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Recent results on the connection between thermodynamics and dynamics in supercooled water☆

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Abstract

We review recent results on the connection between thermodynamics and dynamics in a model for water. We verify the Adam–Gibbs relation between entropy and dynamic properties using computer simulations, which allow direct access to the relevant properties. We combine experimental measurements of entropy with the Adam–Gibbs hypothesis to predict dynamic properties in deeply supercooled states, which are difficult to access experimentally. We find evidence suggesting that the glass transition temperature of water may be significantly higher than previously reported, but is still consistent with recent measurements. Finally, we discuss the hypothesis that the dynamical behavior of deeply supercooled water undergoes a crossover from 'fragile' to 'strong' behavior.
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1. Introduction

The seminal book of Professor Kauzmann taught everyone that water is widely studied for many practical reasons—it is the most ubiquitous fluid on earth, and its unusual properties are thought to be related to basic phenomena in biology, chemistry, and engineering [1–5]. Frequently, non-specialists regard these unusual properties as unique to water. However, recent simulation studies have suggested that the temperature dependence of many dynamic properties are not altogether unlike those of some simple liquids [6–9]. For example, supercooled liquid water seems to be one among many liquids that can be described over a range

☆ Dedicated to Professor W. Kauzmann, whose seminal 1969 book has inspired much of this research.

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of temperatures by the mode-coupling theory (MCT) [10]. MCT provides quantitative predictions for the temperature dependence of relaxation times for the dynamics of supercooled liquids in the 'weakly' supercooled regime, where D decreases by approximately three orders of magnitude from the typical liquid value. However, as temperature decreases toward a 'dynamical critical temperature' T_{MCT} predicted by MCT theory, the MCT breaks down. Typically, T_{MCT} is $\approx 50\%$ larger than the experimentally measured T_{g}, and relaxation times are still approximately 10 orders of magnitude smaller at T_{MCT} than at T_{g}. Hence there is a huge range of $T < T_{\mathrm{MCT}}$, the 'deeply' supercooled region, where dynamic properties change dramatically, but the underlying reasons for this behavior are not understood. Additionally, glass-forming liquids are typically categorized as (i) strong liquids—those having an Arrhenius T dependence of dynamic properties with an activation energy of roughly $37RT$ and (ii) fragile liquids—those having a strongly non-Arrhenius T dependence of dynamics properties [11–13]. Water behaves as a fragile liquid in the experimentally accessible region where MCT predictions seem to apply. In the range $T < T_{\mathrm{MCT}}$, there have been suggestions that water may behave quite differently than other liquids.

Unfortunately, simulations of equilibrium properties for $T < \mathrm{T}_{\mathrm{MCT}}$ are not feasible at the present time due to the excessively large relaxation time, relative to the computational time required. Additionally, experiments on liquid water are hampered by the fact that even carefully prepared samples of supercooled water crystallize at the 'homogeneous nucleation temperature' $T_{\mathrm{H}} = 235$ K [3,14], slightly above the expected value of T_{MCT} for water [15]. On the other hand, liquid water can be vitrified at atmospheric pressure by a variety of methods, including quenching aerosol droplet samples to liquid nitrogen temperatures [16]. Glassy water crystallizes on heating at $T_X \approx 150$ K, making the properties of amorphous water in the range $T_X < T < T_{\mathrm{H}}$ almost unknown. While the properties of glassy water, referred to as low-density amorphous ice (LDA), are intrinsically non-equilibrium, a careful analysis of the thermodynamic properties of glassy water and their relation to the properties of equilibrium samples at $T > T_{\mathrm{H}}$ can possibly help provide insight into the expected properties in the difficult-to-probe region $T_X < T < T_{\mathrm{H}}$.

An evaluation of the thermodynamic data in this range is particularly valuable, owing to the development of a formalism relating thermodynamics to dynamics in deeply supercooled states. These ideas reach back to the seminal work of Kauzmann [17], and have been expanded over time by the work of, among others, Adam and Gibbs [18], Goldstein [19], and Stillinger and Weber [20,21]. The central idea underlying the approach is that dynamics at low temperatures are controlled primarily by the statistical properties of the underlying potential energy landscape [22]; this landscape consists of a tremendous number of local minima corresponding to mechanically stable amorphous states. At sufficiently low T, the system is expected to be localized within one of these basins, with infrequent 'activated processes', which bring the system to a new basin. Several authors have studied the landscape properties explicitly and it appears that, at T_{MCT} (where the MCT predictions break down), the system motion becomes dominated by inter-basin 'hopping' via regions of collective motion [23–34]. Hence the statistical properties of the landscape is key to extending the quantitative understanding of supercooled liquids to the region $T < T_{\mathrm{MCT}}$.

