurement is performed at 30 K. The T_{an} was increased from 77 to 200 K step by step and the set of “the heating up to T_{an} —the cooling down to 30 K—the Raman measurement at 30 K” was repeated. We studied the change of the molecular vibrations of water and glycerol with the increase of T_{an} .

C. Raman measurement

Raman measurement of the sample was performed using a microscopic Raman spectrometer system (Jobin Yvon, Inc., T64000). The exciting light source was an argon ion laser operating at 488 nm with power of 500 mW. The laser light via the optical system was attenuated and the laser power in front of the sample was about 20 mW. Therefore, we can ignore the elevation of sample temperature caused by the laser irradiation.

The intensity of the Raman scattered radiation polarized parallel to the incident light, $I(\nu)$, was recorded in a frequency region from 700 to 4000 cm^{-1} with resolution of 0.2 cm^{-1} , where ν is the Raman frequency. In Fig. 2, the Raman spectra of high-density glassy glycerol- D_2O solution (0.07 mf) at 30 K

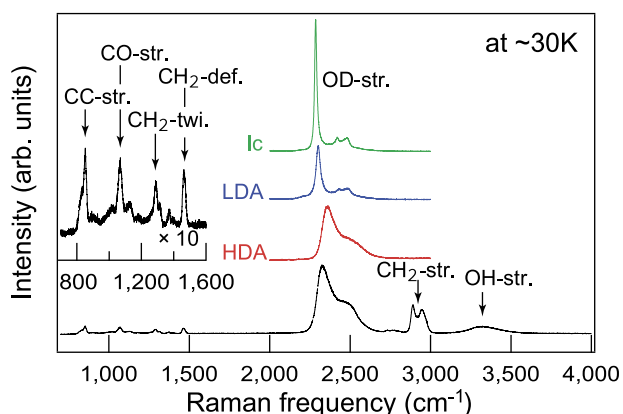


FIG. 2. Raman spectra of the high-density glassy glycerol- D_2O solution at 30 K. The Raman spectrum of initial glassy sample is drawn by black. Comparative Raman profiles of OD-stretching bands of HDA (red), LDA (blue), and ice I_c (green) of pure water (D_2O) at 30 K are shown.^{19,32} The Raman spectrum below 1600 cm^{-1} is expanded to ten times in an inset. The “str.,” “def.,” and “twi.” are abbreviated from “stretching,” “deformation,” and “twist” vibration modes, respectively, and are assigned tentatively by Ref. 69. Although there might be weak Raman bands relating to the bending vibration of D_2O around 1200 cm^{-1} ,⁹² the effect of the bands on the analysis of the CO- and CC-stretching bands of glycerol could be negligible.

in the range of 700-4000 cm^{-1} and the comparative Raman spectra of HDA, LDA, and crystalline ice I_c of pure D_2O at 30 K in the range of 2000-3000 cm^{-1} are shown.

The state of solvent water was identified by the Raman profile of the OD-stretching bands. Assuming the tentative mode assignments of pure glycerol,⁶⁹ the vibration modes relating to the side groups, for example, the OH- and CH_2 -stretching modes, appear in 2700-3700 cm^{-1} and the typical bone vibration modes, for example, the CC- and CO-stretching modes, appear below ~ 1600 cm^{-1} .

D. Analysis of Raman spectra

In order to clarify the subtle change in the Raman profile, the $I(\nu)$ were analyzed by a linear combination of some Gaussian functions, $I(\nu) = \sum_{i=1}^n A_i \left\{ \frac{-(\nu-\nu_i)^2}{\omega_i^2} \right\} + B$, where A_i is the magnitude, ν_i the central frequency, ω_i the dispersion, $n = 2, 3, \text{ or } 4$, and B the background. In this study, the OD/OH stretching band of $\text{D}_2\text{O}/\text{H}_2\text{O}$ was analyzed simply by a linear combination of four Gaussian functions although it is difficult to identify these four modes exactly because of the complex hydrogen bond interaction between water molecules. The OH-, CH_2 -, CO-, and CC-stretching bands of glycerol were deconvoluted by the linear combination of two, three, and two Gaussian functions, respectively.

