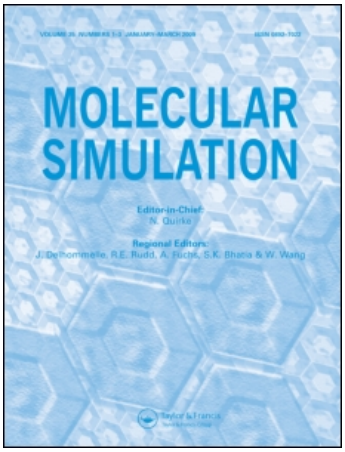

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Structure and Dynamics of Poly(Vinyl Alcohol) Hydrogel

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STRUCTURE AND DYNAMICS OF POLY(VINYL ALCOHOL) HYDROGEL

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Molecular dynamics simulations for models of poly(Vinyl Alcohol) hydrogels and pure water have been carried out over a wide temperature range including the glass transition temperature to examine structure and dynamics of supercooled water in hydrogels. The temperature dependences of thermodynamic properties and rotational relaxation times at atmospheric pressure are investigated. Those properties depend seriously on mobility of polymer chains and network structures of hydrogen bonds. It is found that polymer chains affect significantly the dynamic properties and the fragile-strong character of water. Structure and dynamics of water in PVA hydrogels are characterized by two dynamical modes, the motion of main chains and that of side chains, whose time scales are different from motion of water.

Keywords: Poly(Vinyl Alcohol) hydrogels; supercooled water; hydrogen bond networks

I. INTRODUCTION

We have previously reported molecular dynamics (MD) simulations for various hydrogels at ambient conditions and examined both structural and dynamical aspects. We found that polymer chains affect structure and dynamics of water molecules in hydrogels [1,2]. It is also important to investigate effects of water on structure and dynamics of polymer chains.

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Pure water exhibits various anomalies in thermodynamic response functions such as heat capacity and isothermal compressibility [3, 4]. Those properties in the supercooled state tend to diverge on approaching T_s, 228 K [5]. The origin of the divergences has long been controversial since water always freezes into ice at a temperature higher by a few degree than T_s. Recently, characters of supercooled water have been clarified through simulation studies [6–10]. We have reached a consensus that the phase equilibrium between low density liquid (LDL) and high density liquid (HDL) is responsible for those anomalous properties. The divergent character is suppressed and water is cooled down to the glass transition temperature when alcohol or hydrogen peroxide is dissolved [3]. A possible explanation is that LDL structure cannot exist with those solutes because of the differences in geometry and the number of hydrogen bonding sites.

The strong-fragile classification provides a useful concept as to whether a substance is vitrified [12–14]. For a fragile liquid, temperature dependence of the viscosity (and relaxation time) is described by the Vogel-Tammann-Fulcher (VTF) equation, while its dependence approaches to the Arrhenius type for a strong liquid. The strong-fragile character is related to the topography of the potential surface. The potential surface is rather regular in strong liquid while in fragile liquid the potential surface the trajectory covers is dependent on the temperature [14]. The transition of water from HDL to LDL accompanies a "fragile liquid-to-strong liquid" transition [11]. Aqueous solutions of alcohol or hydrogen peroxide belong to fragile liquids over a wide range of temperature [12, 13]. Aqueous polymer solutions have a different temperature dependence of the relaxation time of rotational motions [15] and are considered to be rather strong liquids. Why water changes its dynamic characters by coexisting solute species from small hydrophilic molecules to polymers? Water, which is classified into the fragile liquid in normal supercooled state, is surrounded by networks of polymer chains in hydrogels. It is important for understanding the mechanism of the glass transition to investigate relaxation phenomena in such a complexed system.

In our previous paper [16], dynamical properties of supercooled water in poly(vinyl alcohol) (PVA) hydrogel are investigated through MD simulation of rather long time runs (6 ns for each temperature). In a present paper, the simulation time is further extended (20 ns). The temperature investigated ranges from 400 to 135 K, which may cover the glass transition temperature of PVA hydrogels. Structure and dynamics of supercooled water in PVA hydrogel are investigated in conjunction with the glass transition, mobility of polymer chains, and network structures of hydrogen bond.

II. MODEL AND SIMULATION DETAILS

MD simulations are performed for pure water and hydrogel models of PVA with two sets of water contents, $c_w = 27.5$ and 50.0 wt%, as listed in Table I. PVA is modeled as H—[—CH_2—CH(OH)—]$_x$—CH_3 with degree of polymerization $x = 81$ ($c_w = 50.0$) or $x = 161$ ($c_w = 27.5$). The fraction of meso dyads of atactic PVA chains is set to 0.5. A polymer chain is confined in a unit cell with 199 ($c_w = 50.0$) or 150 ($c_w = 27.5$) water molecules under the periodic boundary condition. The chain is entangled with its image chains: the network structure of the physical gel is constructed by hydrogen bonds between two —OH groups of polymers. The number of molecules is set to 216 for pure water. The AMBER/OPLS [17, 18] force field is used for the polymers, and the TIP4P [19] for water. The united atom approximation is applied for —CH_3, —CH_2—, and >CH— groups, each of which is treated as a single interaction site. Nonbonded potentials are truncated smoothly at 9 Å. The long range correction for Lennard-Jones part is made. Initial structures are obtained by the same method as described elsewhere [1, 2]. The equations of motion are solved by the Verlet algorithm with a time step of 0.5 fs or 1 fs. The bond angles CH—O—H of PVA and all the bond lengths are constrained by the SHAKE algorithm. The TIP4P water is treated as a rigid molecule by the SHAKE vectorial constraint method [20]. Simulations are performed at various temperatures (135–400 K) and a pressure fixed to 0.1 MPa (atmospheric pressure) using Nosé-Andersen's constant temperature-pressure method [21–23]. A cubic periodic cell is used for the simulations of pure water. For the simulations of hydrogels a rectangular cell is used; three cell lengths are allowed to fluctuate independently. The simulations are performed sequentially from high temperature to low temperature according to the schedule shown in Figure 1. In order to collect data for long time correlations, further simulations are performed for each samples equilibrated at each temperature. The sampling time ranges from 0.4 ns to 20 ns, as listed in Table II. The simulation time is limited at high temperature, which is enough to sample

