

A new scenario of the apparent fragile-to-strong transition in tetrahedral liquids: water as an example

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2003 J. Phys.: Condens. Matter 15 L703

(<http://iopscience.iop.org/0953-8984/15/45/L03>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.125

The article was downloaded on 19/05/2010 at 17:42

Please note that [terms and conditions apply](#).

LETTER TO THE EDITOR

A new scenario of the apparent fragile-to-strong transition in tetrahedral liquids: water as an example

Hajime Tanaka

Institute of Industrial Science, University of Tokyo, Meguro-ku, Tokyo 153-8505, Japan

E-mail: tanaka@iis.u-tokyo.ac.jp

Received 23 October 2003

Published 31 October 2003

Online at stacks.iop.org/JPhysCM/15/L703

Abstract

Recently it was suggested that tetrahedral liquids such as water and silicon exhibit a fragile-to-strong transition while approaching the glass-transition temperature (T_g). Such a drastic change in the fragility of liquid as a function of temperature is very rarely observed. Here we propose that, contrary to the popular fragility transition scenario, this phenomenon should be explained in terms of the crossover from a non-glass-forming to a glass-forming branch. For ordinary glass-forming liquids, there is frustration between long-range density ordering (crystallization) and short-range bond ordering (energetic frustration hidden in the interaction potential), which helps vitrification. For water and silicon, such frustration does not exist near the melting point (T_m) at ambient pressure since the symmetry of their crystals is consistent with that of short-range tetrahedral bond ordering. Thus, we call this high-temperature region near T_m a non-glass-forming branch. In the low-temperature region near T_g , which we call a glass-forming branch, on the other hand, a system tends to have long-range density ordering. Its competition with local tetrahedral ordering induces strong frustration effects, which make the liquid strong. Our scenario suggests that the crossover from a non-glass-forming to a glass-forming branch may be generic to tetrahedral liquids whose specific volume increases upon crystallization.

Water is known to exhibit a variety of unusual thermodynamic and dynamic behaviours [1–4]. Among these, the anomalous temperature dependence of the viscosity of supercooled water at ambient pressure has recently attracted considerable attention. A glass-forming liquid, whose viscosity is low near the melting point T_m but exhibits highly non-Arrhenius behaviour near the glass-transition temperature T_g , is called ‘fragile’, while a liquid whose viscosity shows Arrhenius-like behaviour is called ‘strong’ [5]. Supercooled liquid water is not viscous [1, 6] near T_m and ‘apparently’ behaves as a fragile liquid. Near T_g (~ 136 K [7, 8]), on the other hand, it behaves as a strong liquid [10, 11]; that is, the temperature dependence of the viscosity η , or

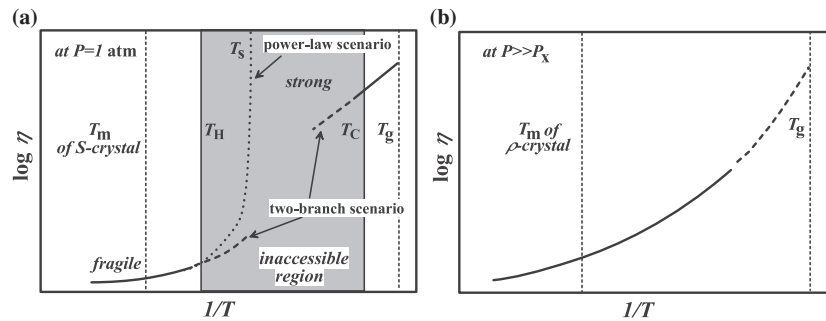


Figure 1. Schematic figures representing the temperature dependence of the viscosity η of water at ambient pressure (a) and at a high pressure far above P_x (~ 2 kbar) (b). See the text on the definition of P_x . Here T_H is the temperature of homogeneous nucleation of a supercooled liquid upon cooling it below T_m , and T_C is the temperature of crystallization of a supercooled liquid into cubic ice upon heating it from T_g . At ambient pressure, water behaves as a fragile liquid near T_m , while it behaves as a strong liquid near T_g (~ 136 K). The prediction of our two-branch scenario (see the text) is indicated by dashed curves, while that of different scenarios [10, 11, 16, 21] based on the power-law divergence at T_s is indicated by a dotted curve. At a high pressure, water is expected to behave as an ordinary glass former, as shown in (b). All the unusual features of water should become less pronounced with increase in pressure and eventually disappear at $P \gg P_x$ [23, 24]. This picture is supported by the results of dynamic measurements at high pressures [18].