III. RESULTS AND DISCUSSIONS

The change in Raman profile of the OD-stretching bands of solvent water in the high-density glassy sample with the increase of T_{an} is shown in Fig. 3(a). The T_{an} dependence of the central frequency, ν_{OD} , of the Gaussian function marked by an arrow in Fig. 3(a) is shown in Fig. 3(f). Below 130 K (the pink region in Fig. 3(f)), the value of ν_{OD} is almost constant and the Raman profile does not change, indicating that the state of solvent water keeps being HDA-like. Around 130 K, the ν_{OD} starts to shift toward the lower frequency side, the decrease of ν_{OD} stops around 140 K, and then between 140 and 160 K (the light blue region in Fig. 3(f)), the value of ν_{OD} is almost equal to that of LDA (D_2O). This indicates that the state of solvent water transforms from HDA-like state to LDA-like state. The gradual decrease of ν_{OD} between 130 and 140 K (the white region in Fig. 3(f)) corresponds to the polyamorphic transition. We consider that the HDA- and LDA-like solvent waters may coexist between 130 and 140 K.^{32,70} Once the T_{an} exceeds ~ 160 K, the ν_{OD} suddenly decreases and its value agrees with the value of ν_{OD} for the crystalline ice I_c , indicating that the part of solvent water crystallizes. Regarding the crystalline structure, we cannot identify from the analysis of Raman spectra whether or not the crystal is the two dimensional ice proposed by Inaba and Andersson.⁷¹ The T_{an} dependences of the other Gaussian function in Fig. 4(a) are analogous to this result.

The T_{an} dependences of the OH-, CH_2 -, CC-, and CO-stretching bands of glycerol are shown in Figs. 3(b)–3(e), respectively. The changes in these Raman profiles are very small, but conspicuous. The central frequencies of the largest Gaussian function marked by an arrow, ν_{OH} , ν_{CH_2} , ν_{CC} , and ν_{CO} ,