TABLE I Degree of polymerization x, number of water molecules n_w, and water content c_w of each sample

Sample	x	n_w	c_w (*wt*%)
PVA/water	161	150	27.5
PVA/water	81	199	50.0
Pure water	–	216	100

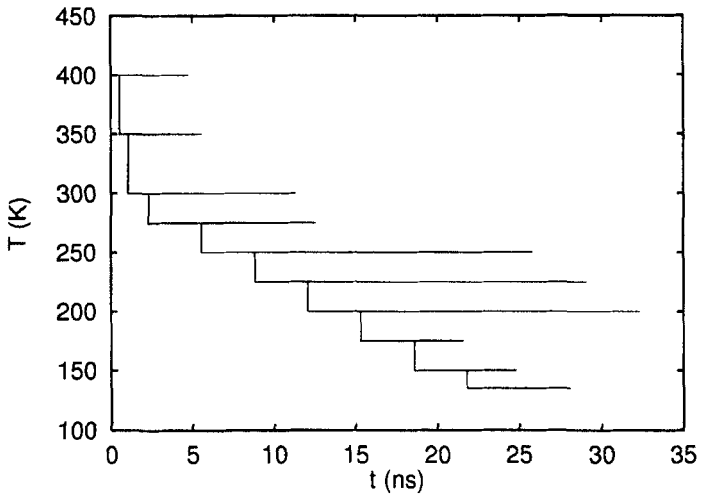


FIGURE 1 Schedule of stepwise cooling procedure for MD simulation of PVA hydrogel of $c_w = 27.5\,\text{wt}\%$. Simulations of the other samples are also performed with a similar procedure.

TABLE II Sampling time of MD simulation

	Sampling time (ns)		
$T(K)$	$c_w = 27.5\,wt\%$	$c_w = 50.0\,wt\%$	$c_w = 100\,wt\%$
400	4.7	0.4	0.5
350	5.0	1.6	0.5
300	10.0	2.8	0.5
275	10.0	10.0	0.5
250	20.0	10.0	0.5
225	20.0	10.0	6.0
213	–	–	6.0
200	20.0	20.0	10.0
175	6.0	6.0	6.0
150	6.0	6.0	6.0
135	6.0	6.0	6.0

the properties we are interested in. Equilibration runs of 0.2–0.5 ns are inserted between two simulations at successive temperatures. Trajectories and velocities of atoms are recorded every 500 steps (0.25 or 0.5 ps) on disk files for later analyses. Quenched (Q-) structures are obtained from instantaneous (I-) structures by the steepest descent energy minimization with the same constraint condition as the MD simulation using gradient-SHAKE method [24].

Orientational time correlation function

$$C_1(t) = \langle \mathbf{u}(t_0) \cdot \mathbf{u}(t + t_0) \rangle \tag{1}$$

are calculated where $\mathbf{u}(t)$ is a unit vector embedded in the molecule at time t. The vectors $\mathbf{u}(t)$ are taken to be unit vectors along the bond vector $\mathbf{b}_{CH\to CH_2}$, the out-of-plane vector $\mathbf{d}_{CH-O-H} = \mathbf{b}_{CH\to O} \times \mathbf{b}_{O\to H}$ of PVA chains, and the dipole vector $\boldsymbol{\mu}_{dip}$ of water molecules. Terminal segments of PVA (5 monomer units for both ends) are excluded from the sampling. Non-Debye response functions are a ubiquitous feature of the dynamics of supercooled liquids and amorphous polymers in their α-relaxation regime. The correlation functions $C_1(t)$ are fitted to the following stretched exponential, or Kohlrausch-Williams-Watts (KWW), function

$$C_1(t) = \exp[-(t/\tau)^{\beta}] \tag{2}$$

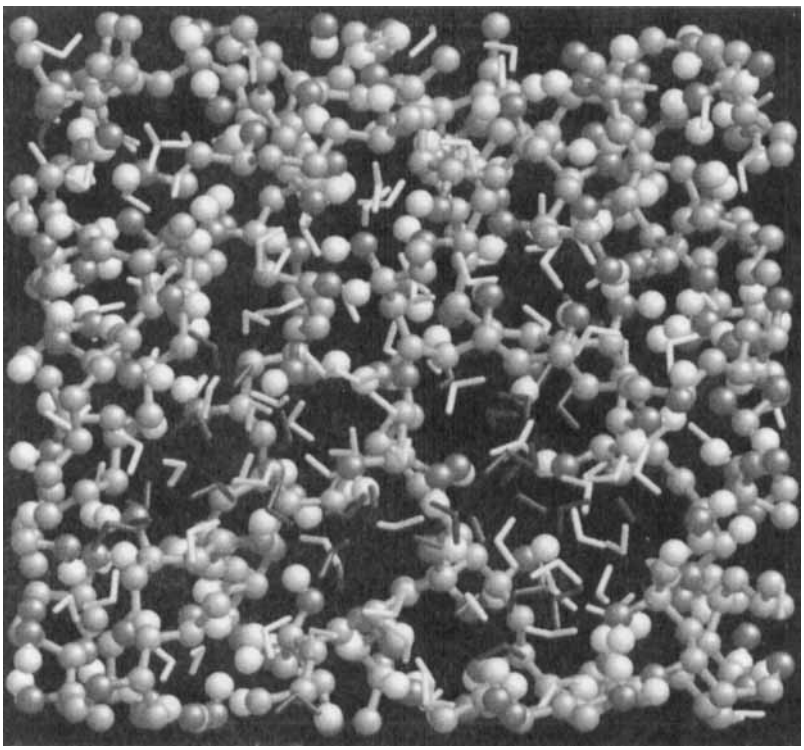
Reorientational relaxation time τ and stretched exponent β ($0 < \beta < 1$) are determined by a nonlinear least-squares method.

