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Effect of Xenon upon the Dynamical Anomalies of Supercooled Water. A Test of Scaling-Law Behavior[†]

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We have studied the molecular reorientation and self-diffusion of water molecules in aqueous solutions of xenon in the approximate temperature range from 273 to 333 K using ²D and ¹H magnetic relaxation and spin-echo techniques. In addition, we report on ¹³¹Xe relaxation rates in this temperature interval. These data, in conjunction with data obtained recently by us for the self-diffusion of xenon, are evaluated in terms of scaling laws which are known to account for the peculiar behavior of transport and relaxation coefficients of pure water in the supercooled regime. In pure water these anomalies are strong enough to suggest a thermodynamic singularity at $T_S = 228$ K. The results for ²D relaxation suggest that xenon shifts this singularity toward higher temperatures. An extrapolation toward the composition of the Xe × 23H₂O clathrate yields $T_S \cong 260$ K. Essentially the same figure is obtained from ¹³¹Xe relaxation, which reflects the local dynamics of water molecules near xenon and may therefore serve as a measure of T_S in clathrate-like domains. This shift of T_S by added xenon confirms expectations that nonpolar solutes stabilize just those structures of water which are responsible for the anomalies observed in the supercooled regime. In this sense, xenon is acting like a negative hydrostatic pressure. It is however difficult to rationalize the data by a universal exponent, as is required by true scaling law behavior. As a further new feature we report on a decoupling of rotational and translational motions of water near T_S , which becomes apparent by largely different values for T_S deduced from relaxation and self-diffusion data. While reorientational motions reflect the slowing down of molecular motions associated with the approach to T_S , diffusion remains comparatively fast at the same temperature. This decoupling shows a striking resemblance with similar processes observed for other liquids near glass transitions.

1. Introduction

This study aims at contributing to an understanding of the fascinating array of unusual properties displayed by liquid water. These peculiarities are most pronounced in the supercooled regime, where many properties appear to head for a singularity near $T_S = 228$ K.¹ An understanding of this singularity is of central importance for a comprehensive molecular theory of water.^{1,2} Here, we study the nature of this singularity by asking for its fate when dissolving an inert test particle. The behavior of water toward nonpolar solutes has long been recognized as unusual and is rationalized by the concepts of “hydrophobic hydration” and “hydrophobic bonding”.³ Noble gases like xenon are the simplest solutes for monitoring these phenomena. We will use here nuclear magnetic relaxation and spin-echo techniques for probing the structure and dynamics of water near xenon.^{4–6}

The existence of a singularity in supercooled water is suggested by several observations: First, below the equilibrium freezing temperature certain thermodynamic response functions like the isothermal compressibility, κ_T , thermal expansion coefficient, α , and isobaric heat capacity, C_p , show peculiarities not found with other liquids. Rather than decreasing with decreasing temperature, these coefficients show an increase. After correction for a nonsingular background contribution, their behavior is described by a power law of the form¹

$$X = X_0(T/T_S - 1)^{-\gamma} \quad (1)$$

with a singular temperature T_S of about 228 K (X stands for κ_T , α , or C_p).

Second, the viscosity¹ and other dynamical quantities like the reorientational correlation time⁷ and self-diffusion coefficient⁸ of water molecules change rapidly in the supercooled regime. While the transport coefficients of many liquids that undergo a glass transition appear to diverge at the ideal glass transition temperature T_0 ,⁹ in water the divergence is so rapid that expressions usually employed for describing the approach toward T_0 cannot explain the observed behavior. Again, it is necessary to introduce a power law of the form of eq 1 with the same singular temperature as that found for the thermodynamic functions.^{1,7,8}

Third, when bypassing the singularity by techniques like vapor deposition, liquid-state hyperquenching, or pressure-induced amorphization, one arrives at a vitreous state. However, the properties of this vitreous phase are so different from what is observed above 228 K that some transition must have occurred during the quenching process.¹¹