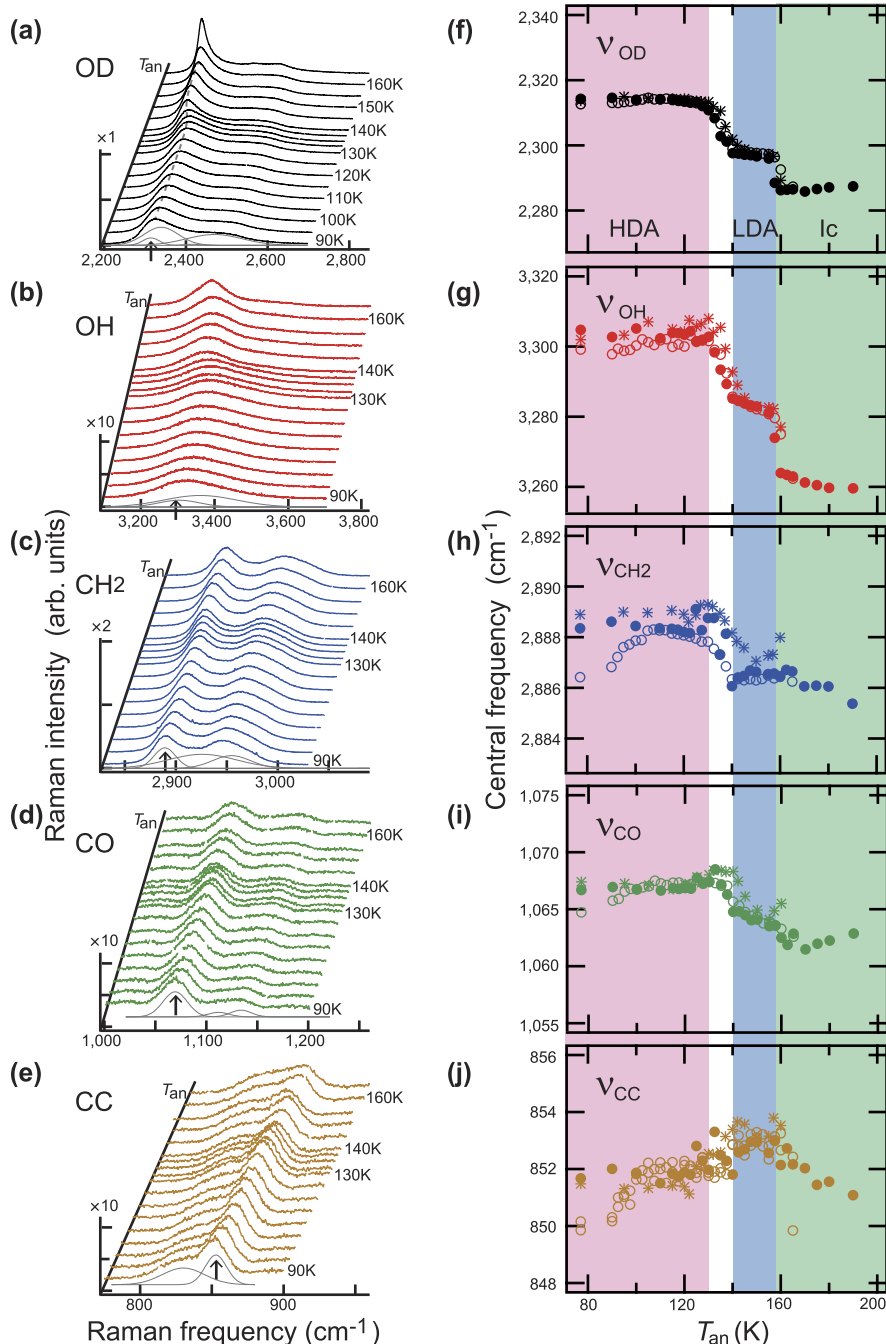


FIG. 3. The T_{an} dependences of Raman spectra of glycerol- D_2O solution. All the Raman spectra were measured at 30 K after cooling from T_{an} ($=90, 95, 100, 105, 110, 115, 120, 125, 130, 132.5, 135, 137.5, 140, 145, 150, 155, 160,$ and 165 K). (a) The change in the OD-stretching bands of solvent water with the increase in T_{an} . The Raman spectra are analyzed by a linear combination of four Gaussian functions (grey thin lines). The change in the position of characteristic large peak around 2300 cm^{-1} is traced by a dashed line. (b)-(e) The changes in the OH-, CH₂-, CO-, and CC-stretching bands of glycerol with the increase in T_{an} . The Raman spectra of the OH-, CH₂-, CO-, and CC-stretching bands are analyzed by a linear combination of two, three, three, and two Gaussian functions, respectively. (f)-(j) The T_{an} dependences of the ν_{OD} , ν_{OH} , ν_{CH_2} , ν_{CC} , and ν_{CO} which are the central frequencies of Gaussian function marked by the arrow in (a)-(e). Three different samples with the same concentration were prepared and the experimental results for the samples were represented by open circle, filled circle, and asterisk. The pink, light blue, and light green regions indicate that the state of solvent water is HDA-like, LDA-like, and crystalline, respectively. The white region indicates that the HDA-like and LDA-like solvent waters may coexist.

were plotted as a function of T_{an} in Figs. 3(g)-3(j), respectively. The value of ν_{OH} , ν_{CH_2} , ν_{CC} , and ν_{CO} hardly changes below 130 K within the error range. The value of ν_{OH} , ν_{CH_2} , ν_{CC} , and ν_{CO} starts to change around 130 K. Although their values are scattered between 140 and 160 K, they are apparently different from those below 130 K. This indicates that the molecular vibration of glycerol in 140-160 K is different from that below 130 K. Moreover, around 160 K, the value of ν_{OH} , ν_{CH_2} , ν_{CC} , and ν_{CO} changes suddenly because of the crystallization of solvent water.

As shown in Figs. 3(f)-3(j), the small, but conspicuous, changes in the molecular vibration of glycerol seem to synchronize with the change in ν_{OD} of solvent water. That is to say, the change in molecular vibration of glycerol is induced by the change in the polyamorphic state of solvent water.

We conclude that the dynamics of glycerol surrounded by the HDA-like solvent water is different from one surrounded by LDA-like solvent water and that the dynamics of glycerol is sensitive to the polyamorphic state of the solvent water. This behavior seems to be conceptually opposite to the generally accepted hydration behavior. Here, we think that the dynamical change of glycerol around 130-140 K is not caused by the glass transition of glycerol because the T_g of pure glycerol locates around 190 K at 1 atm.

In order to check the effect of the hydrogen/deuterium exchange between glycerol and D_2O , we examine the vibration changes of glycerol during the polyamorphic transition of the glycerol- H_2O solution using the same experimental method performed for the glycerol- D_2O system. The T_{an} dependences of Raman spectra for the glycerol- H_2O system and the T_{an}