Calculations are performed on DEC Alpha workstation and CRAY Origin 2000 supercomputer, using the molecular simulation program PAMPS we coded.

III. RESULTS AND DISCUSSION

A. Structure of Hydrogel Model

Figure 2 shows snapshots of PVA hydrogels at 200 K. As colored in the figure, water molecules are classified into three regions: (1) those around hydrophilic groups (yellow), (2) those around hydrophobic groups (green), and (3) the bulk region (blue). The hydrophilic region is defined so as to cover the inner region up to the first peaks of $g(r)$ of water oxygen atoms around —OH groups. The hydrophobic region is similarly defined for hydrophobic groups: >CH—, —CH_2— and —CH_3. The regions which belong to both regions (1) and (2) are incorporated in region (1). The bulk region is defined as a region outside regions (1) and (2) (out of the first hydration shells). Table III lists average numbers of water molecules in each region. In the present samples, 94% (c_w = 27.5 wt%) or 65% (c_w = 50.0 wt%) of water molecules reside in the first hydration shell. As seen from Figure 2(b), the bulk region forms a water ball in the sample of c_w = 50.0 wt%. It is expected that water in this sample preserves bulk nature to a certain extent. On the other hand, character of water is highly perturbed by polymer chains in the sample of c_w = 27.5 wt%, as expected from Figure 2(a).



a)

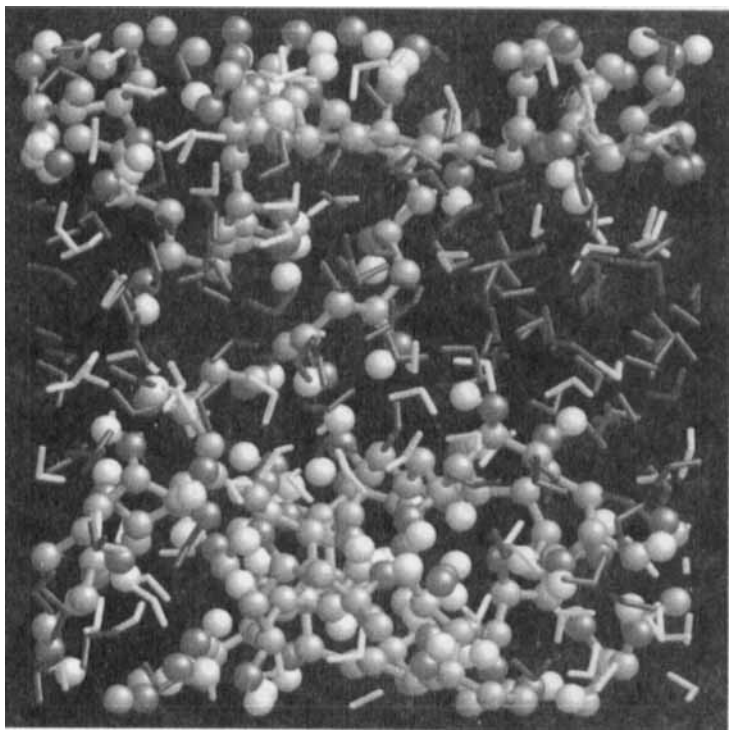
FIGURE 2 Snapshots of PVA hydrogels of (a) water content $c_w = 27.5$ wt% and (b) 50.0 wt% at 200 K. Carbon, oxygen and hydrogen atoms of PVA are shown by gray, red and white balls, respectively. Sticks express water molecules, which are classified into three regions: hydrophilic region (yellow), hydrophobic region (green) and bulk region (blue). (See Color Plate I).

TABLE III Average number of water molecules in each region of hydrogels

c_w (*wt%*)	*hydrophilic*	*hydrophobic*	*bulk*
27.5	112.1	28.3	9.6
50.0	86.7	42.0	70.3

B. Specific Volume

The temperature dependence of the specific volume is given in Figure 3. The individual point is an average over total sampling runs (0.4 – 20 ns) at each temperature. With decreasing temperature, a fairly large increase is found in specific volume for pure water around 210 K where the fluctuation is also



b)

FIGURE 2 (Continued).

large. At high pressure, the volume increase becomes larger while no appreciable temperature dependence is seen at negative pressure. There could be the second critical point around 210 K and 0.1 MPa [8, 9]. Pure water may undergo a phase transition [8, 9] from HDL (normal water) to LDL (water II), or a critical fluctuation [6, 7]. Because of the small number of molecules in this simulation, the transition between two states becomes facile in the vicinity of the critical point where the fluctuation becomes large.

