Different States of Water in Hydrogels?

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Polymers swollen to a high degree by water play a central role in many areas of science and technology, from cell biology over food components to technical separation membranes and personal hygiene products. The role of the water molecules in these systems has been under investigation for many years.[1] At a qualitative level, many aspects of the thermal and the dynamical behavior of water seem to be fairly independent of the other component, which may be a biopolymer or a synthetic polymer, a chemically or physically linked network, or a polyelectrolyte or a neutral species. One of the questions discussed most controversially is the existence or nonexistence of "different states" or "different types" of water in homogeneous mixtures of water and amorphous polymer, i.e., after effects arising from the presence of different phases (crystalline vs amorphous, different composition) have been accounted for. This notion implies that water molecules fall into different classes with qualitatively different thermodynamical or dynamical properties. A frequently used model is that water molecules close to the hydrophilic polymer chains are in some way "bound" to the polymer and, therefore, behave differently from "free" water molecules.

Different behavior of water fractions in a hydrogel is most evident in differential thermal analysis and differential scanning calorimetry (DSC). Upon slow heating of a frozen hydrogel (water content of about 30% and above) one often observes two endothermic peaks, a sharp one corresponding to the melting of ice ($\sim$273 K) and a broader one at 10−40 K below. They are usually associated with freezable free water and freezable bound water.[2,3] Note, however, that a different explanation has also been given for the case of poly(hydroxyethyl methacrylate) (pHEMA) hydrogels: The apparent two endothermic peaks are really only one peak which is interrupted by an exothermic peak caused by amorphous ice undergoing crystallization just below the melting transition.[4,5] A third state of water, so-called "nonfreezing water", is postulated to explain the fraction of water which is unaccounted for in DSC measurements, for instance because it is hidden in a broad continuum. There is no corroboration of the formation of different states of water at low temperatures from structural experimental methods: Raman measurements allow an estimate of defects in water−water hydrogen bonding in hydrogels as compared to liquid water or ice. They show no qualitative difference between pure water and hydrogels when one goes through the temperatures at which the DSC peaks occur.[6] In contrast, Raman spectroscopy is very sensitive to other phase transitions such as the coil-to-globule transition in poly[*N*-(3-ethoxypropyl)acrylamide] hydrogels.[7]

Nuclear magnetic resonance (NMR) relaxation measurements point to a concentration effect on the existence of different states of water. Small amounts of water (up to 2%) display different relaxation behavior:[8] solid-state NMR measurements show that, between 190 and 370 K, there is a constant fraction of water that shows anisotropic reorientation (only rotation *around* the dipole vector, henceforth denoted as perpendicular rotation, subscript $\perp$). The remaining water shows a gradual transition from an amorphous solid with no reorientation to a liquid with isotropic reorientation, i.e., including reorientation *of* the dipole vector (henceforth denoted as parallel rotation, subscript $\parallel$). On the other hand, from ^{17}O relaxation measurements in pHEMA hydrogels with water contents of 20−80% it has been concluded that there either all water molecules reorient on the same time scale or that the exchange between fast and slow reorienting molecules is faster than 1 ms.[9]

The concept of different states of water has also been used to phenomenologically model the temperature or concentration dependence of other properties of hydrogels. The concentration dependence of the water permeability through poly(viny alcohol) (PVA) has been explained by two different diffusion coefficients for bound and free water.[10] Other phenomenological models, however, explain this at least equally well,[11] so that it cannot be taken as additional evidence for different states of water. Up to a water content of 30%, PVA hydrogels show a strong concentration dependence of both the glass transition temperature and the free volume measured by positron annihilation above which both quantities reach a plateau.[12] Identifying the first 30% of water as nonfreezable water was again taken as evidence for the existence of two states of water.

Previous molecular dynamics simulations by us have indicated that, at the level of atomistic dynamics, there is little if any difference between solvent molecules in bulk solvent and close to a polymer solute. The rate at which they exchange members of their first solvation shell is almost equal. This applies to apolar mixtures (benzene and polystyrene)[13] as well as to polar solutions (PVA in water).[14,15] In the present contribution, we use molecular dynamics to answer the questions: (i) Do different water molecules in a hydrogel show qualitatively different dynamical behavior? (ii) How can the different dynamics, if present, be related to the environment of the individual water molecule? (iii) To what extent does the picture of different states of water depend on temperature? To this end, we have performed molecular dynamics simulations of a PVA-based hydrogel consisting of a single PVA chain (400 monomers) and a water volume fraction of 40% at 250, 300, and 375 K and ambient pressure. It has been demonstrated that the motion of small molecules in a polymer is governed by very localized dynamics.[16] Therefore, it is not expected to be different in systems larger than the one simulated here. To study concentration effects, we include a system with 8% water at 375 K which is, however, no longer a hydrogel in the technical sense. All simulations were performed under periodic boundary conditions. The force field[14] and simulation details[11] have been described previously. The simulation at 250 K that has not been reported before was run for 2.4 ns under conditions identical to those used at the other temperatures.