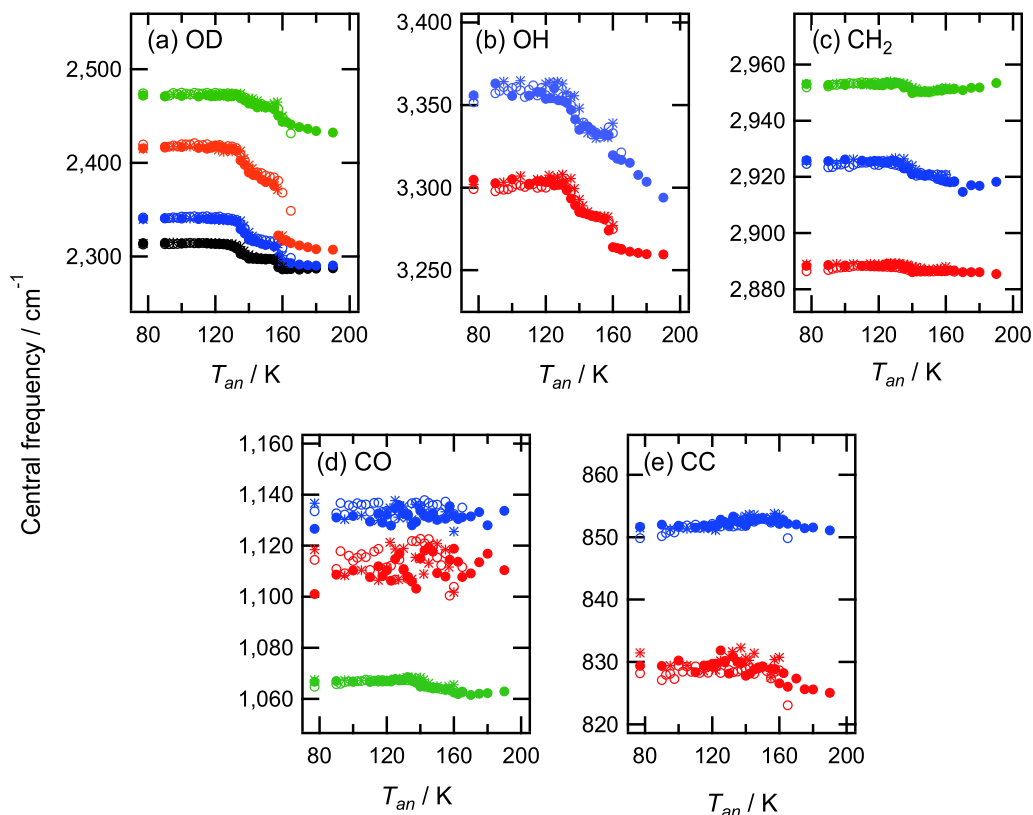


FIG. 4. The T_{an} dependences of the central frequencies of other Gaussian functions for the glycerol-D₂O solution.

dependences of ν_{OH} , ν_{CH_2} , ν_{CC} , and ν_{CO} are shown in Fig. 5. Although the OH-stretching band of solvent water (H₂O) is overlapped with that of glycerol, the polyamorphic change of solvent water is identified by the change of the ν_{OH} around 3100 cm⁻¹ because of the small intensity of the OH-stretching bands of glycerol appearing around 3300 cm⁻¹. In the case of the glycerol-H₂O system, the ν_{OH} starts to decrease around 125 K and the decrease in ν_{OH} stops around 140 K (Fig. 5(e)). This indicates that the polyamorphic transition of glycerol-H₂O solution starts around 125 K and completes around 140 K.

The onset T_{an} of polyamorphic transition is lower than that for the glycerol-D₂O system (~130 K). Although we cannot determine the precise transition temperature because of the experimental errors, the difference of the onset T_{an} may be caused by the different properties between light water and heavy water.⁷² We did not use the deuterated glycerol sample in this study although it would be desirable to clarify the isotope effect.

The ν_{CH_2} of glycerol starts to change around 125 K (Fig. 5(f)) and the ν_{CC} and ν_{CO} start to change around 130 K (Figs. 5(g) and 5(h)). The sudden changes in ν_{CH_2} , ν_{CC} , and ν_{CO} of glycerol seem to synchronize with the polyamorphic transition of solvent water. The similarity between the result for the glycerol-H₂O system and the result for the glycerol-D₂O system proves that there is no effect of the hydrogen/deuterium exchange between glycerol and D₂O on our conclusions in this study.

Previously, we have observed that the CH₂-stretching band of tetrahydrofuran (THF) in the high-density glassy

THF-water solution prepared by the pressure-induced amorphization of THF clathrate hydrate is different from that in the low-density glassy THF-water solution made by 1 atm-heating of high-density glassy THF-water solution.⁷³ This is consistent with the conclusion of the present study.

Now, considering that the structure of water around a macromolecule plays the important roles in the structural stability and the functional expression of the macromolecule,⁷⁴⁻⁷⁶ it is worthwhile to rethink the behaviors of aqueous solutions from a viewpoint of water polyamorphism.^{32,66,68,77-82} Recently, it has been proposed that the polyamorphic transition of solvent water may affect the protein dynamics, for example, the effect of the fragile-to-strong crossover of water on the softening of protein around 220 K⁸³⁻⁸⁵ and the relationship between the high- to low-density transition of amorphous ice confined in the protein crystal and the protein dynamical transition around 110 K.⁸⁶ However, these experiments were performed using the confined water and the direct inter-relationship between the polyamorphic behavior of “bulk” solvent water and the dynamics of solute is unclear. In this study, we showed for the first time that the polyamorphic transition of bulk solvent water affects the molecular vibrations of glycerol directly.