On the other hand, the magnitude of the density fluctuation decreases monotonically with decreasing temperature in hydrogel. This seems to indicate that polymer networks restrain water from the phase transition or critical fluctuation. For PVA hydrogel systems, a change in the slope around 250 K may be identified as a simple break. This seems to be due to the glass transition of polymer chains. On cooling, the specific volume decreases by suppression of thermal motion. Below T_g, contraction of residual specific volume becomes difficult because of the increasingly long characteristic

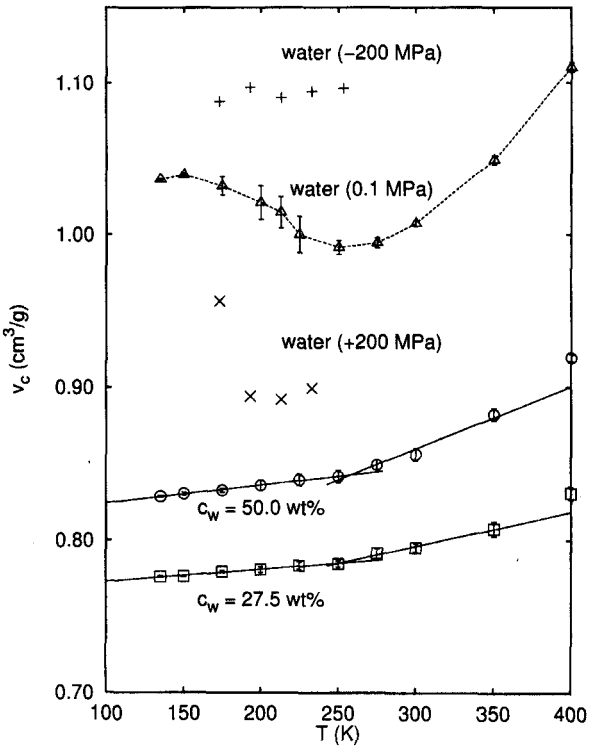


FIGURE 3 Temperature dependence of specific volume of PVA hydrogels with water content $c_w = 27.5$ wt% (square) and 50.0 wt% (circle), and that of pure water (triangle) at 0.1 MPa. Standard fluctuations based on averages of 100 ps interval (50 ps interval for high temperature) are shown by vertical lines. Simulation results of Tanaka [5] at + 200 MPa (cross) and − 200 MPa (plus) are also plotted.

relaxation time. By MD simulation with a stepwise cooling schedule, the glass transition temperature has been determined for bulk polymers [26–28] from the change in the slope of specific volume against temperature. Since the glass transition depends on the observation time, the T_g thus determined may not exactly match the corresponding laboratory T_g. In our present condition (the observation time $\sim 10^{-8}$ s, the effective cooling rate $\sim 10^9$ K/s), T_g of polymer chains in PVA hydrogel is determined to be 260 K. Cooling rate dependence of epoxy resin exhibits 2.2 K shift in T_g per decade of change in the cooling rate, as discussed by Roe [27]. T_g in our present study is approximately 22 K higher than the calorimetric T_g determined by a laboratory experiment (cooling rate on the order of 0.1 K/s).

C. Mobility of Polymer Chain

Polymer chains have two major dynamical modes: motion of main chains and that of side chains. As a measure of these motions, orientational time correlation functions of C—C bond vectors $\mathbf{b}_{CH\to CH_2}$ and that of CH—O—H out-of-plane vectors $\mathbf{d}_{CH-O-H}$ are calculated. The stretched exponents β in Eq. (2) averaged over all samples of $c_w = 27.5$ and 50.0 wt% above 250 K are 0.49 and 0.32 for vectors $\mathbf{b}_{CH\to CH_2}$ and $\mathbf{d}_{CH-O-H}$, respectively. The values of τ are re-determined from the least-squares fitting with fixed β values obtained above. Figure 4 shows the Arrhenius plot of τ of the main chains and that of the side chains. Since the τ values larger than $\sim 10^{-7}$ s have uncertainty, it could not be concluded whether the relaxation times obey the Arrhenius law or not. Assuming the Arrhenius behavior, the value of τ for main chains at T_g (~ 260 K), which is determined from temperature dependence of the specific volume, is approximately 10^{-5} s. This relaxation time is long enough and regarded as an infinite time compared to the observation time $\sim 10^{-8}$ s. Though the motion of main

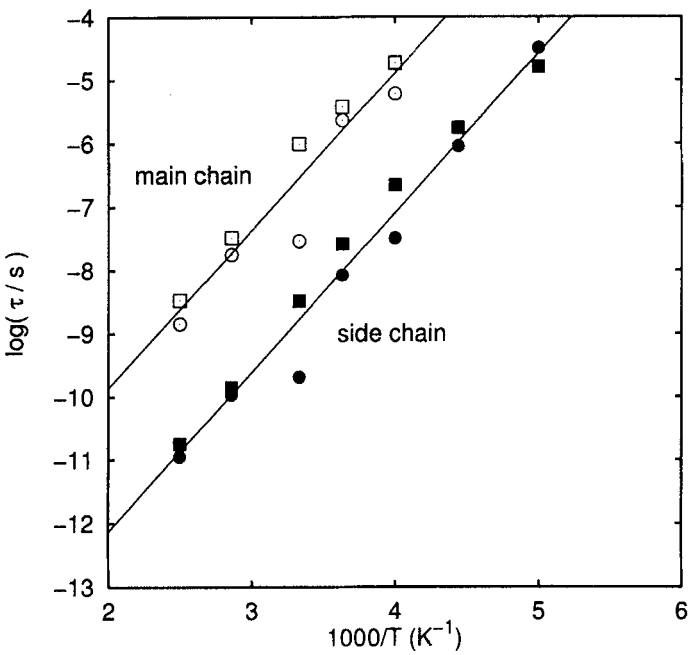


FIGURE 4 Orientational relaxation time of C—C bond vector of main chain (open symbols) and C—O—H out-of-plane vector of side chain (filled symbols) in PVA hydrogels of water content $c_w = 27.5$ wt% (square) and 50.0 wt% (circle).

chains is frozen, side groups can relax at T_g; τ of the vector $\mathbf{d}_{CH-O-H}$ is 10^{-8} s. The motion of side chains is frozen at 200 K, where τ is about 10^{-5} s. Relaxation of the vector $\mathbf{d}_{CH-O-H}$ is slightly slower for the hydrogel of $c_w = 27.5$ wt% than that of 50.0 wt%.