In this testimonial to Professor Kauzmann, we examine the implications of both experimental and computational studies for the dynamic properties of liquid water in the deeply supercooled region, where little equilibrium data are available. From simulations, we establish the validity of the Adam–Gibbs relationship between entropy and dynamic properties, like the diffusion constant D [35–38]. Having validated this approach, we consider experimental measurements of the entropy for the liquid for $T > T_{\mathrm{H}}$ and glassy water at $T < T_X$. By applying simple, but somewhat tedious constraints of thermodynamics, we can predict the expected behavior of the entropy in the range $T_X < T < T_{\mathrm{H}}$. The results for the entropy, when combined with the Adam–Gibbs relation, suggest that water should crossover from fragile liquid behavior to strong liquid behavior at $T < T_{\mathrm{H}}$ [39], as first

proposed in Ref. [40]. If these predictions are valid, water again appears as an anomalous liquid, and deserves careful scrutiny. Additionally, results reported in Ref. [39] suggest that $T_g \approx 160$ K is far above traditionally accepted estimates of T_g, but consistent with recent results based on hyperquenching [41].

2. Background

In 1948, Kauzmann published a seminal paper that focused attention on the interplay of thermodynamics and dynamics of a liquid near its vitrification temperature [17]. We briefly review the theoretical foundations of the thermodynamic viewpoint of the glass transition that grew from his work. This is an incomplete account; a more complete account can be found in Ref. [2].

Kauzmann focused on the entropy of the liquid and its corresponding crystal. On cooling, the liquid entropy decreases at a much faster rate than the crystal entropy. Hence, by naive extrapolation, we expect $S_{\text{liquid}} = S_{\text{crystal}}$ at a temperature T_K, the Kauzmann temperature, and $S_{\text{liquid}} < S_{\text{crystal}}$ for $T < T_K$. While it is strange to imagine a liquid with a smaller entropy than the crystal, it is not thermodynamically inconsistent. The situation is more problematic considering that, for most systems, $S_{\text{crystal}}\ (T \to 0) = 0$, which would require that $S_{\text{liquid}} < 0$, which is inconsistent with the classical expression $S = k_B \ln\Omega$ since the number of states Ω cannot be less than unity.

The 'Kauzmann paradox' refers to the fact that, in practice, the kinetic glass transition intervenes so as to avoid the thermodynamic 'entropy catastrophe'—dynamics saving thermodynamics. To avoid the possibility of an entropy catastrophe without a paradox, Kauzmann proposed that the barrier to crystallization vanishes at some T between T_K and T_g, thereby avoiding the equal entropy point by simple crystallization. Subsequent work considered the possibility that crystallization might not intervene, and put forth the notion that T_K may be the point of an 'ideal' thermodynamic glass transition, attainable only by an infinitely slow cooling of the liquid [42]. In practice, such a transition is never observed, as laboratory measurements of T_g depend on the cooling rate.

The notion of a thermodynamic singularity underlying the glass transition was expanded on by the work of Adam, Gibbs' and DiMarzio. They developed a theoretical framework in which the liquid at low T evolves through cooperatively rearranging regions, rather than simple Brownian motion as at high T, and associated the size of the cooperatively rearranging regions with a configurational entropy S_{conf}. Most importantly, since the rearranging region controls the relaxation of the liquid, they proposed that the relaxation time τ (or other dynamic properties, like the diffusion constant D) are related to S_{conf} via

$$\ln\tau \sim (TS_{\text{conf}})^{-1}. \tag{1}$$

In this scenario, an ideal glass forms when the relaxation time diverges, and hence $S_{\text{conf}} = 0$. Thus, it has become common to refer to T_K also as the T where S_{conf} vanishes. The concept of cooperative rearrangement and a close relation of the dynamics to the configurational entropy have remained central to the development of the theoretical approach.