the structural relaxation time τ_α , is well described by the Arrhenius law, as shown schematically in figure 1(a). This scenario where water changes its character from a fragile to a strong liquid has been supported by the following recent experimental studies [9–11]:

- (i) Jenniskens and Blake [9] studied the kinetics of ice crystal growth in liquid water near T_g . They confirmed that the liquid just above T_g is very viscous and its temperature dependence is well described by the Arrhenius law, and concluded that water is a strong liquid near T_g .
- (ii) Ito *et al* [10] carefully established the correlation between the width of a liquid–glass transformation range measured by differential scanning calorimetry (DSC) and the strong nature of liquid near T_g , for a number of liquids with a wide range of fragility. From the fact that the liquid–glass transformation range of water measured by DSC is quite wide, they concluded that supercooled water near T_g is a very strong liquid.
- (iii) Recently, Bergman and Swenson [11] succeeded in directly observing the Arrhenius temperature dependence of the dielectric relaxation time of supercooled water confined between clay plates and also concluded that water is a strong liquid near T_g .

Thus, the scenario of the fragile-to-strong transition in water now becomes more convincing [9–12].

It should be noted, however, that there were a few experimental results [13, 14] seemingly contradicting this scenario. Johari *et al* [14] measured the dielectric relaxation in water in a polymer network and found that liquid water near T_g is rather fragile. Smith and Kay [13] measured diffusion kinetics in a liquid near T_g and found non-Arrhenius temperature dependence, suggesting that liquid water near T_g is fragile.

All these experimental studies were very carefully done, but there might be the following technical problems in some of these experiments:

- (a) The experiments on water confined in a polymer network may suffer from the fact that the polymer network, which prevents the crystallization of water, might affect the hydrogen-bonding state of water and thus change the character of the water itself.

- (b) The experiments on water confined between clay plates might suffer from a similar problem (surface charge effects).
- (c) The diffusion experiments on a thin film of water might suffer from the problem of hydrodynamic flow, which may apparently accelerate the diffusion. This is because the structure of ice films prepared by vapour deposition is in a mechanically metastable state and a decrease in viscosity may produce a hydrodynamic flow which induces the convective mixing of H₂O and D₂O and accelerates the mixing kinetics. Such a change in the structure of water films was actually observed by Jenniskens *et al* [15].

Although it is difficult to draw a definite conclusion in the above-described confusing situation, we believe that the experiments on the crystallization kinetics and on the width of a liquid–glass transformation range measured by DSC are most reliable. Note that both experiments suggest that liquid water is ‘strong’ near T_g , which supports the existence of the apparent fragile-to-strong transition in water. To explain this unusual behaviour, a few interesting models [10, 16, 17] have been proposed. However, the physical origin is still far from being fully understood. As pointed out by Sastry [12], this fragile-to-strong transition in water is a challenge to any theoretical model of ‘liquid–glass transition’ in the sense that any model must explain it in a physically reasonable manner. To settle this difficult problem, we need to logically consider its validity or to devise a new experiment. In this letter, we take the former approach. We pay special attention to the fact that the dynamic behaviour of water is known to approach that of ordinary liquids [18] with increase in pressure, as shown schematically in figure 1(b).

Before proposing a physical picture that can explain this unusual behaviour, first we reconsider the statement that water is a fragile liquid near T_m . This statement gives the impression that water is similar to a typical fragile liquid, but this is *not* appropriate from the following reasons:

- (A) For fragile liquids, the temperature distance between T_m and T_g is usually small [19, 20]. For water, it is ~ 140 K, which is unusually large compared to those for typical fragile liquids. Note that for typical fragile liquids $T_m/T_g \sim 1.3$ – 1.5 while for water $T_m/T_g \sim 2.0$.
- (B) Bulk water can never be vitrified and always crystallizes below T_H . In other words, water is an extremely poor glass former.
- (C) More importantly, the viscosity of water first decreases with increase in pressure (or density) [1, 18], and then increases above ~ 2 kbar (see figure 2(b)). This unusual behaviour is markedly different from the typical behaviour of ordinary liquids, in which viscosity always increases with increasing pressure (or density). Such unusual behaviour cannot be explained by the conventional knowledge about supercooled liquids.