D. Orientational Relaxation of Water

To get insight into the strong-fragile character, we calculate the orientational time correlation function of water. Average values of the fitted β in Eq. (2) are 0.33 and 0.47 in PVA of $c_w = 27.5$ and 50.0 wt%, respectively, and 0.77 for pure water. No marked temperature dependence is observed. The small value of β, 0.33, in $c_w = 27.5$ wt% hydrogel indicates broad distribution of relaxation time, which is also reported for proteins: $\beta = 0.2-0.4$ [15]. Figure 5 shows the reorientational relaxation times τ, which are redetermined by the least-squares fits with fixed values of β obtained above. For pure water, deviation from the Arrhenius behavior is obvious; water is classified into fragile liquid. In PVA aqueous solutions, the temperature

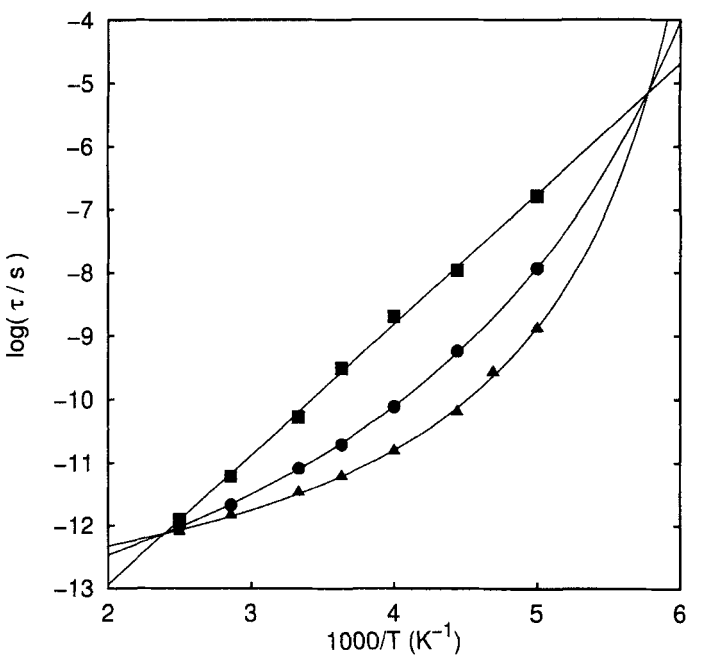


FIGURE 5 Reorientational relaxation time of water in PVA hydrogels of water content $c_w = 27.5$ wt% (square) and 50.0 wt% (circle) and that in pure water (triangle). The data points are fitted to the VTF equation (Eq. 3).

dependence of τ approaches the Arrhenius type with decreasing water content. The data points for the samples of $c_w = 27.5$ wt% can be fitted by the Arrhenius equation. The data for the other samples are well fitted by the modified VTF equation for the relaxation time

$$\tau(T) = \tau_0 \exp\left(\frac{D_s T_0}{T - T_0}\right) \tag{3}$$

Best fitted values of fitting parameters τ_0, D_s and T_0 are listed in Table IV. As is clear from the strength parameter D_s, water surrounded by PVA chains is rather strong at low water content. Slow dynamics of polymer chains affects dynamic properties of water through strong hydrogen bonds between polymer and water. The ideal glass transition temperature T_0, at which relaxation time diverge, coincides with the Kauzmann temperature and should lie below T_g by an amount which depends on the parameter D_s. In our simulation, the value of T_0 for pure water is a little higher than the experimental T_g, 136 K [29]. Because of rapid cooling rate, the T_g of water in our simulation is higher than experiments and lies around 175 K.

Experimental values of dielectric relaxation time of water in poly(2-hydroxyethyl methacrylate) hydrogel were reported in temperature range 195 – 160 K [30]. These values are around the extrapolated line of the present result at $c_w = 27.5$ wt%. The phase transition of water into LDL seems not to occur in hydrogels. This does not contradict with the phase transition reported in Ref. [8], since the character of water is changed from pure water by polymer – water interactions as demonstrated in the present study.

E. Temperature Dependence of Hydrogen-bond Number

Hydrogen bonds are defined by a geometry criterion, in the same manner as our previous study [1, 2]. A pair of water molecules are defined to be hydrogen-bonded if distances and an angle satisfy the following conditions:

$$\begin{aligned} R_{OO} &\leq 3.60\,\text{Å} \\ R_{OH} &\leq 2.45\,\text{Å} \\ \phi &\leq 30^\circ \end{aligned} \tag{4}$$

TABLE IV Fitted parameters of the modified VTF equation (Eq. 3)

c_w (wt%)	D_s	T_0 (K)	$\log(\tau_0/s)$
50.0	9.4	117	−13.7
100	3.8	143	−13.0

where R_{OO} and R_{OH} are distances $O_1 \cdots O_2$ and $O_1 \cdots H_2$, and ϕ is an angle $O_1 \cdots O_2 — H_2$, where the subscripts 1 and 2 show indices of water molecules. This is the same definition as Luzar and Chandler [25]. The cutoff distances, R_{OO} and R_{OH}, are taken to be the distance of the first minimum in the corresponding radial distribution functions, $g(r)$, in pure water. The hydrophilic groups of the polymers also form hydrogen bonds to water. The hydrogen bonds are defined also for —OH of PVA in the same manner.