The strong implication is that some kind of phase transition must be at work near 228 K. According to a conjecture by Speedy,¹² this transition may correspond to a line of stability limits which defines the end of the liquid phase in the temperature–pressure plane. A more recent hypothesis suggests the existence of a line of liquid–liquid phase transitions in the supercooled region of the phase diagram which ends in a critical point.¹³ Possibly both proposals may be different realizations of a single behavior.¹⁴

On the molecular level, this behavior can be rationalized by the following scenario:² Due to their ability to participate in four hydrogen bonds, water molecules form an approximately four-coordinated random network structure with preference for tetrahedral geometry, but containing a large proportion of strained and broken bonds. At low temperatures, more bulky, less-strained configurations are stabilized, resembling structures in the low-pressure polymorphs of ice and of clathrates. The

[†] This paper is dedicated to Prof. Harold Friedman, who has inspired much of our work over the years.

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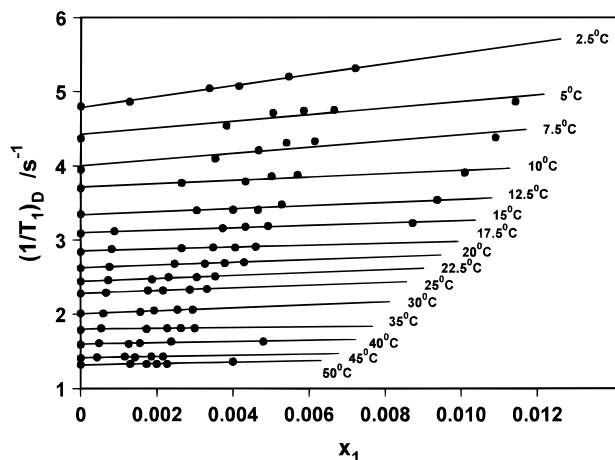


Figure 1. Isotherms of ^2D relaxation rates $(1/T_1)_\text{D}$ of water (D_2O) as a function of the mole fraction x_1 of added xenon. The temperatures are shown in the figure.

anomalies in the supercooled regime reflect the formation and growth of such domains, which then compete with the relatively strained structures.

Adopting this picture, a logical connection should exist between the water structure near hydrophobic solutes like xenon and the structures generating the anomalies of supercooled water.² Xenon forms a solid clathrate, the major residues of which are known to be retained in solution.¹⁵ Dissolution of xenon should therefore favor just those patterns of the water structure which become important in supercooled water. Thus, one may expect that xenon reinforces the anomalous properties of water and shifts this regime toward higher temperatures.^{2,16}

Here, we present a comprehensive study of molecular motions in the xenon + water system. In the first place, we consider the effect of xenon on the reorientational and translational motions of water molecules, as studied by ^2D magnetic relaxation and ^1H spin-echo self-diffusion measurements. In the second place, we report on ^{131}Xe relaxation in water. Quadrupolar relaxation of ^{131}Xe forms a very short-range probe for the structure and dynamics of solvent molecules in the immediate vicinity of the solute.^{6,17,18} Finally, we reconsider our recently published data for the self-diffusion coefficient of xenon in water in light of the new results.⁵ The measurements were expected to shed light on the following questions:

- (1) Is the translational and reorientational dynamics in aqueous solutions of xenon consistent with the general picture of the water anomalies and more specifically, with the predicted rise of T_S by hydrophobic solutes?
- (2) Does the approach toward T_S affect the various modes of motion to the same degree?
- (3) Is there evidence for universal behavior of molecular dynamics near T_S , as exemplified by a universal value of the exponent γ ?

2. Experimental Section

Sample Preparation. Samples were prepared by condensing a known volume of gaseous xenon into a given amount of water (H_2O or D_2O). Since pressures were generally less than 10 MPa, glass tubes of 0.9-mm external and 0.6-mm internal diameter could be employed. When sealing the sample, the pressure and temperature were recorded. Xenon concentrations at the temperatures of interest were then calculated from these volumetric data by use of known gas solubilities.¹⁹ In addition, xenon concentrations were determined by integration of the ^{131}Xe NMR signals. The results derived from both methods agreed satisfactorily.

