

Diffusion in Supercooled Water to 300 MPa

F. X. Prielmeier, E. W. Lang, R. J. Speedy,^(a) and H.-D. Lüdemann

Institut für Biophysik und Physikalische Biochemie, Universität Regensburg, D-8400 Regensburg, Federal Republic of Germany
(Received 18 February 1987)

Measurements of the self-diffusion coefficient in supercooled water to 300 MPa are reported. Translational diffusion in liquid water at 243 K is enhanced by 60% when the pressure is increased from 0.1 to 150 MPa, and rotational diffusion is enhanced by almost 250% between 0.1 and 250 MPa. These striking anomalies are interpreted in terms of the proximity of a conjectured line of spinodal-like stability limits in the supercooled liquid.

PACS numbers: 66.10.-x

It is an intriguing anomaly of cold water that it becomes more fluid¹ and the rates of translational² and rotational diffusion³ increase when pressure is applied to the liquid. This behavior is apparently unique to a class of liquids, like water and silicon dioxide, which prefer four coordination and have open network structures at low pressure. It is just one of a remarkable variety of odd behaviors displayed by water,⁴ all of which become most pronounced when the liquid is cooled below its equilibrium freezing temperature.

The isobaric temperature dependence of the transport properties of water are also unusual, having the form⁴⁻⁶

$$X = A_x (T/T_s - 1)^{\gamma}, \quad (1)$$

where X represents the fluidity or inverse viscosity $1/\eta$,⁷ the self-diffusion coefficient D ,^{8,9} inverse reorientational correlation time $1/\tau_2$,⁵ or the electrical conductance of dilute electrolyte solutions Λ .¹⁰ Equation (1) suggests that mobility in the liquid would cease at the temperature $T_s(p)$, which at atmospheric pressure has the value¹¹ $T_s(1 \text{ atm}) \approx -46^\circ\text{C}$. That the transport coefficients extrapolate to zero at some temperature below the melting point is not unusual: Many liquids can be supercooled to a glass transition where $1/\eta$ and D go effectively to zero, but there are strong indications that the phenomenon in water is not simply a glass transition.⁶ One such indication is that below 0°C the thermal expansivity α and the temperature dependence of the heat capacity C_p and isothermal compressibility κ_T have the opposite signs to those in normal liquids, and their isobaric temperature dependence can be described by¹²

$$X = A_x (T/T_s - 1)^{-1/2} + B_x. \quad (2)$$

The first term in Eq. (2) is consistent with divergences at T_s of $X = C_p$, κ_T , and $-\alpha$, and the second term B_x is a slowly varying "background" contribution. Equation (2) has the form implied by the conjecture¹³ that $T_s(p)$ represents a spinodal line or locus of stability limits, and the exponent value of $\frac{1}{2}$ is characteristic of the divergences of C_p , κ_T , and α at a mean-field spinodal.¹⁴ The suggestion is that the slowing down of the transport properties as $T \rightarrow T_s$ is related to diverging thermodynamic fluctuations and correlation lengths in the liquid, as at a spinodal line rather than as at a glass tran-

sition.

A related indication that Eq. (1) is not describing the approach to a glass transition is that the homogeneous nucleation temperature for the freezing of water, T_H , is -41°C at atmospheric pressure,⁴ just 5° above T_s . While this might be coincidental if observed only at atmospheric pressure, the relation $T_s < T_H < T_s + 10^\circ$ is preserved over a wide pressure range⁵ as shown in Fig. 1. In contrast, other supercooled liquids either display homogeneous nucleation at temperatures well above any impending glass transition, or crystallization can be bypassed and a glass transition observed.

The relation between T_s and T_H shown in Fig. 1 is a natural consequence of the conjecture that T_s represents a line of stability limits.^{6,13} If the metastable liquid becomes unstable as $T \rightarrow T_s$, then it will transform to some other phase (i.e., freeze or boil) at T_H before T_s is reached. This means that T_s is inherently inaccessible so that the properties of the liquid at T_s (including the conjectured existence of a stability limit) can only be inferred by extrapolation. It also presents an experimental challenge: to measure the properties of water as close as possible to T_s over a wide pressure range, the main difficulty being that very small samples are needed to minimize the chance that the water will freeze before the measurements are complete.