These facts (A)–(C) cast strong doubts on the validity of the statement that water is a fragile liquid near T_m , which implicitly assumes that water is a glass former in the usual sense. The question that should be answered first is, thus, whether the viscosity anomaly of water near T_m is caused by slow dynamics associated with a glass transition or has other origins. The dynamic anomaly of viscosity η and the structural relaxation time τ in water have often been explained by mode-coupling theory (MCT) [3, 16] or the model based on the existence of a critical-like end-point of the hydrogen-bond network formation process [10, 21]. Both models predict the power-law anomaly $\eta \propto (T - T_s)^{-\nu}$ (T_s : a critical temperature; ν : a critical exponent) and T_s was determined as 228 K at ambient pressure [3, 10, 21]. Figure 2(a) shows such a fitting, which describes the viscosity anomaly well. To confirm this type of power-law divergence, however, we need to approach very close to T_s . Since T_s is hidden by crystallization in reality

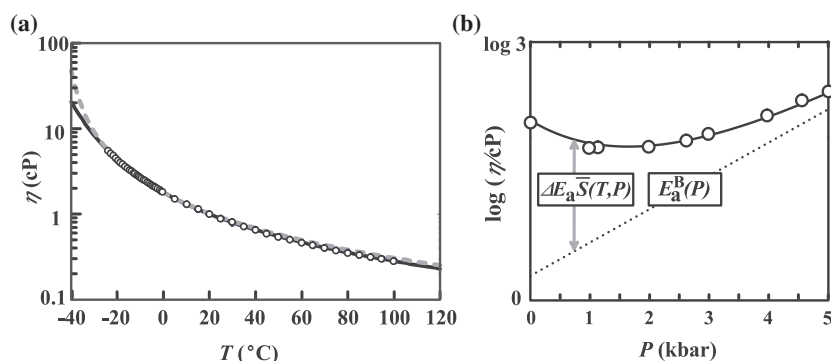


Figure 2. (a) The viscosity anomaly of water at ambient pressure. The black solid curve is the prediction of equation (3), while the grey dashed curve is that of the power law with $T_s = 228 \text{ K} \sim -45^\circ\text{C}$ and $\nu = 1.5$. (b) The pressure dependence of the viscosity of water at $T = -5.0^\circ\text{C}$ and the fitting curve for our prediction. As shown here, our scenario explains well both the T - and P -dependences of the viscosity of water.

(see figure 1(a)), however, this scenario cannot be confirmed in an unambiguous manner. More importantly, it should be noted that in a real system such a sharp singularity is smeared out by thermal fluctuation effects, which are thermally activated hopping processes and fluctuations of the order parameter, respectively, for MCT and spinodal-singularity scenarios.

We point out some problems associated with these scenarios.

- (1) The pressure dependence of the viscosity anomaly is ascribed to the pressure dependence of $T_s(P)$ and $\nu(P)$. This pressure dependence itself is, however, rather difficult to explain in a natural manner within its own framework.
- (2) There seems to be no obvious justification for the applicability of the mean-field MCT for a system of finite-range interactions. Or—why does it work so well only for water? It is well established that such divergence near the mode-coupling T_c is not observed in ordinary glass formers and it is smeared out by the thermally activated hopping process.
- (3) Furthermore, the absence of the activation process in a molecular liquid with hydrogen bonding above T_s seems not to be reasonable. In other words, there should be a background part in the viscosity, but fitting is usually carried out without it.
- (4) More importantly, these scenarios cannot explain facts (A)–(C).

Although the MCT scenario is attractive, thus, it is worth reconsidering the origin of the viscosity anomaly from a different standpoint.