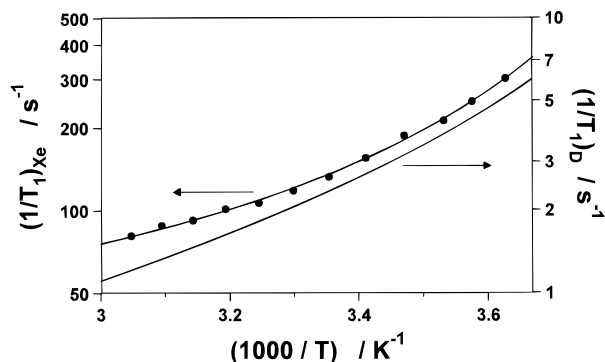


Figure 2. ^{131}Xe relaxation rate (left hand scale) as a function of the inverse temperature. Within experimental resolution ^{131}Xe relaxation does not depend on the xenon concentration. For comparison the ^2D relaxation rate $(1/T_1)_\text{D}$ at a mole fraction $x_1 = 0.004$ is shown as a solid line (right hand scale).

The upper limit of the xenon concentration is given by the precipitation of the solid clathrate, $\text{Xe} \times 23\text{H}_2\text{O}$, which at equilibrium and at atmospheric pressure melts at 289 K. The melting point rises with rising pressure; at 298 K, the melting pressure is about 2.3 MPa. By trial and error, we could prepare samples which even near 273 K remained liquid up to 9 MPa. Hence, many data points reported below refer to metastable liquid samples. We did not succeed in supercooling such samples below 273 K.

Measurements. ^2D and ^{131}Xe spin–lattice relaxation times were measured with a Bruker pulsed NMR spectrometer at resonance frequencies of 46.1 and 24.6 MHz, respectively. Self-diffusion coefficients of water were measured by ^1H pulsed field gradient spin-echo experiments, as described elsewhere,²⁰ and refer to calibration against pure water with $D_w = 2.30 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at 298.15 K. Sample temperatures were controlled to 0.2 K by liquid thermostating of the probe. We estimate the reported data to be accurate to within $\pm 1\%$.

3. Experimental Results and Data Evaluation

^2D Relaxation. We have measured the effect of xenon upon the ^2D spin–lattice relaxation rate, $(1/T_1)_\text{D}$, of D_2O between about 273 and 333 K. Figure 1 displays the experimental results for isotherms of $(1/T_1)_\text{D}$ vs the mole fraction, x_1 , of xenon.²¹ Addition of xenon leads to a perceptible enhancement of ^2D relaxation. At high temperatures this effect is scarcely seen in a large-scale plot such as Figure 1 but evolves from the more detailed data analysis. Near 273 K the increase of $(1/T_1)_\text{D}$ with rising xenon concentration is more clearly visible and amounts to 15% at the highest concentrations. As one has to apply hydrostatic pressure for varying the xenon concentration, it is interesting to note that in the range of interest here the effect of pressure upon $(1/T_1)_\text{D}$ in pure D_2O is very small and opposite to what is observed here.^{7,22} In order to characterize the temperature dependence of $(1/T_1)_\text{D}$, we have read off from the curves in Figure 1 smoothed values at rounded concentrations. Figure 2 shows an example for the resulting Arrhenius-type $\log(1/T_1)_\text{D}$ vs $1/T$ plots.

Angell¹ has noted that ^2D magnetic relaxation time measurements provide some of the best evidence for the putative singularity in supercooled water. ^2D relaxation reflects the rotational correlation time τ_2 for the O–D axis of the water molecule. Standard relaxation theory yields²³

$$\left(\frac{1}{T_1}\right)_\text{D} = \frac{3}{2}\pi^2\chi_\text{D}^2\tau_2 \quad (2)$$

where χ_D is the nuclear quadrupole coupling constant. The

available evidence^{7,24} suggests that in the range of interest the temperature dependence of χ_D is negligible, if compared with the diverging behavior of τ_2 . Following Lang and Lüdemann,⁷ we therefore presume the relaxation rates can be directly fitted to eq 1. The resulting fit parameters are shown in Table 1.²⁵ Equation 1 represents the data within their experimental accuracy.