Lang and Lüdemann^{5,15,16} have measured spin-lattice relaxation times T_1 for H, D, and ^{17}O in emulsions of dispersed water droplets to temperatures approaching $T_H(p)$ and to 300 MPa. Viscosity and self-diffusion have not been studied in supercooled water above atmospheric pressure.

We measured the self-diffusion coefficient, D , in supercooled water using the pulsed gradient spin-echo technique.¹⁷ The results reported here derive from measurements on water samples contained in a 200- μm -diam capillary. The capillary was oriented in line with the magnetic field gradient so that diffusion was measured along the capillary axis rather than across its radius. The magnetic field gradient was calibrated with use of the values of Mills,¹⁸ as recommended by Weingärtner.¹⁹ Measurements were made at each of the pressures listed in Table I from 273 K down to the temperature at which the sample froze.

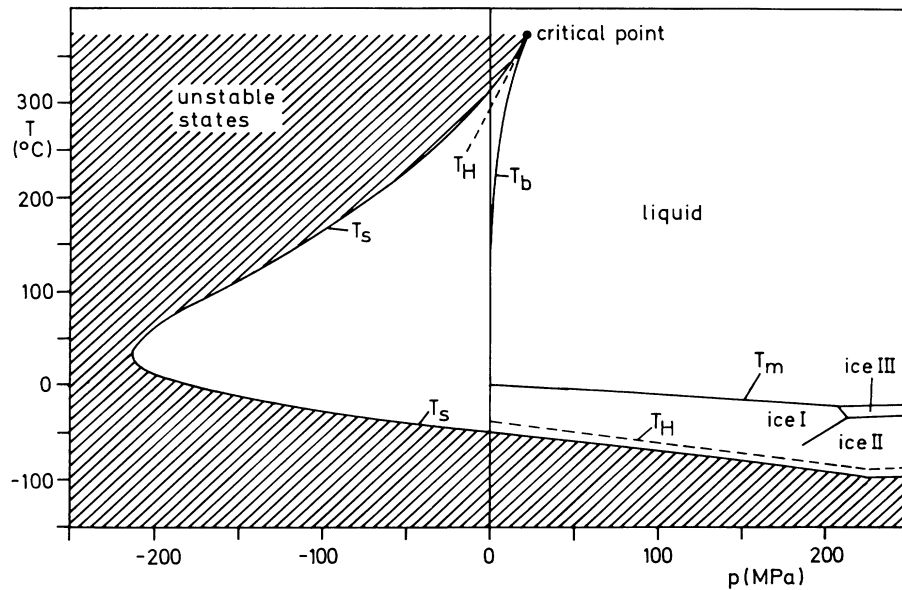


FIG. 1. Locus of the conjectured stability limits of water $T_s(p)$ shown in relation to the equilibrium phase diagram and the experimental kinetic limits of stability T_H . The methods of locating T_s are detailed in Ref. 13.

Our results below 273 K together with previous results at higher temperatures, which are assessed and tabulated by Weingärtner,¹⁹ were fitted with the equation

$$D = D_0 T^{1/2} (T/T_s - 1)^\gamma, \quad (3)$$

with the best-fit parameter listed in Table I. The standard deviations reflect the precision of the measurements which is 1% to 2%.

It should be emphasized that Eq. (3) is an empiricism. While such a form might be justified in the limit $T \rightarrow T_s$, when the leading term dominates the temperature dependence of D , no explanation has been offered as to why Eqs. (1) or (3) seem to apply over a wide temperature range. There are, no doubt, several factors, with different temperature dependences (variation of the density being one example) which influence D and which Eq. (3) is being forced to accommodate when fitted over the 80- to 220-K temperature ranges shown in Table I, with consequent effects on the parameter values. The fitting parameters can be varied interdependently by about 10%

in D_0 , 10 K in T_s , and 0.3 in γ before the standard deviation exceeds twice the best-fit value in Table I.

The data were also fitted with the empirical Vogel-Tamman-Fulcher equation in the form

$$D = D_0 \exp[-B/(T - T_0)]. \quad (4)$$

The standard deviation from Eq. (4) were larger than those from Eq. (3) at the highest and lowest pressures, but comparable around 200 MPa.