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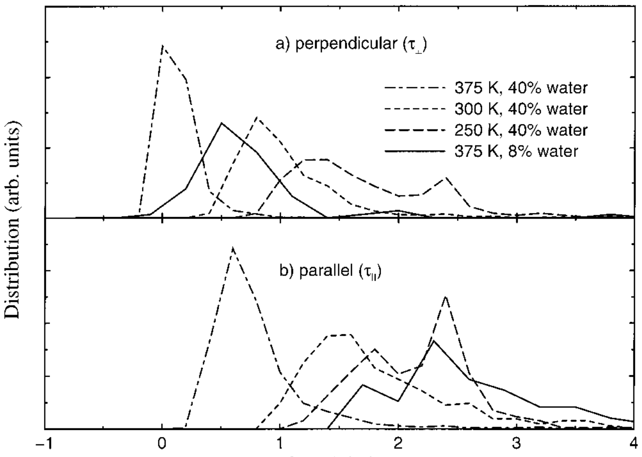

Figure 1. Distribution of correlation times for the reorientation of water molecules: (a) reorientation of the plane normal (perpendicular); (b) reorientation of the dipole vector (parallel). The third reorientational mode of water (reorientation of a unit vector through the H atoms) is very similar to the perpendicular reorientation and is not shown. All distributions are normalized to integrate to 1.

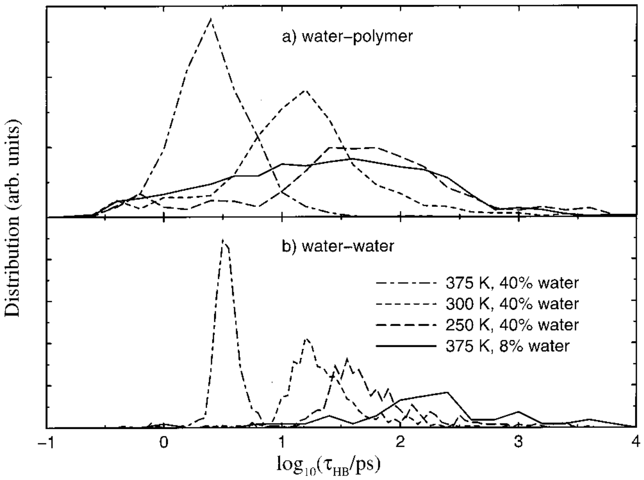

Figure 2. Distribution of average hydrogen bond correlation times of water molecules. For every water molecule, the correlation functions of all hydrogen bonds it is involved in are averaged. It is then integrated to give the average hydrogen bond correlation time of the molecule. Key: (a) hydrogen bonds between water and OH groups of poly(vinyl alcohol); (b) hydrogen bonds between water molecules. All distributions are normalized to integrate to 1.

Since it is to be determined if and how individual molecules differ in their dynamics, local dynamical properties are needed. This rules out the diffusion coefficient. We chose the reorientational correlation times $\tau_{\|}$ and $\tau_{\perp}$ as a measure of single-molecule rotation, and the hydrogen bond correlation time as a measure of how quickly a molecule changes its local environment. The reorientational correlation times are calculated by first defining molecule-fixed unit vectors **u** (the dipole vector for $\tau_{\|}$, the plane normal for $\tau_{\perp}$) and obtaining their time correlation function $\langle \mathbf{u}(t)\mathbf{u}(0)\rangle$. The integral of the correlation function from zero to infinity gives the correlation time. It is calculated by first fitting $\langle \mathbf{u}(t)\mathbf{u}(0)\rangle$ with a stretched exponential function $\exp[-(t/\alpha)^{\beta}]$ whose time integral is analytic.[17] For the correlation time τ_{HB} of an individual hydrogen bond, the integral over the correlation function $\langle h(t)h(0)\rangle$ is evaluated in the same way. The state function $h(t)$ takes the value 1, if a hydrogen bond according to geometric criteria (distance between oxygens less than 0.3 nm, O−H−O angle larger than 130°) is present, and 0 otherwise. The correlation time thus defined allows for re-formation of the hydrogen bond after breaking. In the analysis, we use average hydrogen-bond correlation times which are obtained by taking the integral over the average of the correlation functions of all hydrogen bonds a particular molecule is involved in during the simulation.