The primary remaining question is: what is S_{conf} and how can it be measured? The first steps to resolving this question were made by Goldstein [19], who focused on the underlying potential energy landscape, arguing that the dynamics of a liquid can be split into two contributions at low T: (i) vibrations localized within a single basin of a landscape, and (ii) infrequent hops between basins that give rise to structural relaxation. In this context, there is a natural separation of S into a vibrational contribution S_{vib} and a configurational contribution S_{conf}, arising from the number of basins the liquid samples. From the point of view of the energy landscape, the ideal glass is formed when the liquid becomes trapped in a single landscape basin.

Stillinger and Weber formalized the concept of a basin in the energy landscape by introducing the inherent structure (IS) formalism. Specifically, the set of points that map to the same minimum, or IS, are those which constitute a basin. This approach is particularly well suited to simulated liquids, since it is possible to explicitly calculate the steepest descent to a local minimum from an equilibrium configuration [43]. Moreover, the par-

tition function can be explicitly rewritten in terms of the basins. By introducing the density of states $\Omega(E_{IS})$, i.e., the number of minima with energy in the interval of energy E_{IS} to $E_{IS}+dE_{IS}$, we can rigorously define

$$S_{conf}=k_B \ln \Omega(E_{IS}). \tag{2}$$

The Helmholtz free energy is given by

$$F=E_{IS}-TS_{conf}+f_{basin}(T,E_{IS}). \tag{3}$$

Here f_{basin} captures the vibrational contribution and kinetic degrees of freedom. Eq. (3) is a formal expression for the separation of configurational and vibrational contributions. For our purposes, we will focus on the fact that one can define $S_{conf}=S-S_{vib}$, and evaluate S and S_{vib} to obtain S_{conf}.

3. Calculation of configurational entropy of simulated water

We calculate the absolute entropy at all state points simulated by following the procedure described in Ref. [44]. We use the ideal gas as a reference state and use thermodynamic integration to link to a system at high T and small ρ (large volume V), where interactions are far less important. The entropy at all other (ρ, T) simulated are then obtained by a numerical integration of the relationship $dS=\frac{1}{T}dE-\frac{p}{T}dV$. The only additional complication beyond previous calculations for Lennard–Jones systems is that we must consider the reference state to be a tri-atomic ideal gas, rather than a monatomic one. The tri-atomic ideal gas entropy is given by

$$S_{id}(V,T)=Nk_B\left[\ln\frac{\pi^{1/2}V}{Nh^6}+\frac{3}{2}\ln(2\pi m k_B T)+\frac{1}{2}\sum_{i=1}^{3}\ln(8\pi^2 I_i k_B T)+4-\ln 2\right], \tag{4}$$

where I_i are the moments of inertia, and h is Planck's constant.

Our primary goal is to calculate S_{conf} so that we may test proposed relations between the dynamic properties and thermodynamic properties. We exploit the hypothesized relationship that $S=S_{conf}+S_{vib}$. For T not far from the mode-coupling temperature T_{MCT}, Ref. [44] observed that the vibrational contribution may be well approximated by a classical harmonic solid, with the eigenfrequencies defined by the inherent structures sampled below the 'onset temperature' [43,45,46]. Unfortunately, even at the lowest T studied, the extended simple point charge (SPC/E) model of water displays a significant anharmonic contribution to U. To approximate the contribution due to the anharmonicity of the potential, we include higher order terms in an expansion of the vibrational energy

$$U_{vib}=3k_B T+aT^2+bT^3 \tag{5}$$

Here a and b are fitting parameters, and the harmonic contribution to the energy is given by $3k_B T$. Since $(dU/dT)_v=T(dS/dT)_v$, we may express the vibrational entropy as

$$S_{vib}=S_{harmonic}+S_{anharmonic} \tag{6}$$

$$=\frac{k_B}{N}\sum_{i=1}^{6N-3}\left[\ln\left(\frac{k_B T}{\hbar\omega_i}\right)+1\right]+2aT+\frac{3}{2}bT^2, \tag{7}$$

where $\{\omega_i\}$ are the eigenvalues of the Hessian matrix $\partial^2 V/\partial x_j \partial x_k$. We calculate $\{\omega_i\}$ from the normal mode spectrum of the liquid after quenching to the inherent structure at each (ρ, T) system point simulated.