Figure 2 shows the pressure dependence of D , $1/\tau_2$, and $1/\eta$ at three temperatures. At 363 K, water behaves as a normal liquid in which all three measures of molecular motion decrease with increasing pressure, although the decrease in $1/\tau_2$ is less than the experimental error of about 5%. D and $1/\eta$ show very similar variations and the Stokes-Einstein ratio $D\eta/T$, while it is not constant, does not vary by more than 10% from its average value over the range of pressures and temperatures shown in Fig. 2.

The anomalous increase in D , $1/\eta$, and $1/\tau_2$ is already

TABLE I. Best-fit parameters in the equation $D = D_0 T^{1/2} (T/T_s - 1)^\gamma$, where D is the self-diffusion coefficient in H_2O . (Data above 273 K from Ref. 8.)

p (MPa)	T range (K)	D_0 ($10^{10}/m^2 s^{-1}$)	T_s (K)	γ	% standard deviation
0.1	252–448	8.66	220	1.809	1.3
10	248–448	8.68	221	1.771	1.5
50	243–448	7.34	213	1.850	1.2
100	243–448	6.22	205	1.967	1.5
150	229–448	5.50	200	2.038	2.6
200	218–298	5.28	190	2.429	1.6
250	213–298	5.36	190	2.462	2.1
300	218–298	5.30	193	2.349	1.8

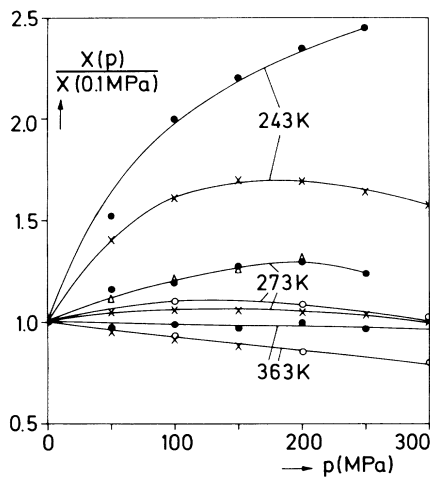


FIG. 2. The effect of pressure on the transport properties of water at three temperatures. The value of $X(p)$ at pressure p , relative to its atmospheric pressure value $X(0,1 \text{ MPa})$ is plotted against pressure. $X=D, x; 1/\tau_2$ (Ref. 5), filled circles; $1/\tau_1$ (Ref. 2), triangles; $1/\eta$ (Ref. 3), open circles; where D is the self-diffusion coefficient, τ_2 is the relaxation time for rotational diffusion, τ_1 is the dielectric relaxation time, and η is the shear viscosity.

evident at 273 K. We note that there is good agreement between the effects of pressure on rotational diffusion, as measured by either $1/\tau_2$ which derived from ^{17}O longitudinal relaxation times, or as measured by the inverse dielectric relaxation time²⁰ $1/\tau_1$. The most striking variations are apparent in the supercooled region. At 243 K, D is increased by 60% at 150 MPa and $1/\tau_2$ by almost 250% at 250 MPa. Some of the trends shown in Fig. 2 can be interpreted in terms of the proximity of the points to the stability-limit line $T_s(p)$ shown in Fig. 1. At the stability limit, D , $1/\eta$, and $1/\tau_2$ are zero, and so the anomalous pressure effect is accounted for by the fact that they can only increase when the pressure is increased along an isotherm moving away from that line. The observed increases are greatest where the measurements are closest to the line. Well away from the line, normal behavior takes over and D , $1/\eta$, and $1/\tau_2$ decrease with pressure.

The unusual phenomenon, that rotational diffusion (proportional to $1/\tau_2$) is evidently enhanced much more strongly by pressure than is translational diffusion, calls for a more specific structural explanation, as follows. At low temperatures and pressures the water molecules form an open network structure with most molecules hydrogen bonded to four neighbors, which tend to be tetrahedrally disposed as in the low-density ices or clathrate crystals. The quasitetrahedral force field presented by the surrounding network constrains a molecule to reside in one of a few well-defined orientational states which are separated by potential barriers. When the system is compressed, however, the number of near