Furthermore, when compared with the previous studies of the relationship between the polyamorphic transition of solvent water and the protein dynamics,⁸³⁻⁸⁶ our Raman measurements were done at a constant temperature of 30 K, which removed the effect of the temperature change on the dynamics of solute molecules. Consequently, the difference between the molecular vibration of solute surrounded by

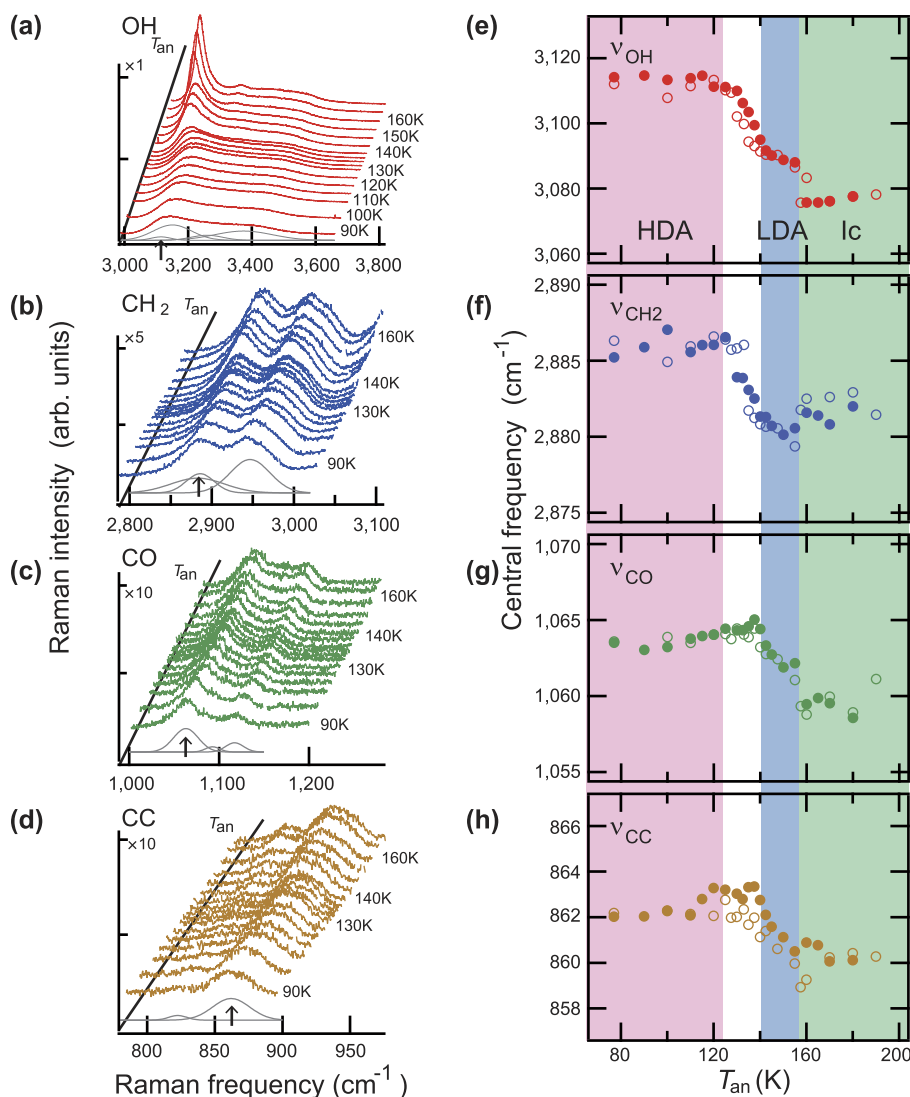


FIG. 5. The T_{an} dependences of Raman spectra of glycerol- H_2O solution. (a) The change in the OH-stretching bands of solvent water with the increase in T_{an} . (b)-(d) The changes in the CH_2 -, CO -, and CC -stretching bands of glycerol with the increase in T_{an} . (e)-(h) The T_{an} dependences of the ν_{OH} , ν_{CH_2} , ν_{CO} , and ν_{CC} which are the central frequencies of Gaussian function marked by the arrow in (a)-(d). Two different samples were prepared, and the experimental results for the samples were represented by open and filled circles. The pink, light blue, and light green regions indicate that the state of solvent water is HDA-like, LDA-like, and crystalline, respectively. The white region indicates that the HDA-like and LDA-like solvent waters may coexist.

the HDA-like bulk water and that surrounded by LDA-like bulk water becomes clear. This suggests a possibility that the dynamics of solute molecule in water under ambient conditions is influenced by the polyamorphic change of solvent water, for example, the polyamorphic fluctuation of water structure emanated from the presumed LLCP.

It is natural to expect that the solute is generally perturbed by the structural change in solvent and, in our case, the change in solvent is the polyamorphic transition. Now, our statement in this paper is that there exists the specific temperature-pressure region in which the vibration of solute molecule changes relatively drastically in the aqueous solution. The specific region will locate near the LLT line and near the Widom line.⁸⁷ The specific region is thought to include the region around the room temperature around 1 atm because of the far-reaching influence of LLCP. We note that the recent simulation studies have demonstrated the existence of HDA- and LDA-like structures in the inherent potential energy surface of the ambient water.⁸⁸⁻⁹⁰ The experimental study suggests also a sign that the two liquid waters exist.⁹¹ Therefore, in order to understand the dynamic behavior of solute, it may be important to consider a degree of the

polyamorphic fluctuation of water, that is, the LDL/HDL ratio in the inherent potential surface.⁸⁸⁻⁹⁰

This conclusion is derived from the measurements of glassy states at low temperatures, suggesting a possibility that the polyamorphic fluctuation of solvent water affects the molecular vibrations of solute at high temperatures. In order to verify the conclusion, the *in situ* measurements of LLT in the liquid regions are necessary in future, though the actual experiment will be challenging because of the difficulty in quick measurement.