Contrary to these popular scenarios, we recently demonstrated a new possibility: that the viscosity anomaly of water could be due to short-range hydrogen-bond tetrahedral ordering in water [22–24]. We propose that a liquid is generally neither homogeneous nor completely disordered. In any liquid there are competing orderings: density (ρ) ordering driven by an isotropic part of the attractive interactions and bond (S) ordering driven by symmetry-selective interactions. Locally favoured structures (LFSs) in a lower energy state (S -state) are rather randomly created in a sea of normal-liquid structures (NLSs) in a higher energy state (ρ -state). Their energy difference is ΔE . The specific volume of the former is ‘larger’ than that of the latter by Δv . The most probable candidate LFS in water may be a tetrahedral structure made of five water molecules. The average fraction of the LFS, \bar{S} , is given by the following Boltzmann factor [23, 24]:

$$\bar{S} = S_0 \exp[\beta(\Delta E - P \Delta v)]. \quad (1)$$

where $\beta = 1/k_B T$ (k_B : Boltzmann's constant). For water, we estimated $\Delta E = 3.56 \text{ kcal mol}^{-1}$ and $\Delta v = 9.98 \text{ cm}^3 \text{ mol}^{-1}$ [23]. Note that these values are for 1 mol of LFSs and not for one mole of molecules. On the basis of this two-order-parameter (TOP) model of liquid, the viscosity anomaly of water can be explained as follows. In usual liquids the activation energy required for viscous flow or diffusion is associated with the creation of a hole, or the disruption of local interactions with its neighbouring molecules. The existence of the unique activation energy for this process is the origin of the Arrhenius behaviour. With the existence of the LFS, however, an additional activation energy, ΔE_a , is required for molecules participating in these structures to flow. Here we note that the lifetime of the LFS, which is longer than that of the NLS, is still quite short ($\ll \mu\text{s}$) and thus a liquid cannot be regarded as a mixture of stable NLSs and LFSs. Thus, the activation energy averaged over all molecules participating and not participating in the LFS is estimated as

$$E_a(T, P) = E_a^B(P) + \Delta E_a \bar{S}(T, P), \quad (2)$$

where $E_a^B(P)$ is the background activation energy for normal water without LFSs. The T, P -dependence of the viscosity is thus predicted as [23]

$$\eta(T, P) \propto T^{3/2} \exp[\beta E_a(T, P)]. \quad (3)$$

The fitting of equation (3) to the T -dependence of the viscosity is shown in figure 2(a). We obtain $E_a^B(P) = [1832 + (0.37 - 0.0002 \times (T/\text{K})) \times (P/\text{bar})] \text{ K}$ and $\Delta E_a = 2612 \text{ K}$. Since our prediction and the MCT one give equally good descriptions, we cannot judge solely from this comparison which scenario is more reasonable. However, we stress that our scenario can explain the unusual P -dependence of the viscosity, or fact (C), in a natural manner. As shown in figure 2(b), it is well explained by the competition between the background part, $E_a^B(P)$, which is a linearly increasing function of P as often seen in ordinary liquids, and the part related to the LFS, $\Delta E_a \bar{S}(T, P)$, which is an exponentially decreasing function of P (see equation (1)). In our model, further, all the unusual T, P -dependence of the density, compressibility, heat capacity, and viscosity can be described solely in terms of the T, P -dependence of a single common Boltzmann factor, $\bar{S}(T, P)$ (see equation (1)) *in a unified manner* [23, 24].