Before considering our results for the other transport coefficients, it is convenient to discuss some alternative scenarios for data evaluation. Our first remark concerns the contribution of the nonsingular background contribution to $(1/T_1)_D$. Equation 1 implies a temperature-independent background. There are however other options, in which a temperature-dependent background term, e.g., of Arrhenius-type, $X_0 = A \exp(E/RT)$, is assumed.^{1,16} We have examined various scenarios of this type,¹ resulting in the following observations: (1) In general, we did not achieve significant reductions of the standard deviations of the fits, but severe problems occurred when there was an increase in the number of parameters in the fit, which then became highly correlated. (2) The figures for T_S were little affected by the choice of the background and never changed by more than 4 K from those in Table 1. (3) The exponent γ proved to be more sensitive than T_S to the form of the background term.

The latter observation is of relevance, as in true scaling law behavior encountered near critical points the exponents are universal. We have therefore examined whether the concentration dependence of γ in Table 1 can be removed by choosing an appropriate form of the noncritical background. Again, we consider for illustration an Arrhenius-type background, $X_0 = A \exp(E/RT)$. To get physically significant positive values of the activation energy E , the true universal exponent γ must lie below the lowest value in Table 1. This can be easily fulfilled, e.g., by choosing $\gamma = 1$, but the cost is paid by obtaining a strong concentration dependence of E which *decreases* with increasing xenon concentration. With consideration of the presumed strengthening of hydrogen bonds by added xenon, such a behavior seems unlikely. Several other possibilities have been examined without obtaining convincing evidence for the existence of a universal exponent. As, anyway, the use of such modified equations is highly speculative, we do not follow up this path for the remainder of this paper.

Our second remark concerns the description of our data by the so-called “Vogel–Fulcher–Tamman (VFT)” equation

$$X = A \exp\left(\frac{B}{T - T_0}\right) \quad (3)$$

which for many liquids successfully describes the divergent behavior of transport coefficients at a glass transition.⁹ The “ideal glass temperature” T_0 is expected to lie below the caloric glass transition temperature T_g , which is operationally defined by experiments at a well-defined finite cooling rate.⁹ If dynamical data for pure water are evaluated in terms of this equation, one finds T_0 to be of the order of 170 K. All available evidence indicates, however, the existence of a caloric glass transition at 135 K.¹ Hence, if transport coefficient data are evaluated in terms of eq 3, a faster divergence is obtained than that predicted with T_0 values corroborated from any other experimental results. Hence, this approach seems not to be physically acceptable.^{1,7,8}

The same result was obtained when data for solutions containing xenon were fitted to eq 3. At a first glance, the standard deviations were comparable to those of eq 1. Thus, the quality of the fits did not permit a decision in favor of one of the two descriptions. However, as in the case of pure water,

TABLE 1: Best Fit Parameters for the Description of Transport and Relaxation Coefficients in Aqueous Solutions of Xenon to the Scaling Law $X = X_0(T/T_S - 1)^{-\gamma}$ ^a

X	solvent	$10^3 \chi_1$	X_0	T_S	γ
$(1/T_1)_D$	D ₂ O	0	0.237	227.0	1.92
		2	0.239	236.1	1.70
		4	0.243	242.0	1.53
		6	0.251	246.2	1.44
		8	0.266	252.0	1.33
$(1/T_1)_{Xe}$	H ₂ O	0–8	21.98	257.5	0.99
$1/D_w$	H ₂ O	0	0.0616×10^9	216.0	2.02
		1	0.0639×10^9	213.1	2.10
		2	0.0658×10^9	210.9	2.14
		3	0.0693×10^9	207.0	2.27
		4	0.0707×10^9	206.0	2.30
$1/D_{Xe}$	D ₂ O	0–8	0.1704×10^9	200 (fixed)	1.59

^a For $(1/T_1)_D$ and $(1/T_1)_{Xe}$ the prefactor X_0 of the scaling law is given in units of s^{-1} , for $1/D_w$ and $1/D_{Xe}$ in $s^2 m^{-1}$, and for T_S in K.

the T_0 values were found to be far above any values for glass transition temperatures in aqueous solutions of hydrophobic solutes.¹ Again, VFT behavior seems not to be physically acceptable.