Our result suggests that not only the polyamorphic change of the interfacial water near the solute but also that of bulk solvent water directly induces the change in the molecular vibration of solute. The structural similarity between the interfacial water near the solute and two kinds of glassy water (LDA/HDA)^{32,66,70,78-82} has been reported previously, suggesting that it is important to reconsider the hydration of aqueous solution from a viewpoint of water polyamorphism. If enough amount of water to form the LDA-like/HDA-like structure exists near the solute, the solvent water including the interfacial water adjacent to the solute will be classified into either the LDA-like or the HDA-like water, even if the

structure of the interfacial water is deformed by the interaction between the solute and the water.

Now, we suppose that, if the LLC exists, the solvent water in the solution under the ambient environment would be essentially the supercritical state of the two kinds of water, LDL- and HDL-like waters, and then the reaction between the solute molecules would be more active in the low-temperature and low-pressure regions near the LLC from the analogy of the active reaction in the liquid-gas supercritical region. The change in the solute dynamics suggested in this work is consistent with this supposition. We expect in future that the complex hydration dynamics occurring under aqueous environment will be elucidated and simplified by reconsidering the solvent water in the aqueous solution from the polyamorphic viewpoint.

ACKNOWLEDGMENTS

This work was supported by JSPS KAKENHI Grant No. 25400432.