Next we check whether our TOP scenario can also explain facts (A) and (B). To do so, we first focus on the following unusual features of the T - P phase diagram of water: (a) density decreases upon crystallization (freezing into ice Ih) at ambient pressure [1] and (b) the melting point has a minimum as a function of pressure [1] (see figure 3). To explain these features, we also use our TOP model of liquid [24–26]. On noting that the tetrahedral symmetry of the LFS is compatible with the crystallographic symmetry of ice Ih, we argue that the freezing into ice Ih is primarily driven by the bond order parameter S and ‘not’ by the density order parameter ρ (see figure 3). This is consistent with the volume increase upon crystallization into ice Ih. Thus, we conclude that crystallization of water below the crossover pressure P_x ($\sim 2 \text{ kbar}$) is a result of *long-range bond ordering*, while that above P_x is a result of *long-range density ordering*. We call crystals formed below P_x S -crystals (e.g., ice Ih) and those formed above P_x ρ -crystals (e.g., ices III and V). The change of a sign in the pressure dependence of the melting point, dT_m/dP , is naturally explained by the Clausius–Clapeyron relation, on noting that S -crystal and ρ -crystal, respectively, have larger or smaller specific volumes than liquid water. This is a natural consequence of the fact that the degree of density ordering increases and that of bond ordering decreases in the order S -crystal, liquid water, ρ -crystal. Below the melting point of ρ -crystal (T_m^ρ) there appears a driving force of crystallization into ρ -crystal, while below the melting point of S -crystal (T_m^S) there is a driving force of crystallization into S -crystal. Below both T_m^S and T_m^ρ , thus, there are competing orderings, which cause frustration effects. We propose that this unusual feature of the phase diagram is the most essential origin of all the unusual features of water, which makes water so different from other molecular

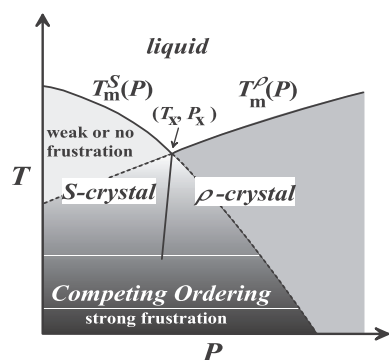


Figure 3. A schematic phase diagram of water. Water may be the only *molecular* liquid having P_x at a positive pressure. For all the other molecular liquids, the symmetry of the LFS selected by S is not consistent enough with the symmetry of the equilibrium crystal. For ordinary molecular liquids, thus, no long-range bond ordering is allowed at positive pressure and only long-range density ordering is allowed. In other words, P_x does not exist in the positive-pressure region, or $P_x < 0$. We note that liquid Si and Ge have similar phase diagrams [26].

liquids [22–24]. Water may be the only molecule in which anisotropic interactions, or the symmetry of the LFS (S), can be consistent enough with a crystallographic symmetry to allow the formation of the crystal favoured by S (S -crystal).

In the light of the above-described view on the phase diagram of water (see figure 3), we consider why water is a very poor glass former and can never be vitrified *in a bulk state* even with the fastest temperature cooling rate. According to our TOP model of liquid–glass transition [19, 20], vitrification is due to energetic frustration between different symmetries (global and local symmetries) favoured by the interaction potential, namely, competing ordering between long-range density ordering (crystallization) and short-range bond ordering: LFSs formed in a liquid, which are more stable than NLSs, play a similar role to random magnetic impurities in spin glass and prevent crystallization. Our model suggests [19, 20] that stronger disorder effects make a liquid ‘stronger’ or ‘less fragile’. However, these frustration effects help vitrification *only when the symmetry of the LFS is ‘not’ consistent with the symmetry of the equilibrium crystal into which a liquid tends to crystallize*. For water, the symmetry of the LFS is compatible with the structure of ice Ih, and bond ordering itself is the driving force of crystallization into ice Ih (see figure 3). Thus, few frustration effects on crystallization into ice Ih are caused by bond ordering (LFS). Note that since the ρ -state is a higher energy state than the S -state, it cannot disturb the S -ordering. Thus, crystallization of water into ice Ih should be free from any frustration effects. This picture naturally explains why water is such a poor glass former at ambient pressure and suggests that the viscosity anomaly is primarily not due to the slow dynamics associated with the glass transition. Thus, our TOP scenario is consistent with all the facts (A)–(C) at least on a qualitative level.