Figure 6 shows the average hydrogen-bond number, $\langle n_{HB} \rangle$, of a water molecule in each region classified above. In the bulk region, $\langle n_{HB} \rangle$ values of a water molecule are equal to those in pure water irrespective of water contents. At low temperature, the values approach to 4: $\langle n_{HB} \rangle$ value in ice structure. In the region out of the first hydration shell, the hydrogen-bond numbers are not changed by polymers. Figure 6(a) shows $\langle n_{HB} \rangle$ in *I*-structure. In the hydrophobic region, $\langle n_{HB} \rangle$ is smaller than that in pure water. In the hydrophilic region, dependence on temperature is different from that in bulk and hydrophobic regions. At high temperature, $\langle n_{HB} \rangle$ is not so different from that in the bulk region. At low temperature, the dependence on temperature approaches to that in the hydrophobic region. The values of $\langle n_{HB} \rangle$ depend on c_w at low temperature: those are smaller for the sample of lower water content. In *Q*-structure, the values of $\langle n_{HB} \rangle$ are different from those in *I*-structure above 200 K.

Figure 7 shows $\langle n_{HB} \rangle$ of an —OH group of PVA. The values are around 2 and temperature dependence is smaller than that of water molecules as shown in Figure 6. Dependence on c_w is small for total hydrogen-bond number, which includes both polymer–polymer and polymer–water hydrogen bonds. The ratio of polymer–polymer/polymer–water hydrogen bonds varies with c_w: fraction of polymer–polymer hydrogen bonds is large for the samples of smaller water content.

F. Perfectness of Hydrogen Bond

Fraction of water molecules which have four hydrogen bonds, $p(4)$, is shown in Figure 8 for each region defined above. With decreasing temperature, the network structure of hydrogen bonds of water tends to be more enhanced; defects of tetrahedral network structure decrease. Since a water molecule forms four hydrogen bonds in ice, $p(4)$ could be a measure of perfectness of hydrogen bonds. In pure water, $p(4)$ reaches to a limiting value 0.97 at low temperature. Around 210 K, water is supposed to undergo a phase transition from HDL to LDL, the latter of which includes only a few defects of tetrahedral network structure, as shown by Tanaka [9]. In PVA

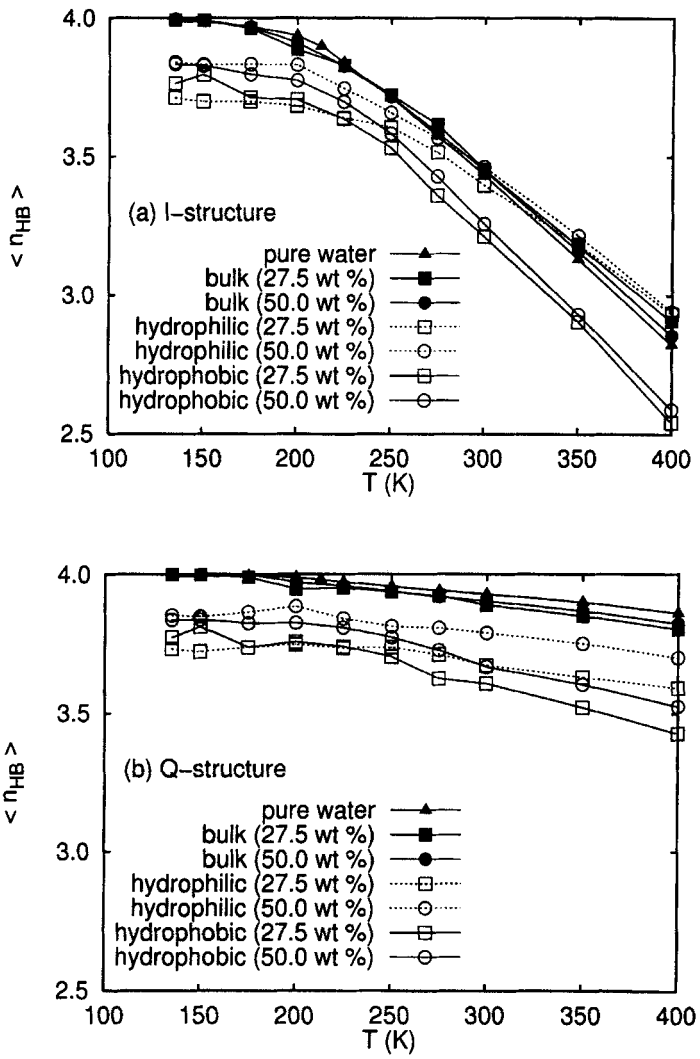


FIGURE 6 Average hydrogen-bond number $\langle n_{HB} \rangle$ of a water molecule (a) in *I*-structure and (b) in *Q*-structure of PVA hydrogel and pure water. Both water–water and water–polymer hydrogen bonds are included.

hydrogel, the values of $p(4)$ in hydrophilic region strongly depend on water contents at low temperature. For hydrogel of $c_w = 27.5$ wt%, freezing of main chain motion directly affects the network structure of water. For