- ¹P. G. Debenedetti, *J. Phys.: Condens. Matter* **15**, R1669 (2003).
- ²O. Mishima and H. E. Stanley, *Nature* **396**, 329 (1998).
- ³P. H. Poole, F. Sciortino, U. Essmann, and H. E. Stanley, *Nature* **360**, 324 (1992).
- ⁴J. C. Palmer, F. Martelli, Y. Liu, R. Car, A. Z. Panagiotopoulos, and P. G. Debenedetti, *Nature* **510**, 385 (2014).
- ⁵R. S. Singh, J. W. Biddle, P. G. Debevebetti, and M. A. Anisimov, *J. Chem. Phys.* **144**, 144504 (2016).
- ⁶J. L. F. Abascal and C. Vega, *J. Chem. Phys.* **123**, 234505 (2005).
- ⁷T. Sumi and H. Sekino, *RSC Adv.* **3**, 12743 (2013).
- ⁸T. Yagasaki, M. Matsumoto, and H. Tanaka, *Phys. Rev. E* **89**, 020301 (2014).
- ⁹O. Mishima, L. D. Calvert, and E. Whalley, *Nature* **310**, 393 (1984).
- ¹⁰O. Mishima, L. D. Calvert, and E. Whalley, *Nature* **314**, 76 (1985).
- ¹¹O. Mishima, *J. Chem. Phys.* **100**, 5910 (1994).
- ¹²K. Winkel, M. S. Elsaesser, E. Mayer, and T. Loerting, *J. Chem. Phys.* **128**, 044510 (2008).
- ¹³L. Bosio, G. P. Johari, and J. Teixeira, *Phys. Rev. Lett.* **56**, 460 (1986).
- ¹⁴A. Bizid, L. Bosio, A. Defrain, and M. Oumezzine, *J. Chem. Phys.* **87**, 2225 (1987).
- ¹⁵M. C. Bellissent-Funel, J. Teixeira, and L. Bosio, *J. Chem. Phys.* **87**, 2231 (1987).
- ¹⁶M. A. Floriano, E. Whalley, E. C. Svensson, and V. F. Sears, *Phys. Rev. Lett.* **57**, 3062 (1986).
- ¹⁷J. C. Li and P. Jenniskens, *Planet. Space Sci.* **45**, 469 (1997).
- ¹⁸J. L. Finney, A. Hallbrucker, I. Kohl, A. K. Soper, and D. T. Bowron, *Phys. Rev. Lett.* **88**, 225503 (2002).
- ¹⁹D. D. Klug, O. Mishima, and E. Whalley, *Physica B+C* **139-140**, 475 (1986).
- ²⁰H. Kanno, K. Tomikawa, and O. Mishima, *Chem. Phys. Lett.* **293**, 412 (1998).
- ²¹Y. Suzuki, Y. Takasaki, Y. Tominaga, and O. Mishima, *Chem. Phys. Lett.* **319**, 81 (2000).
- ²²E. L. Gromnitskaya, O. V. Stal'gorova, V. V. Brazhkin, and A. G. Lyapin, *Phys. Rev. B* **64**, 094205 (2001).
- ²³O. Andersson and H. Suga, *Phys. Rev. B* **65**, 140201 (2002).
- ²⁴T. Loerting, C. Salzmann, I. Kohl, E. Mayer, and A. Hallbrucker, *Phys. Chem. Chem. Phys.* **3**, 5355 (2001).
- ²⁵P. Brüggeller and E. Mayer, *Nature* **288**, 569 (1980).
- ²⁶O. Mishima and Y. Suzuki, *J. Chem. Phys.* **115**, 4199 (2001).
- ²⁷C. U. Kim, Y.-F. Chen, M. W. Tate, and S. M. Gruner, *J. Appl. Crystallogr.* **41**, 1 (2008).
- ²⁸O. Mishima, *Nature* **384**, 546 (1996).
- ²⁹K. Amann-Winkel *et al.*, *Proc. Natl. Acad. Sci. U. S. A.* **110**, 17720 (2013).
- ³⁰O. Mishima, K. Takemura, and K. Aoki, *Science* **254**, 406 (1991).
- ³¹C. U. Kim, M. W. Tate, and S. M. Gruner, *Proc. Natl. Acad. Sci. U. S. A.* **112**, 11765 (2015).
- ³²Y. Suzuki and O. Mishima, *J. Chem. Phys.* **141**, 094505 (2014).
- ³³Z. Zhao and C. A. Angell, *Angew. Chem., Int. Ed.* **55**, 2474 (2016).
- ³⁴K. Murata and H. Tanaka, *Nat. Mater.* **11**, 436 (2012).
- ³⁵L.-S. Zhao, Z.-X. Cao, and Q. Wang, *Sci. Rep.* **5**, 15714 (2015).
- ³⁶I. Popov, A. Greenbaum, A. P. Sokolov, and Y. Feldman, *Phys. Chem. Chem. Phys.* **17**, 18063 (2015).
- ³⁷O. Mishima and Y. Suzuki, *Nature* **419**, 599 (2002).
- ³⁸M. M. Koza, H. Schober, H. E. Fischer, T. Hansen, and F. Fujara, *J. Phys.: Condens. Matter* **15**, 321 (2003).
- ³⁹S. Klotz *et al.*, *Phys. Rev. Lett.* **94**, 025506 (2005).
- ⁴⁰K. Winkel, E. Mayer, and T. Loerting, *J. Phys. Chem. B* **115**, 14141 (2011).
- ⁴¹Y. Yoshimura, S. T. Stewart, H.-K. Mao, and R. J. Hemley, *J. Chem. Phys.* **126**, 174505 (2007).
- ⁴²C. A. Tulk *et al.*, *Science* **297**, 1320 (2002).
- ⁴³M. Guthrie *et al.*, *Phys. Rev. B* **68**, 184110 (2003).
- ⁴⁴M. M. Koza, T. Hansen, R. P. May, and H. Schober, *Studying Kinetics with Neutrons* (Springer, 2010), p. 77.
- ⁴⁵K. Amann-Winkel *et al.*, *Rev. Mod. Phys.* **88**, 011002 (2016).