¹³¹Xe Relaxation. Within experimental resolution, ¹³¹Xe relaxation rates, $(1/T_1)_{Xe}$, were found to be independent from xenon concentration up to the highest concentrations achieved in our experiments. Figure 2 shows the temperature dependence of this concentration-independent relaxation rate (in H₂O). ¹³¹Xe ($I = 3/2$) relaxes by intermolecular interaction of the nuclear electric quadrupole moment with electric field gradients produced by the electric dipoles of the surrounding water molecules.^{6,17,18} The mean-square electric field gradient entering into the expression for the relaxation rate $(1/T_1)_{Xe}$ depends on $1/r^5$, where r is the distance between the xenon nucleus and the point dipole of the water molecule. Hence, ¹³¹Xe relaxation represents a very short-range probe for local motions of water molecules. Denoting the correlation time by τ_{QF} , we have

$$\left(\frac{1}{T_1}\right)_{Xe} = \frac{2}{5} \pi^2 \chi_{Xe}^2 \tau_{QF} \quad (4)$$

The quadrupole coupling constant χ_{Xe} is not known exactly. It can be estimated from a simple electrostatic model or from computer simulations of the water structure near xenon.^{17,18} We argue here again that its variation with temperature is insignificant, if compared with the divergent behavior of the correlation time. Then, a fit of $(1/T_1)_{Xe}$ to the scaling law directly yields T_S for the dynamical process under consideration. The corresponding fit parameters are also given in Table 1.

Self-Diffusion of Water. In contrast to the relaxation rates, the self-diffusion coefficients directly reflect the relevant dynamical processes. Figure 3 gives an overview over self-diffusion data for water (H₂O) as a function of the xenon concentration from about 273 to 333 K.²¹ D_w shows a weak decrease with rising xenon concentration, which above 298 K corresponds to the increase of $(1/T_1)_D$. In contrast to what has been found for ²D relaxation, this effect is *not* enhanced at low temperatures.

We have again evaluated our data in terms of eq 1, where X now stands for $1/D_w$. The fit parameters are compiled in Table 1.²¹ Our results for the scaling parameters of pure water differ slightly from those obtained from ²D relaxation, but as the parameter surface in the fit was very flat, this difference may still be in the range of experimental uncertainty. On the other hand, at finite xenon concentrations the parameter sets deduced from relaxation and diffusion become increasingly discrepant, the difference exceeding largely the experimental uncertainty.

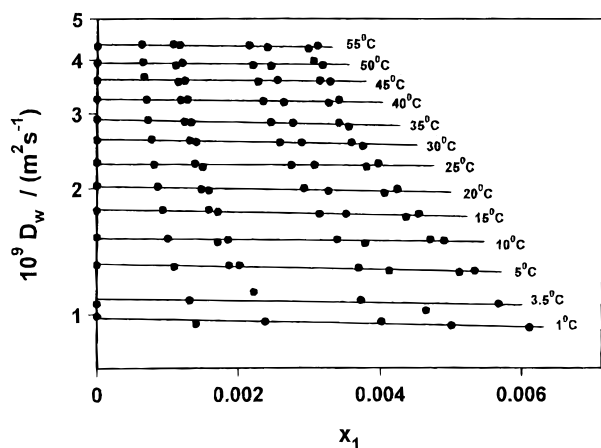


Figure 3. Isotherms of self-diffusion coefficients D_w of water (H_2O) as a function of the mole fraction x_1 of added xenon. The temperatures are shown in the figure.