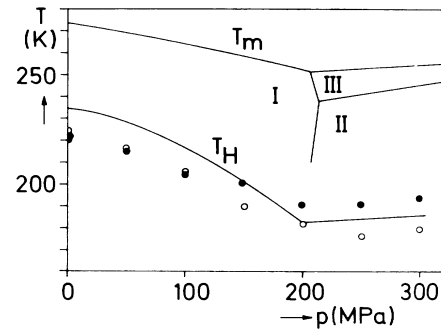


FIG. 3. Homogeneous nucleation temperatures T_H for the freezing of water (Ref. 26) and the values of $T_s(D)$ filled circles and $T_s(\tau_2)$ open circles (Ref. 5), at which translational and rotational mobilities extrapolate to zero according to Eq. (1), compared with the phase diagram for water. Roman numerals indicate the stable ice polymorphs. T_m is the melting temperature. The similarity of the pressure dependence of $T_s(D)$, $T_s(\tau_2)$, T_H , and T_m suggests a correspondence between local structures in the supercooled liquid at a given pressure and the structure of the ice which is most stable at the pressure. Note that uncertainties in the estimates of T_s could accommodate the expectation that $T_s(D)$ and $T_s(\tau_2)$ are the same, and lie below T_H .

neighbors increases and the tetrahedrality of the imposed force field is broken down. The potential-energy surface for rotation is then less sharply partitioned and there is a greater variety of orientational states, separated by smaller energy barriers, so that rotational diffusion is enhanced. In all ice and clathrate networks each molecule is hydrogen bonded to four neighbors with bond lengths of $2.8 \pm 0.1 \text{ \AA}$.²¹ The significant difference is that whereas in the clathrates and in ice I, the distance of closest approach of the nonbonded neighbors is $\approx 4.5 \text{ \AA}$,²¹ in ices II, III, IV, and V they lie in the range $3.2\text{--}3.5 \text{ \AA}$.²¹ Studies of the ices^{22,23} show that dielectric relaxation, and hence rotational diffusion, is about 100 times faster in ices III, IV, and V than in ice I. (It is, of course, much slower in the proton ordered ice II.)

Those structural considerations point to an explanation of why supercooled water manifests a stability limit rather than a glass transition. The energetically stable amorphous state is a four-connected network of hydrogen bonded molecules. Embedded within such a network will be local structures which can be identified as fragments of the nine (at least) ice polymorphs²¹ and the various aqueous clathrate crystals. It is presumably the competition between such different structural elements and the cooperative growth of domains of particular structures^{24,25} which give rise to the thermodynamic fluctuations, long-range correlations, and correlation times associated with the stability limit.

We now discuss some implications of the fit with Eq. (3) and the values of its parameters. The best-fit parameters T_s are compared in Fig. 3 with values of T_s ob-

tained by Lang and Lüdemann⁵ from fitting their τ_2 data with Eq. (1) and with the measured²⁶ homogeneous nucleation temperatures T_H . If T_s locates a stability limit, then the values of T_s obtained from the τ_2 and D data should agree and both should lie below T_H . Those expectations are satisfied at low pressures, but above 200 MPa the values of T_s obtained from our self-diffusion data are systematically higher than T_H by up to 10 K. The implication that $D \rightarrow 0$ before the sample freezes is physically unreasonable, which indicates that Eq. (3) does not correctly describe the temperature dependence of D beyond the range of the measurements.

With the caveat that the precise location of T_s , and perhaps the existence of a stability limit, remain uncertain, the apparent close relation between T_s and T_H , is sufficiently striking to suggest a causal connection. Such a connection has radical implications: The properties of the liquid are explicitly related to T_s and thereby to T_H , but T_H reflects properties of the crystalline polymorph which nucleates; so the properties of the liquid are related to, and contain information about, the crystal which nucleates. Furthermore, if the discontinuous slope of T_H vs p is reflected by a discontinuity in T_s vs p (which is not inconsistent with the estimates of T_s shown in Figs. 1 and 3), then it may be reflected by some higher-order discontinuity in the properties of the liquid. While that seems unlikely, such a discontinuity might be related to the existence of two amorphous solid forms of water which are apparently connected by a first-order phase transition.²⁷

Finally, we note that in the pressure range 0.1–50 MPa the exponent γ in Eq. (3) is close to the value 1.76 predicted by a mode-coupling model,²⁸ for the shear viscosity divergence at an ergodic \rightarrow nonergodic transition. That formalism has been taken to describe the dynamics of the glass transition phenomenon.^{28–31} It might, however, with equal justification, be applied to the stability-limit phenomenon observed in water.