- ⁴⁶K. Binder, *Proc. Natl. Acad. Sci. U. S. A.* **111**, 9374 (2014).
- ⁴⁷O. Mishima and H. E. Stanley, *Nature* **392**, 164 (1998).
- ⁴⁸O. Mishima, *Phys. Rev. Lett.* **85**, 334 (2000).
- ⁴⁹Y. Zhang *et al.*, *Proc. Natl. Acad. Sci. U. S. A.* **108**, 12206 (2011).
- ⁵⁰J. A. Sellberg *et al.*, *Nature* **510**, 315 (2014).
- ⁵¹G. Pallares *et al.*, *Proc. Natl. Acad. Sci. U. S. A.* **111**, 7936 (2014).
- ⁵²M. E. M. Azouzi, C. Ramboz, J.-F. Lenain, and F. Caupin, *Nat. Phys.* **9**, 38 (2013).
- ⁵³D. Liu *et al.*, *Proc. Natl. Acad. Sci. U. S. A.* **104**, 9570 (2007).
- ⁵⁴O. Mishima, *J. Chem. Phys.* **133**, 144503 (2010).
- ⁵⁵V. Holten, C. E. Bertrand, M. A. Anisimov, and J. V. Sengers, *J. Chem. Phys.* **136**, 094507 (2012).
- ⁵⁶L. Ter Minassian, P. Pruzan, and A. Soulard, *J. Chem. Phys.* **75**, 3064 (1981).
- ⁵⁷V. Holten, J. V. Sengers, and M. A. Anisimov, *J. Phys. Chem. Ref. Data* **43**, 043101 (2014).
- ⁵⁸O. Mishima, *J. Phys. Chem.* **126**, 244507 (2007).
- ⁵⁹P. H. Poole, I. Saika-Voivod, and F. Sciortino, *J. Phys.: Condens. Matter* **17**, L431 (2005).
- ⁶⁰A. Faraone, L. Liu, C.-Y. Mou, C.-W. Yen, and S.-H. Chen, *J. Chem. Phys.* **121**, 10843 (2004).
- ⁶¹L. Liu, S.-H. Chen, A. Faraone, C.-H. Yen, and C.-Y. Mou, *Phys. Rev. Lett.* **95**, 117802 (2005).
- ⁶²M. Oguni, Y. Kanke, and S. Namba, *AIP Conf. Proc.* **982**, 34 (2008).
- ⁶³K. Ito, C. T. Moynihan, and C. A. Angell, *Nature* **398**, 492 (1999).
- ⁶⁴V. Holten and M. A. Anisimov, *Sci. Rep.* **2**, 713 (2012).
- ⁶⁵Y. Suzuki and O. Mishima, *J. Chem. Phys.* **138**, 084507 (2013).
- ⁶⁶Y. Suzuki and O. Mishima, *Phys. Rev. Lett.* **85**, 1322 (2000).
- ⁶⁷J. Bachler *et al.*, *Phys. Chem. Chem. Phys.* **18**, 11058 (2016).
- ⁶⁸D. A. Jahn *et al.*, *Phys. Chem. Chem. Phys.* **18**, 11042 (2016).
- ⁶⁹E. Mendelovici, R. L. Frost, and T. Klopogge, *J. Raman Spectrosc.* **31**, 1121 (2000).
- ⁷⁰J. W. Biddle, V. Holten, and M. A. Anisimov, *J. Chem. Phys.* **141**, 074504 (2014).
- ⁷¹A. Inaba and O. Andersson, *Thermochim. Acta* **461**, 44 (2007).
- ⁷²A. K. Soper and C. J. Benmore, *Phys. Rev. Lett.* **101**, 065502 (2008).
- ⁷³Y. Suzuki, *Phys. Rev. B* **70**, 172108 (2004).
- ⁷⁴Y. Levy and J. N. Onuchic, *Annu. Rev. Biophys. Biomol. Struct.* **35**, 389 (2006).
- ⁷⁵P. Ball, *Chem. Rev.* **108**, 74 (2008).
- ⁷⁶P. Ball and J. E. Hallsworth, *Phys. Chem. Chem. Phys.* **17**, 8297 (2015).
- ⁷⁷D. Paschek, *Phys. Rev. Lett.* **94**, 217802 (2005).
- ⁷⁸S. Chatterjee and P. G. Debenedetti, *J. Chem. Phys.* **124**, 154503 (2006).
- ⁷⁹A. Paciaroni *et al.*, *Phys. Rev. Lett.* **101**, 148104 (2008).
- ⁸⁰D. Russo *et al.*, *J. Am. Chem. Soc.* **133**, 4882 (2011).
- ⁸¹L. Le and V. Molinero, *J. Phys. Chem. A* **115**, 5900 (2011).
- ⁸²Y. Suzuki and Y. Tominaga, *J. Chem. Phys.* **134**, 244511 (2011).
- ⁸³S.-H. Chen *et al.*, *Proc. Natl. Acad. Sci. U. S. A.* **103**, 9012 (2006).
- ⁸⁴F. Mallamace, C. Corsaro, P. Baglioni, E. Fratini, and S.-H. Chen, *J. Phys.: Condens. Matter* **24**, 064103 (2012).
- ⁸⁵F. Mallamace *et al.*, *J. Chem. Phys.* **141**, 165104 (2014).
- ⁸⁶C. U. Kim, M. W. Tate, and S. M. Gruner, *Proc. Natl. Acad. Sci. U. S. A.* **108**, 20897 (2011).
- ⁸⁷L. Xu *et al.*, *Proc. Natl. Acad. Sci. U. S. A.* **102**, 16558 (2005).
- ⁸⁸B. Santra, R. A. DiStasio, Jr., F. Martelli, and R. Car, *Mol. Phys.* **113**, 2829 (2015).
- ⁸⁹S. R. Accorino, J. A. Rodriguez Fris, F. Sciortino, and G. A. Appignanesi, *Eur. Phys. J. E* **34**, 48 (2011).
- ⁹⁰K. T. Wikfeldt, A. Nilsson, and L. G. M. Pettersson, *Phys. Chem. Chem. Phys.* **13**, 19918 (2011).
- ⁹¹A. K. Soper and M. A. Ricci, *Phys. Rev. Lett.* **84**, 2881 (2000).
- ⁹²G. E. Walrafen and L. A. Blatz, *J. Chem. Phys.* **59**, 2646 (1973).