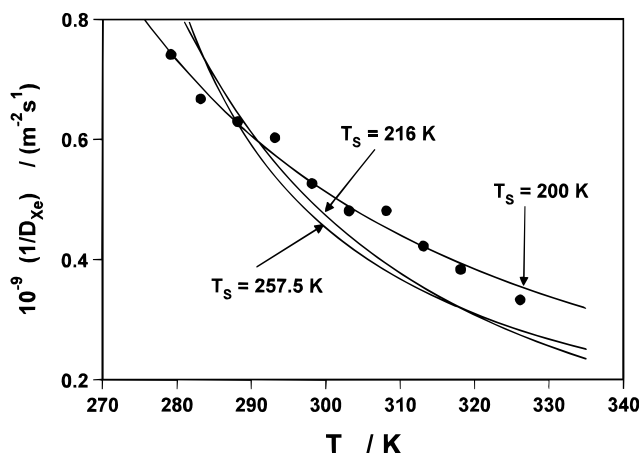


Figure 4. Fit of self-diffusion coefficients D_{Xe} of xenon in H_2O to eq 1 with different sets of scaling parameters. Within experimental resolution D_{Xe} is independent from the xenon concentration.

This behavior can be traced back to the primary experimental data in Figures 1 and 3, where the increase of the slope of $(1/T_1)_D$ vs x_1 at low temperatures is not reflected by a decrease of the slope of D_w .

Self-Diffusion of Xenon. We reconsider in Figure 4 our results⁵ for the self-diffusion coefficient of xenon. D_{Xe} does not depend on the xenon concentration within experimental resolution. Due to the limited accuracy of our data, we did not obtain unambiguous figures for T_s and γ in unconstrained fits to eq 1. We have therefore fitted the data with fixed γ and T_s . Figure 4 shows three representative fits: The first one refers to $T_s = 257.5$ K and $\gamma = 1.0$, as found for ^{131}Xe relaxation; the second one, to $T_s = 217$ K and $\gamma = 1.81$, as obtained for the self-diffusion coefficient of pure water. Both fits are unsatisfactory. The third fit refers to an arbitrarily selected value of $T_s = 200$ K, which yields an acceptable representation of the data. Fits of about the same quality were obtained by changing interdependently T_s toward lower and γ toward higher values, so that $T_s = 200$ K represents an upper bound. The unambiguous result is that xenon self-diffusion does not scale with any of the other processes considered in this paper.

4. Discussion

Summary of Experimental Results. It is now generally accepted that in pure water there exists a thermodynamic singularity near 228 K.^{1,2} The addition of hydrophobic solutes like xenon should favor the processes leading to this singularity.

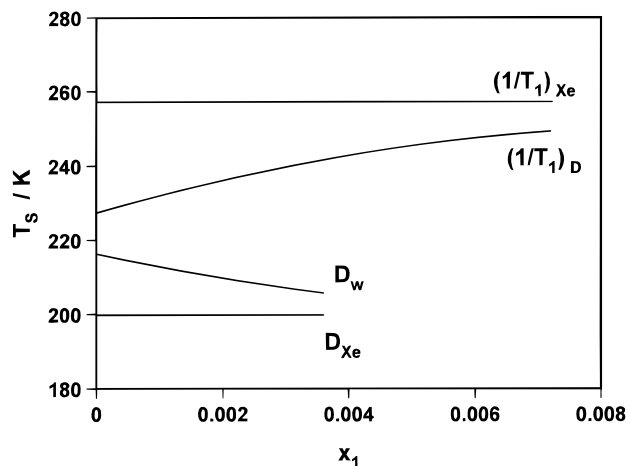


Figure 5. Apparent values for the singular temperature T_s deduced from various dynamical quantities. As discussed in the text, only the data set for 2D relaxation is expected to reflect the “true” behavior of T_s .

We have attempted to examine this hypothesis by studying various dynamical quantities in aqueous solutions of xenon, but we have learned from the results in Table 1 that the different dynamical quantities give quite different answers. To prepare for the subsequent discussion, we first summarize which major facts we believe to be established from our experiments:

(1) All dynamical properties considered in this study are well described by a scaling relation of the form of eq 1.

(2) At a given xenon concentration it is *not* possible to represent the temperature dependence of the various dynamical quantities by the same set of scaling parameters. The apparent values for T_s deduced from the various quantities are summarized in Figure 5.

(3) Within the simple form of the scaling law in eq 1, concentration-dependent exponents γ are obtained. Universal exponents can be formally restored by assuming alternative forms for the nonsingular background, but in all cases considered by us the physical relevance of the background parameters remained unclear.