We only need to evaluate the constants a and b to obtain S_{vib}. We heat the quenched structures and measure the dependence of U on T, which allows us to fit U to the form specified in Eq. (5). In order to obtain reliable fits of the constants, the heating schedule follows the following sequence:

- The temperature is first increased to 50 K for 10 ps to anneal the effect of any nearby minima that may be lower in energy due to the extreme roughness of the landscape.
- The temperature is reduced to 1 K for 10 ps, to allow the vibrational degrees of freedom to

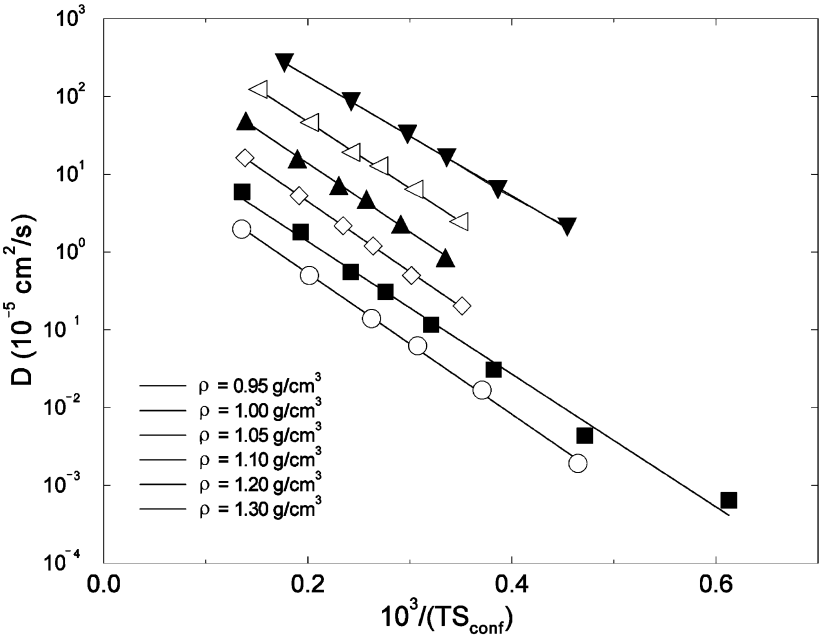

Fig. 1. The diffusion constant D as a function of $1/TS_{conf}$ for the SPC/E model, confirming the predicted relation of Adam and Gibbs. Note that the curves for each density have been shifted for clarity. Figure redrawn from Ref. [35]. Verification of the proposed relation for simpler models is reported in Refs. [46–49].

equilibrate, followed by 10 ps of data collection in the NVE ensemble.

- The temperature is then increased to 10 K, and then by 10 K intervals following the same schedule of 10 ps for the equilibration of vibrational degrees of freedom and 10 ps of data collection in the NVE ensemble up to 190 K; at higher T, diffusive motion becomes significant on these time scales.

At this point, we have both the total and vibrational entropy for all state points simulated and can now calculate $S_{conf} = S - S_{vib}$.

We also briefly discuss the calculation of the entropy of crystalline forms, since we want to compare the properties of S_{conf} and the excess entropy $S_{ex} = S_{liquid} - S_{crystal}$. From the landscape point of view, a crystalline arrangement corresponds to only a single basin, since significant rearrangement of the molecules would destroy the crystalline structure. Hence, one expects the crystal entropy to be entirely vibrational in nature. Thus, we calculate $S_{crystal}$ using the same techniques used to calculate S_{vib} of the liquid inherent structures. However, since the crystal structure does not change (i.e. the system is always exploring the same crystalline basin), the normal modes $\{\omega_i\}$ are independent of T, but of course still depend on ρ. Quenches from several T confirm this.

4. Testing the Adam–Gibbs hypothesis

Having obtained S_{conf} over a wide range of density at supercooled temperatures, we can test the proposed relation

$$\ln D \sim (A/TS_{conf}). \tag{8}$$

In the range of D values where bulk water experiments have been performed, we find agreement with the proposed relationship for the SPC/E model of water, as shown in Fig. 1.