Under high pressures, a crystal into which a liquid crystallizes generally tends to have a more compact, denser structure¹. Thus, pressure destabilizes S -crystal but stabilizes ρ -crystal. Accordingly, the equilibrium crystal switches from S -crystal to ρ -crystal at the crossover pressure P_x with increasing pressure (see figure 3). In other words, the primary order parameter responsible for crystallization into the equilibrium crystal switches from

¹ The reason that the nucleation of ρ -crystal is more favoured at higher pressure than that of S -crystal is primarily due to the effect of the volume change Δv_c upon crystallization. For S -crystal, Δv_c is positive, while for ρ -crystal, it is negative. This affects the free energy difference between the crystal and liquid and also gives an extra free energy barrier related to $\Delta v_c P$ upon nucleation.

bond order parameter S to density order parameter ρ there. Our TOP model [19, 20] predicts that above P_x LFSs have strong frustration effects acting against crystallization into ρ -crystal and thus a liquid should be more easily vitrified there. Thus, water should behave as an ordinary glass-forming liquid at very high pressures (see figure 1(b)), consistently with the experimental indication [18]. Here we mention two examples supporting our argument. First, Mishima and Suzuki [27] found that the glass-forming ability of water is significantly enhanced at a high pressure (~ 5 kbar), where water tends to crystallize into ice IX (ρ -type crystal in our terminology): more precisely, the critical cooling rate for producing a glassy state of water is 10^6 – 10^7 K s $^{-1}$ at ambient pressure, while it is 10^3 – 10^4 K s $^{-1}$ around 5 kbar. Second, a similar behaviour was also reported for liquid Ge [28]. Liquid Ge cannot be vitrified at ambient pressure by a temperature quench and just crystallizes into Ge-I crystal (S -crystal). But it can be vitrified at high pressures (~ 30 kbar) by a temperature quench into the competing ordering region (see figure 3). More importantly, the amorphous phase coexists with the high-pressure form of Ge crystal, Ge-II (ρ -crystal) just after the quench (see footnote 1) [28], although it seems to eventually transform into a Ge-I crystal (S -crystal). This indicates that switching of the crystal form into which a liquid tends to crystallize from S -crystal to ρ -crystal is indeed related to the glass-forming ability.

One might think that this greater glass-forming ability at higher pressure in water and Ge can be explained by the increase in viscosity with pressure. However, we point out that the viscosity of water decreases with increase in pressure up to $\sim P_x$ (see figure 2(b)) and then increases with its further increase. Thus, we cannot expect a drastic increase in the viscosity at the pressure applied in the above experiments for either water or liquid Ge.

Thus, we propose that frustration between long-range crystalline ordering and short-range bond ordering (energetic frustration hidden in the interaction potential) is one of the key factors determining the glass-forming ability (see also [19] and [20]). We emphasize that this tendency is difficult to explain in terms of the other existing theories of liquid–glass transition.

Now we are ready to explain why water behaves like strong liquids near T_g at ambient pressure. According to our model, the unusual behaviour can be explained as follows. Water tends to crystallize into ice Ih at high temperatures close to T_m . However, the driving force of crystallization into its high-pressure crystalline form (ρ -crystal), which has a higher density than liquid water, sets in below the extrapolated melting-point curve of ρ -crystal, $T_m^\rho(P)$, even at ambient pressure, and becomes stronger and stronger while further decreasing the temperature (see figure 3). This may induce the switching of the crystalline phase into which the water tends to crystallize, from S -crystal to ρ -crystal. Once the driving force of ρ -ordering wins over that of S -ordering, short-range bond ordering can cause ‘strong’ frustration effects against long-range ρ -ordering, as in ordinary glass-forming liquids. This makes a liquid ‘strong’ [19, 20]. It is this switching of the primary order parameter that leads to the apparent transition of water from a fragile to a strong liquid. Our scenario of order-parameter switching strongly suggests an intrinsically nonequilibrium nature of the transition.

In relation to this, it is worth noting that the fragile-to-strong transition is supposed to occur in the temperature region between the temperature of homogeneous nucleation (T_H) and the temperature of crystallization into cubic ice (T_C). This temperature region is sometimes called ‘no-man’s land’ [4], since there we can realize neither a liquid state nor an amorphous state of water experimentally. Its existence (see figure 1(a)) can be regarded as a sign of the fact that the switching of the primary driving force of crystallization from S -ordering to ρ -ordering is necessary for vitrification. On noting this intrinsically nonequilibrium nature of the transition, it may not be appropriate to call the phenomenon a ‘transition’. It is much more reasonable to say that there is a crossover from a non-glass-forming to a glass-forming branch (see figure 1(a)): one is supercooled water obtained by cooling liquid water while the other