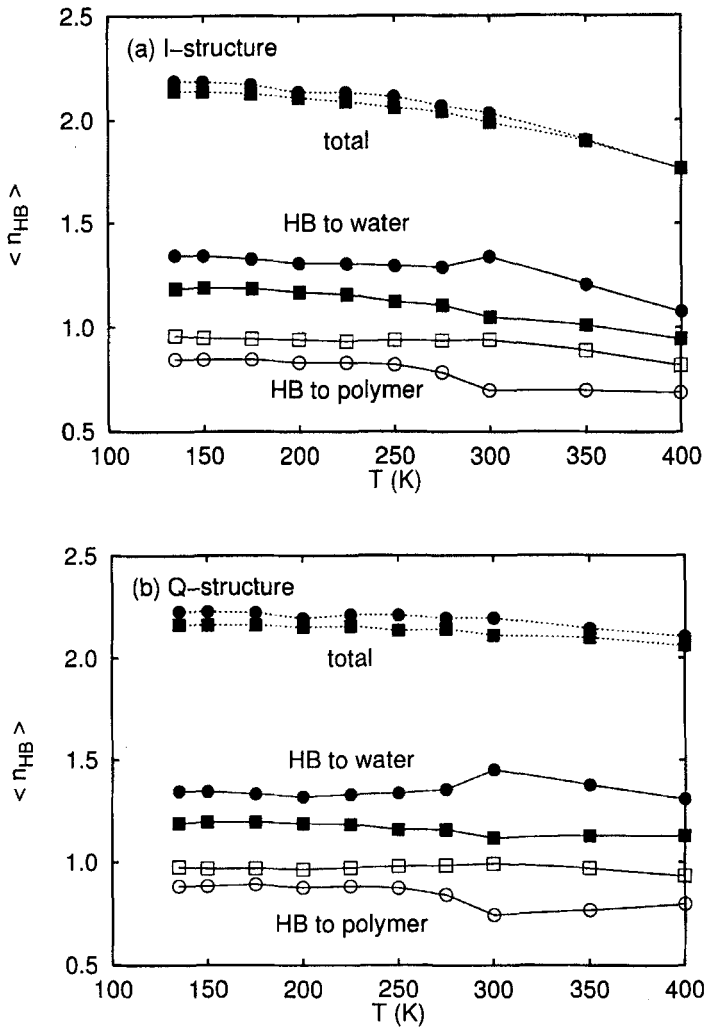


FIGURE 7 Average hydrogen-bond number $\langle n_{HB} \rangle$ of an —OH group of PVA (a) in *I*-structure and (b) in *Q*-structure of PVA hydrogels of water content c_w = 27.5 wt% (square) and 50.0 wt% (circle).

hydrogel of c_w = 50.0 wt%, water molecules can relax gradually to more stable configurations even below T_g and $p(4)$ reaches to an asymptotic value 0.80 below 195 K. In *I*-structure, the values of $p(4)$ are apparently independent of c_w above T_g, in spite of the strong dependence on c_w in *Q*-structure. The greater $p(4)$ at high water content in *Q*-structure is canceled

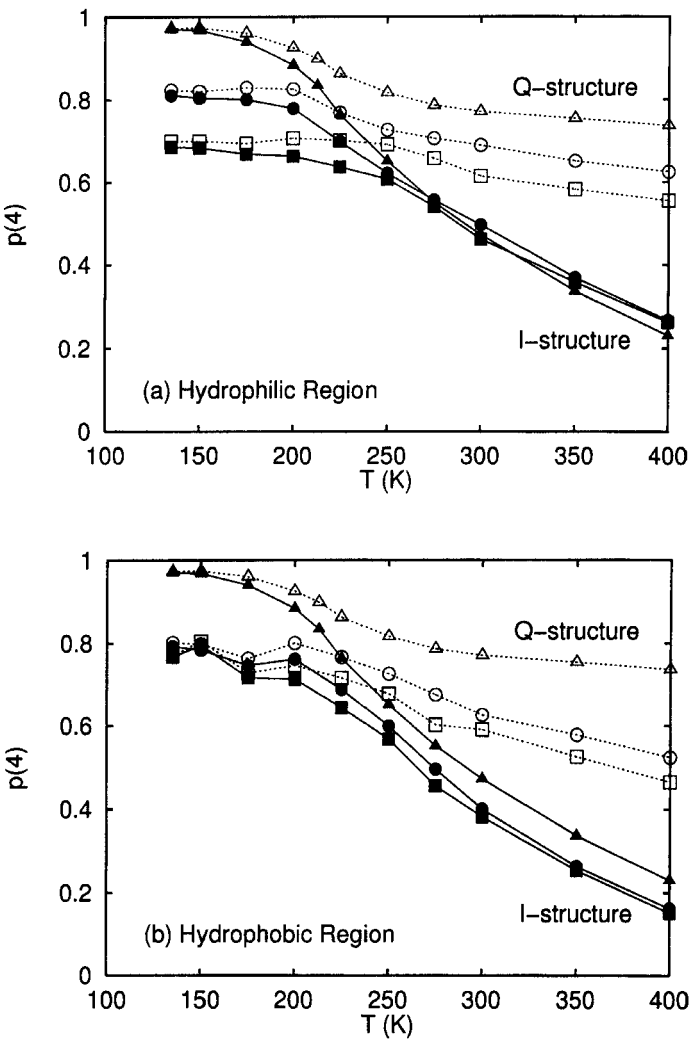


FIGURE 8 Fractions of water molecules which have four hydrogen bonds in *I*-structures (filled symbols) and that in *Q*-structures (open symbols) of PVA hydrogels of water content c_w = 27.5 wt% (square) and 50.0 wt % (circle). Data for pure water is also plotted in the figures (triangle): (a) hydrophilic, (b) hydrophobic, (c) bulk and (d) all region.

by larger amplitude thermal motions, which arise from the anharmonic vibrations. In the system of low water content, the number of configurations to form local tetrahedral structure is small, though $p(4)$ values in *I*-structures are the same as in pure water.