Evaluation of S_{conf} relies on the ability to perform instantaneous quenches that follow a steepest descent path (or alternatively, a conjugate gradient minimization). Since this approach is not experi-

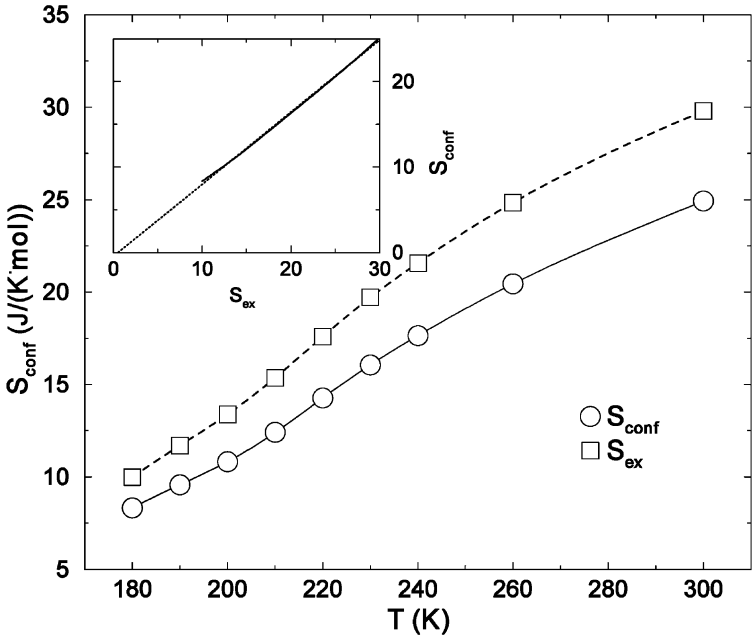

Fig. 2. S_{conf} and S_{ex} at a fixed density $\rho = 1.0$ g/cm^3 for the SPC/E model. The inset shows a parametric plot (solid line) to demonstrate proportionality. Figure redrawn from Ref. [39].

mentally feasible, many experimentalists have exploited the fact that crystalline entropy is vibrational in nature and have approximated $S_{vib} = S_{crystal}$, and hence $S_{conf} \approx S_{ex}$. This approximation has been found to work well in the approach of Adam and Gibbs. However, we do not in general expect that $S_{ex} = S_{conf}$, since it would imply that the liquid and crystalline basins have the same eigenfrequencies (or, loosely speaking, shape) and that the liquid frequencies are invariant [36,50]. Indeed, we see that S_{ex} and S_{conf} differ for the SPC/E model (Fig. 2). Details of the ice simulation are given in Ref. [36]. Hence the successful use of S_{ex} can only be explained if $S_{ex} \propto S_{conf}$, as pointed out in Ref. [51,52]; in such a case, the constant of proportionality can be absorbed into the free parameter of the Adam–Gibbs equation. To test this possibility, we have made a parametric plot of S_{conf} and S_{ex} in the inset of Fig. 2, demonstrating the linear proportionality and hence explaining why S_{ex} can be substituted for S_{conf}.

5. Application of the Adam–Gibbs hypothesis to experimental data

5.1. Estimation of entropy for $T < T_H$

To determine a reasonable form for the entropy $S = S(T, P)$ in the range $T_X < T < T_H$, we first focus on thermodynamic properties that facilitate the calculation of S in the easily-accessible regions $T > T_H$ and $T < T_X$, and whose values also place strict limits on the possible behavior of S in the region $T_X < T < T_H$. Like S_{ex}, all other 'excess' quantities, such as specific heat C_P^{ex} and enthalpy H_{ex}, refer to the difference between liquid and crystalline states. Each of these three quantities is known experimentally for $T > T_H$ as well as $T < T_X$.