The orientational correlation times show an anisotropy (Figure 1). The parallel reorientation is slower than the perpendicular. For both modes, we find that the distribution shifts to longer times as the temperature is lowered at constant composition. At 375 and 300 K, both distributions are unimodal; their shape can be described as lognormal plus a long-time tail. At 250 K, however, both modes display bimodal distributions. The perpendicular mode has maxima around 20 and 250 ps, and the parallel mode has maxima around 65 and 250 ps. The perpendicular mode, however, has more density at the faster reorientation, whereas the parallel mode has a significantly larger intensity at the slower reorientation. The behavior of water at much lower concentrations (8%) is worth mentioning, too. While lowering the water content leads to the same trend as lowering the temperature, namely to slow down water reorientation, the two modes are affected in a qualitatively different way. The perpendicular mode is merely slowed, and this effect is not even as big as that of lowering the temperature from 375 to 300 K. In contrast, the parallel mode is not only slowed down as much as by cooling to 250 K, but also the bimodal distribution appears. The fact that reorientational anisotropies of solvent molecules in polymers are more affected by concentration than by temperature has been alluded to previously,[13,17] and it is also in keeping with the aforementioned NMR measurements.[8,9]

The hydrogen-bond correlation times are unimodal throughout (Figure 2). Decreasing the temperature leads to longer correlation times. Water−polymer and water−water hydrogen bond distributions at corresponding temperatures have roughly the same center. However the water−water ones tend to be sharper. Decreasing the water content increases the correlation times of both types of hydrogen bond significantly, the effect being larger than for the reorientation. The apparent bimodality of the water−water hydrogen bond distribution at 8% water content, however, is probably not physical but a statistical artifact of the small number of water molecules and, hence, water−water contacts.

To determine the connection between the environment of a water molecule and its dynamics, we have calculated numerous cross-correlation coefficients between the logarithms of the respective correlation times (perpendicular and parallel reorientation, water−water and water−polymer hydrogen bonds) and the average number of hydrogen bonds, separately for water−water, water−polymer, and all hydrogen bonds. As a more robust estimator, we have also evaluated the corresponding rank correlation coefficients. These results indicate that there is no correlation between the number and type of hydrogen bonds a water molecule has and the hydrogen bond dynamics, the corresponding correlation coefficients r typically being between −0.1 and +0.1. In marked contrast, both reorientational modes are significantly influenced by the local environment of water molecules. There is a positive correlation ($r = 0.35-0.69$) between the reorientational correlation times and the number of hydrogen bonds to polymer: molecules close to the polymer reorient more slowly. On the other hand, there is a negative correlation of similar magnitude ($r = -0.67$ to -0.41) between these times and the number of hydrogen bonds with other water molecules: water molecules in contact with other water reorient more rapidly. Both correlations are statistically significant. As a consequence, there is almost no correlation between reorientation time and the total number of hydrogen bonds of a water molecule, since the effects from both types of hydrogen bonds cancel.

With the caveat that these results were obtained for one specific hydrogel (PVA based) at time scales of a few nanosecond, we conclude the following points: (i) Whether water in hydrogels is found in different dynamical states or whether there is just a single albeit broad distribution of characteristic times depends on the dynamical process used as a probe and, hence, on the experimental method that uses this process. (ii) We have found evidence for two states of water only at the lowest temperature which is below the freezing point of bulk water. Therefore, while it is perfectly acceptable to speak of different fractions of water undergoing phase transitions at different temperatures during a DSC experiment, the concept of different states of water must not be carried over to hydrogels above 273 K. In the present simulations we cannot identify a possible third state of water. (iii) In the only case where there is evidence for a connection between the local environment of water molecules and their mobility, namely reorientation, the water molecules are more mobile if they are surrounded by other water than if they are in contact with polymer. This is also true at 250 K, i.e., below the freezing transition of pure water. In other words, there is not sign that the “free” water freezes while the “bound” water stays mobile, as is widely believed, but rather the opposite. The model assumption can only be made compatible with the present simulations if one allows for microscopic inhomogeneities (presence of different phases) on length scale larger than considered here (~3.5 nm) in the system during the formation of ice crystallites.

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