Model for Data Interpretation. We propose here an interpretation which seems to offer a resolution of these phenomena, but it may be noted at the outset that we do not know whether it is unique in that respect. The starting point is the thermodynamic anomaly indicated by the response functions, from which the isothermal compressibility is of prime interest, as it reflects density fluctuations in the liquid. The behavior of κ_T at low temperatures indicates that these density fluctuations increase strongly, when the temperature is lowered. Near a critical point or spinodal line, this increase of density fluctuations must mirror an increase of their correlation length.²⁶ This should, in principle, be observable in small-angle X-ray or neutron scattering, but such experiments have yielded rather discrepant results.^{27,28} According to the most recent data of Xie et al.,²⁸ an increasing correlation length cannot be proved by small-angle scattering. Rather the authors have attributed the increase in density fluctuations to an increasing number of water molecules participating in clusters.

The point made here is that, in the presence of clusters and large domains with different structural arrangements of water molecules, the increasing fluctuations when approaching T_s may affect the various motional degrees of freedom quite differently. Such a behavior is indeed already known from mechanical and dielectric relaxation in pure water. Angell¹ has analyzed these data and has suggested that faster dielectric relaxation than mechanical relaxation may signify clustering phenomena near

T_S , as the dielectric strength may be carried by dipole-correlated clusters of water molecules. Similar phenomena are known from liquids near the glass transition, where, among others, a decoupling of rotational and translational motions has been observed.²⁹ In the latter case, rotational motions appear to signify the glass transition, while other dynamical properties including the self-diffusion coefficient remain shorter at T_g . An analogous interpretation seems also appropriate for the results reported here.

Fate of the Singularity upon Dissolution of Xenon.

According to our data, rotational motions reflected by ^2D relaxation show the fastest divergence and thus should represent the quantity of choice for locating T_S . Then, we conclude from Figure 5 that T_S , as deduced from ^2D relaxation, increases upon dissolution of xenon from $T_S = 228\text{ K}$ for pure water to values of about 250 K at the highest concentrations achieved. Hence, our findings are concordant with the view^{1,2} that hydrophobic solutes reinforce the water structures that are responsible for the anomalies in the supercooled regime. In other words, our results are in harmony with the picture of supercooled water and hydrophobic effects, e.g., advocated by Stillinger,² and described in the Introduction of this paper.

It may be noted that the same general trend in T_S has been deduced from electrical conductance measurements for the hydrophobic salt tetrabutylammonium bromide (Bu_4NBr) dissolved in water.¹⁶ The displacement of T_S extracted from the latter data is considerably smaller than that reported here. Conceptually, xenon does, of course, represent a more prototypical hydrophobic solute than Bu_4NBr . Also, in view of the decoupling of rotational and translational motions observed by us, it is not clear to what degree the electrical behavior can be used to locate T_S in a quantitative manner.

In concluding this section, we note that the effect of xenon upon the scaling law behavior of water is opposite to the effect of hydrostatic pressure, both with regard to the displacement of T_S and the apparent exponent γ . Hydrostatic pressure is known to suppress the structural processes leading to the anomalous behavior of water, and eventually, with the decrease of T_S , VFT behavior instead of scaling law behavior becomes prevalent.^{7,8} In this regard, by addition of xenon, one should learn about the processes occurring in water at negative pressure. This is of some relevance, as there is considerable interest in the location of stability boundaries in pure water which may cross from positive to negative pressures.^{1,12}