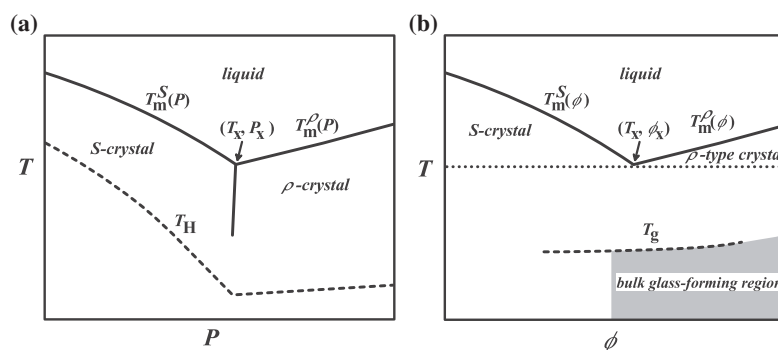


Figure 4. Schematic figures of the T - P phase diagram of water (a) and the ϕ - T phase diagram of a mixture of water and LiCl (b). Here ϕ is the concentration of LiCl and ϕ_x is the eutectic point.

is that obtained by heating hyperquenched (HQW) or vapour-deposited glassy water (ASW). In the former branch (the non-glass-forming branch) water is a very poor glass former and ‘apparently’ looks extremely fragile, while in the latter (the glass-forming branch) it behaves as a better glass former and looks like a strong liquid. We stress that the slowing down of the kinetics in the non-glass-forming branch is *not* associated with the glass transition.

As described before, our model also suggests that at $P \gg P_x$ the apparent fragile-to-strong transition disappears and water behaves as an ordinary liquid (see figure 1(b)). This is because short-range hydrogen-bond tetrahedral ordering causes strong frustration effects and tends to disturb crystallization into ρ -crystal there at any temperature. This is consistent with the known pressure dependence of the viscosity and the diffusivity [1, 18].

Our physical picture is further supported by the similarity between the P - T phase diagram [29] of water and the ϕ - T phase diagram [30, 31] of a mixture of water and LiCl (ϕ : the concentration of LiCl), although the difference in number of components causes an essential difference in the meaning of the phase diagram. Figure 4 shows schematically the characteristic features of these phase diagrams. In pure water (see (a)), the temperature distance between T_m and T_H increases with increase in pressure. Thus, water can be more deeply supercooled at higher pressures. In other words, the glass-forming ability of water is enhanced with increasing pressure (see also [27]). In a mixture of water and LiCl (see (b)), the crystalline form into which water attempts to crystallize switches from S -crystal to ρ -type crystal (pentahydrate crystal, $\text{LiCl} \cdot 5\text{H}_2\text{O}$) at ϕ_x with increasing ϕ . This is consistent with the fact that the density of a crystal increases with increase in ϕ [31]. Reflecting this, a glassy state of water starts to be formed *even in bulk* under usual quenching conditions (see (b)) [30, 31] with increase in ϕ . Both examples clearly demonstrate that the switching of the crystalline phase into which water tends to crystallize from S -crystal to ρ -crystal is crucially related to the significant enhancement of the glass-forming ability of water.

This similarity between the two types of phase diagram shown in figure 4 arises from the fact that both densification and the addition of LiCl lead to the break-up of LFSs and help crystallization into ρ -crystal. For pure water, since the LFS has a larger specific volume than the normal-liquid structure, the number density of the LFS decreases with increase in pressure [22–24]. For a mixture of water and LiCl, on the other hand, since LiCl is a hydrogen-bond breaker, its addition decreases the number density of the LFS (S -state) and instead increases that of hydration structures, which we call the ρ -state for this mixture. For both cases, the reduction of hydrogen-bonding ability destabilizes S -crystal and makes ρ -crystal more stable than S -crystal. In the region where water tends to crystallize into ρ -crystal, water can be vitrified rather easily in both cases.