In the difficult-to-probe $T_X < T < T_H$ region, we construct two possible forms for S_{ex}. To connect the regions $T > T_H$ and $T < T_X$, we must consider the thermodynamic constraints on the entropy. These constraints are:

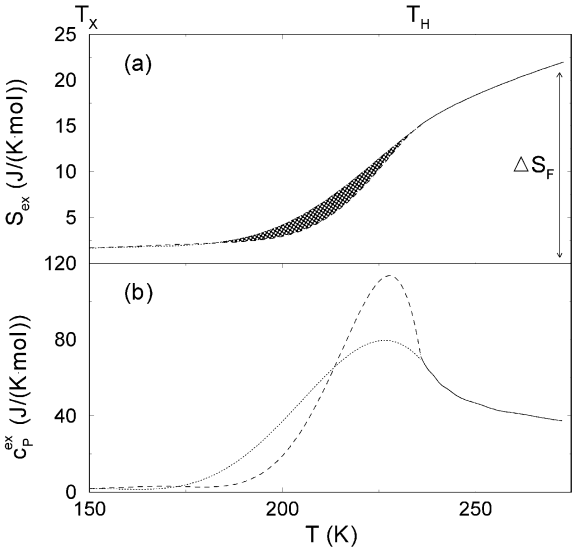

Fig. 3. (a) Possible forms for the excess entropy S_{ex} in the experimentally inaccessible region. The two curves show the fits obtained using the upper and lower bounds on the area under S_{ex}. The entropy of fusion $\Delta S_F = 21.8$ J/(K mol) for freezing at 273 K is indicated by the arrow, (b) Constant pressure excess specific heat $C_P^{ex} = T(dS_{ex}/dT)p$ for the possible forms of S_{ex} shown in (a). Figure redrawn from Ref. [39].

(I–IV) S_{ex} and C_P^{ex} at the endpoints and the slopes of S_{ex} at T_X and T_H—four constraints.
(V) $S(T)$ must be a monotonic increasing function because $C_P^{ex} \geq 0$. Note that this is not a uniquely defined constraint.
(VI) The area A under the curve $S(T)$ is defined by the excess Gibbs free energy G_{ex}.

$$A = [TS_{ex} - H_{ex}]_{T_X}^{T_H}. \tag{9}$$

Our challenge is to determine a functional form for $S_{ex}(T)$, given only its values at the limiting temperatures T_X and T_H, the area A under $S(T)$, and the monotonicity of $S(T)$. Related work on the possibility of a liquid–liquid phase transition [53–69] suggests that $S(T)$ should not contain a discontinuity at atmospheric pressure, and hence we aim to develop a form for $S(T)$ (and its derivatives) that varies continuously [70–72].

We show possible forms of S_{ex} that satisfy the upper and lower bounds on the area constraint of S_{ex} in Fig. 3. These two curves represent approximate bounds on the form of S_{ex} in the unknown region; these bounds are somewhat larger if the uncertainty in S_{ex} is also included. Fig. 3 shows that S_{ex} and C_P^{ex} both display these significant changes in their behavior below 230 K. This is a result of the fact that S_{ex} must remain nearly constant near T_X in order to satisfy the constraint of Eq. (9). The inflection in S_{ex} (Fig. 3) must occur at $T \gtrsim 215$ K; were the inflection to occur at a significantly lower temperature, the area A bounded by $S(T)$ would be too large.

5.2. Prediction of dynamic properties

Having established the legitimacy of the Adam–Gibbs equation, as well as the proportionality between S_{conf} and S_{ex}, we now consider applying the Adam–Gibbs equation to our estimated values for S_{ex} in the deeply supercooled region $T < T_H$.

We select proportionality constants in the Adam–Gibbs equation to fit S_{ex} to η [73,74] and D [75] (Fig. 4) for $T > 235$ K, where experimental measures of all quantities are available. The super-Arrhenius behavior for $T \gtrsim 230$ K is typical for a fragile liquid [12,13]. The maximum in C_P^{ex} (approximately 225 K) is reflected by the inflection of η and D; this change is not clearly evident in η or D until $T \lesssim 190$, where the dynamic properties are approximately Arrhenius. In contrast to the fragile behavior for T close to T_H, the behavior for T near T_X is characteristic of a strong liquid [12,13] which is Arrhenius behavior with an appropriate activation energy. Here we find an activation energy $E \approx 74$ kJ/mol, which converts to a 'fragility index' $m = E/2.303RT_g = 28$, if we use $T_g = 136$ K, or $m = 24$, if we use $T_g = 160$ K, comparable to m for sodium trisilicate (a very strong liquid) [77]. Such a crossover from fragile-to-strong behavior is not typical of liquids [78], but does appear in simulations of BeF_2 and SiO_2 [79,80], which, like water, have a tetrahedral network structure [81]. The value of E is consistent with that obtained experimentally from crystallization kinetics [82–84] expected to correspond to the activation energy of the diffusion constant of the crystallizing phase [85]. However, we point out that these crystallization kinetics-based results