Dynamical Processes in Clathrate-Like Domains. At high concentrations the T_S vs x_1 curve deduced from ^2D relaxation data levels off. Note that "high concentrations" means mole fractions of the order of 0.01 only. It is then tempting to extrapolate these data to the composition of the clathrate $\text{Xe}:\text{H}_2\text{O} = 1:23$, corresponding to $x_1 \approx 0.04$. Rough extrapolation yields $T_S \approx 260\text{ K}$ for water in clathrate-like domains. This is impressively confirmed by the data for ^{131}Xe relaxation. As noted, ^{131}Xe relaxation reflects the local dynamics of water molecules in the immediate vicinity of xenon. In the low-concentration regime under consideration here, one may expect the water structure surrounding a given xenon atom, and hence ^{131}Xe relaxation, to be independent from the xenon concentration. This is indeed observed. As the water structure around xenon should bear much resemblance to that in clathrates,^{15,18} it is tempting to attribute the value $T_S = 257\text{ K}$ obtained from ^{131}Xe relaxation to solvent dynamics in clathrate-like domains. Note that this figure practically coincides with that obtained by concentration extrapolation of ^2D relaxation data. Moreover, in both cases the exponents γ approach one another as well.

We consider this close numerical agreement as striking evidence in favor of our interpretation.

Nonuniversal Behavior of the Scaling Law Exponent. In terms of the simple scaling law, eq 1, one obtains from ^2D relaxation rates concentration-dependent exponents γ which cover a range from about 1.9 to 1.3 (see Table 1). A similar trend in the exponents has been obtained for solutions of Bu_4NBr .¹⁶ On the other hand, in pure water at elevated pressures, values up to about 2.4 have been obtained.⁷ Of course, a concentration-dependent exponent is not in the spirit of a true scaling law, as, e.g., encountered near critical points. As discussed above, we did not find a background correction for restoring universal behavior which seemed physically plausible. In this context, it is again worth drawing attention to the fact that recent small-angle scattering data have not yielded evidence for a diverging correlation length of the density fluctuations, as would be expected near a critical point or a spinodal line.²⁸ Also, one should note that the viscosity, but not single particle quantities like τ_2 or D_w , is expected to diverge near critical points. Thus, in our opinion, there is no convincing evidence from our experimental results for a thermodynamic state near a spinodal line or critical point.

Decoupling of Rotational and Translational Motions. We find unambiguous evidence that in solutions containing xenon the temperature dependence of the self-diffusion coefficient of water, like that of the self-diffusion coefficient of xenon, does not reflect the strong divergence exhibited by the reorientational correlation time of water. Rather, below 298 K the self-diffusion coefficient of water is bending over to a weaker temperature dependence, resulting in a lower effective value for T_S , when fitted to eq 1. Such a decoupling³⁰ has recently been observed for liquids near the glass transition,²⁹ and has been termed the "translation-rotation paradox".

While an unambiguous explanation is not yet at hand, we draw attention to two possible scenarios, both developed originally in models for molecular dynamics near the glass transition: Stillinger and Hodgdon³⁰ have proposed a "fluidized domain model" in which, depending on the domain parameters (size, life time, concentration, and internal viscosity of the domains), the observed decoupling can be rationalized within a hydrodynamic model. Possibly, a suitable modification of this model may account for the processes near T_S .

An alternative interpretation may be based on a change in the translational diffusion mechanism from small-step to jump diffusion, when approaching T_S . Incoherent quasi-elastic neutron scattering data at low temperatures have indeed been evaluated in terms of a jump model for translational motions,³¹ suggesting that protons move from one site to another one via partial rotation through the tetrahedral angle. It may however be noted that the jump model has formed the input rather than the result of this analysis. If the explanation in terms of a crossover from small-step to jump rotational diffusion is correct, molecular dynamics simulations could perhaps shed light on this point.

In both scenarios, the role of xenon in initiating this decoupling needs to be clarified. One speculation is that the translation-rotation paradox would also become visible in pure water, if measurements were conducted sufficiently close to T_S . Then, the role of xenon would just be to displace this regime to higher temperatures, where measurements are feasible. In pure water at atmospheric pressure Lüdemann and co-workers^{7,8} have performed ^2D relaxation and self-diffusion measurements down to about 243 K , i.e., some 15 K above T_S . Reanalysing their data, we have found no definite evidence for such a behavior, but on the other hand, in the deeply supercooled

regime experimental uncertainties increase largely. Again, molecular dynamics simulations may perhaps shed light on this new aspect of dynamical behavior near T_S . In any case the close analogy to the behavior of transport processes near glass transitions is worth being considered in more detail.

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