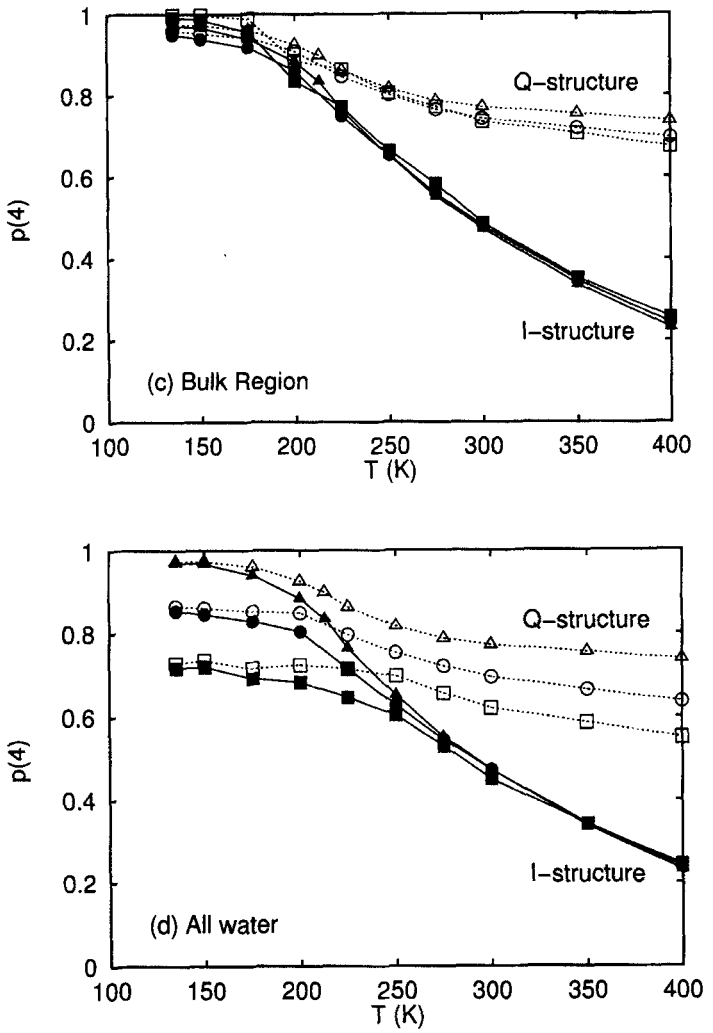


FIGURE 8 (Continued).

Figure 9 show $p(2)$, fraction of —OH groups which have two hydrogen bonds, of PVA. Approximately 80% of —OH groups have two hydrogen-bonds. The temperature dependence of $p(2)$ is very small below T_g.

For the system of $c_w = 27.5\,wt\%$, 94% of water molecules reside in the first hydration shell (either hydrophilic or hydrophobic regions classified above). Therefore, freezing of the main chain motion necessarily suppresses the relaxation of water molecules into more stable (low energy) configura-

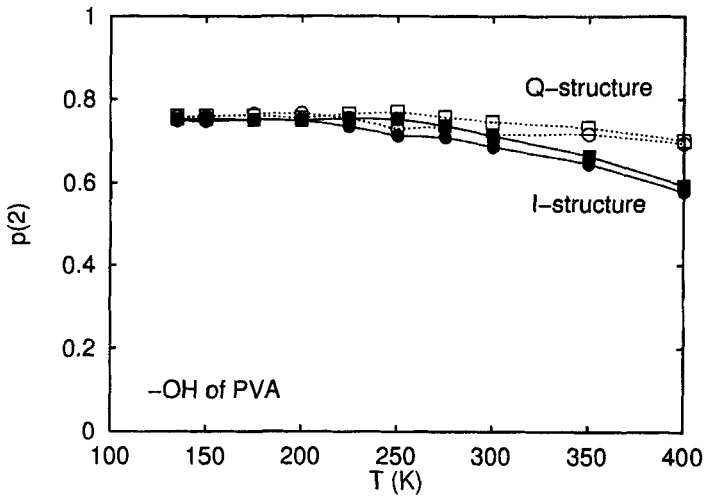


FIGURE 9 Fractions of —OH groups which have two hydrogen bonds in *I*-structures (filled symbols) and that in *Q*-structures (open symbols) of PVA hydrogels of water content c_w = 27.5 wt% (square) and 50.0 wt% (circle).

tion. On the other hand, for the system of c_w = 50.0 wt%, fraction of water molecules which reside in the first hydration shell is 65%; the size of *water ball* becomes large. Water molecules can relax more stable configuration in this sample even below T_g, where the motion of the main chains is frozen. Since freezing of the side chains causes the suppression of motion of water molecules which form strong hydrogen bonds to the side chains, water in the first hydration shell cannot form more stable defect-free hydrogen-bond networks below the freezing temperature of the side chains. It is conceivable that structure and dynamics of water in hydrogels are characterized by two dynamical modes (the motion of main chain and side chains of polymers), whose time scales are a few order of magnitude different from motion of water molecules.

IV. CONCLUSION

MD simulations of rather long time runs are performed for pure water and PVA hydrogels over a wide temperature range including the glass transition temperature. Structure and dynamics of supercooled water in PVA hydrogel are investigated and related to the mobility of polymer chains and network

structures of hydrogen bond. It is found that polymer chains affect significantly the dynamic properties and the fragile-strong character of water. Structure and dynamics of water in PVA hydrogels are characterized by two dynamical modes (the motion of main chain and that of side chains), whose time scales are different from motion of water. The dynamical properties of polymer chains restrict structure and dynamics of water molecules in hydrogels through strong hydrogen bonds between water and polymers, as suggested by the analysis of perfectness of hydrogen bonds. This may alter not only the dynamic properties but thermodynamic properties.

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