In summary, we show that the apparent fragile-to-strong transition of liquid water can be naturally explained by our TOP model of liquid on a qualitative level. We propose that it should be interpreted as the crossover from a non-glass-forming to a glass-forming branch. Our model predicts that this crossover should become less pronounced with increasing pressure and it should disappear for $P \gg P_x$, as shown schematically in figure 1(b). Water should behave as an ordinary glass former there, which seems to be supported by experimental results [18]. Further studies on how pressure affects the crossover behaviour are highly desirable to check the validity of our model. Finally, we point out that the same scenario can be applied to atomic liquids with covalent-bond tetrahedral order, such as Si and Ge, which also exhibit a volume expansion upon crystallization at ambient pressure and have a positive P_x [26]. Although the discussion here is speculative, our model provides us with a simple scenario that explains the thermodynamic and dynamic anomalies of water including the apparent fragile-to-strong transition as well as the poor glass-forming ability of water in a coherent manner.

References

- [1] Eisenberg D and Kauzmann W 1969 *The Structure and Properties of Water* (Oxford: Oxford University Press)
- [2] Angell C A 1995 *Science* **267** 1924
- [3] Debenedetti P G 1997 *Metastable Liquids* (Princeton, NJ: Princeton University Press)
- [4] Mishima O and Stanley H E 1998 *Nature* **396** 329
- [5] Angell C A 1991 *J. Non-Cryst. Solids* **131–133** 13
- [6] Hallett J 1963 *Proc. Phys. Soc.* **82** 1046
- [7] Johari G, Hallbrucker A and Mayer E 1987 *Nature* **330** 552
- [8] Hallbrucker A, Mayer E and Johari G 1989 *J. Phys. Chem.* **93** 4986
- [9] Jenniskens P and Blake D F 1996 *Astrophys. J.* **473** 1104
- [10] Ito K, Moynihan C T and Angell C A 1999 *Nature* **398** 492
- [11] Bergman R and Swenson J 2000 *Nature* **403** 283
- [12] Sastry S 1999 *Nature* **398** 467
- [13] Smith R S and Kay B D 1999 *Nature* **398** 788
- [14] Johari G P 1996 *J. Chem. Phys.* **105** 7079
- [15] Jenniskens P, Banham S F, Blake D F and McCoustra M R S 1997 *J. Chem. Phys.* **107** 1232
- [16] Starr F W, Sciortino F and Stanley H E 1999 *Phys. Rev. E* **60** 6757
- [17] Jagla E J 1999 *J. Phys.: Condens. Matter* **11** 10251
- [18] Bett K E and Cappi J B 1965 *Nature* **207** 620
DeFries T and Jonas J 1977 *J. Chem. Phys.* **66** 896
Lang E W and Ludemann H D 1981 *Ber. Bunsenges. Phys. Chem.* **85** 1016
- [19] Tanaka H 1998 *J. Phys.: Condens. Matter* **10** L207
Tanaka H 1999 *J. Chem. Phys.* **111** 3163
Tanaka H 1999 *J. Chem. Phys.* **111** 3175
- [20] Tanaka H 2003 *J. Phys.: Condens. Matter* **15** L491
- [21] Speedy R J and Angell C A 1976 *J. Chem. Phys.* **65** 851
- [22] Tanaka H 1998 *Phys. Rev. Lett.* **80** 5750
- [23] Tanaka H 2000 *J. Chem. Phys.* **112** 799
- [24] Tanaka H 2000 *Europhys. Lett.* **50** 340
- [25] Tanaka H 2000 *Phys. Rev. E* **62** 6968
- [26] Tanaka H 2002 *Phys. Rev. B* **66** 064202
- [27] Mishima O and Suzuki Y 2001 *J. Chem. Phys.* **115** 4199
- [28] Zhang F X and Wang W K 1995 *Phys. Rev. B* **52** 3113
He D W, Zhang F X, Yu W, Zhang M, Yu Y P and Wang W K 1998 *J. Appl. Phys.* **83** 5003
- [29] Kanno H and Angell C A 1980 *J. Chem. Phys.* **73** 1940
- [30] Angell C A and Sare E J 1968 *J. Chem. Phys.* **49** 4713
Angell C A, Sare E J, Donnella J and MacFarlane D R 1981 *J. Phys. Chem.* **85** 1461
Kanno H 1987 *J. Phys. Chem.* **91** 1967
- [31] Fornazero J, El Hachadi A and Dupuy-Philon J 1992 *J. Non-Cryst. Solids* **150** 413