Financial support by the Deutsch Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. One of us (F.X.P.) was supported by a scholarship from the Friedrich-Ebert-Stiftung.

^(a)Permanent address: Department of Chemistry, Victoria University of Wellington, Wellington, New Zealand.

¹J. Kestin, H. E. Khalifa, H. Sookiazian, and W. A. Wakeham, *Ber. Bunsenges. Phys. Chem.* **82**, 180–188 (1978).

²C. A. Angell, E. D. Finch, L. A. Woolf, and P. Bach, *J. Chem. Phys.* **65**, 3063 (1976).

³T. De Fries and J. Jonas, *J. Chem. Phys.* **66**, 896 (1977).

⁴C. A. Angell, in *Water: A Comprehensive Treatise*, edited by F. Franks (Plenum, New York, 1983), Vol. 7.

⁵E. W. Lang and H.-D. Lüdemann, *Ber. Bunsenges. Phys. Chem.* **85**, 603 (1981).

⁶R. J. Speedy and C. A. Angell, *J. Chem. Phys.* **65**, 851 (1976).

⁷Ye. A. Osipov, B. V. Zhelenznyi, and N. F. Bondarenko, *Russ. J. Phys. Chem.* **51**, 1264 (1977); J. Hallett, *Proc. Roy. Soc. London* **82**, 1046 (1963).

⁸H. R. Pruppacher, *J. Chem. Phys.* **56**, 101 (1972).

⁹K. T. Gillen, D. C. Douglass, and M. J. R. Hoch, *J. Chem. Phys.* **57**, 5117 (1972).

¹⁰R. J. Speedy, *J. Phys. Chem.* **87**, 320 (1983).

¹¹B. D. Cornish and R. J. Speedy, *J. Phys. Chem.* **88**, 1888 (1984).

¹²R. J. Speedy, *J. Phys. Chem.* **91**, 3354 (1987).

¹³R. J. Speedy, *J. Phys. Chem.* **86**, 982 (1982).

¹⁴R. J. Speedy, *J. Phys. Chem.* **86**, 3002 (1982).

¹⁵E. W. Lang and H.-D. Lüdemann, *J. Chem. Phys.* **67**, 218 (1977).

¹⁶E. W. Lang and H.-D. Lüdemann, *Ber. Bunsenges. Phys. Chem.* **84**, 462 (1980).

¹⁷E. O. Stejskal and J. E. Tanner, *J. Chem. Phys.* **42**, 288 (1965).

¹⁸R. Mills, *J. Phys. Chem.* **77**, 685 (1973).

¹⁹H. Weingärtner, *Z. Phys. Chem.* **132**, 129 (1982).

²⁰R. Pottel, private communication.

²¹D. Eisenberg and W. Kauzmann, *The Structure and Properties of Water* (Oxford Univ. Press, New York, 1969).

²²G. J. Wilson, R. K. Chen, D. W. Davidson, and E. Whalley, *J. Chem. Phys.* **43**, 2384 (1965).

²³R. K. Chen, D. W. Davidson, and E. Whalley, *J. Chem. Phys.* **43**, 2376 (1965).

²⁴F. H. Stillinger, *Science* **209**, 451 (1980).

²⁵R. J. Speedy, *J. Phys. Chem.* **88**, 3364 (1984).

²⁶H. Kanno, R. J. Speedy, and C. A. Angell, *Science* **189**, 880 (1975).

²⁷O. Mishima, L. D. Calvert, and E. Whalley, *Nature (London)* **310**, 393 (1984), and **314**, 76 (1985).

²⁸E. Leutheusser, *Phys. Rev. A* **29**, 2765 (1984).

²⁹U. Bengtzelius, W. Götze, and A. Sjölander, *J. Phys. C* **17**, 5915 (1984).

³⁰W. Götze, *Z. Phys. B* **56**, 139 (1984), and **60**, 195 (1985).

³¹F. Mezer, W. Knaak, and B. Farago, *Phys. Rev. Lett.* **58**, 571 (1987).