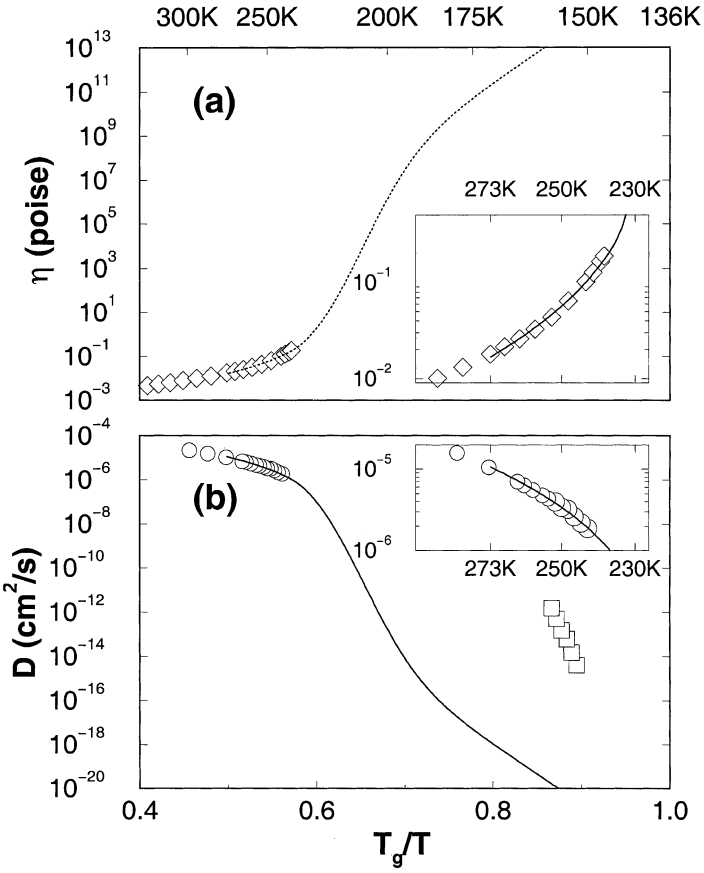

Fig. 4. (a) Fit of S_{ex} and viscosity η. Experimental data (◇) are from [73,74]. Diffusion constant D predicted using the same method. The experimental data (○) for $T>235$ K are from [75]. The data for $T<160$ K (□) are from [76]. (b) Both (a) and (b) show behavior expected for a strong liquid for $T\lesssim 220$ K—i.e. Arrhenius behavior with an activation energy $\approx T_g/3$ (in units of kJ/mol) [12]. The insets show the quality of the fit in the region where experimental data are available. Figure redrawn from Ref. [39].

are in conflict with the evaporation-rate based diffusivity results of Ref. [76], which obtain $E\approx 170$ kJ/mol, indicating that further tests are necessary to determine the properties of water in this region.

For most systems, the value of $\eta(T_g)\approx 10^{13}$ Poise, while Fig. 4a shows that η reaches this value at $T\approx 160$ K, significantly higher than the expected $T_g=136$ K. This may be an indication of the limitations of our approach for estimating dynamic properties. Alternatively, this may be an indication that T_g of water is in fact significantly higher than 136 K. Velikev et al. [41] shows that the thermal data for hyper-quenched glassy water are incompatible with what is known about the relaxation of trapped enthalpy from other hyper-quenched glasses, and that the incompatibility can only be resolved if the data for water are re-scaled using a glass transition temperature of 165–170 K. This roughly coincides with the T_g predicted by Fig. 4. While a simple linear extrapolation of binary aqueous solution data suggests $T_g=136$ K for pure water, linear extrapolations are unreliable if the target substance is a network forming liquid, like water [86]. An alternate extrapolation, applicable to other network forming liquids, suggests

that T_g for water is considerably higher than 136 K [86]. However, this remains a matter of controversy [87].

If the assignment of $T_g \approx 160$ K is correct, then the data used at $T = 150$ K refers to a glassy state, and hence S_{ex} (150 K) would be smaller for an equilibrium state. Fortunately, even if the data at 150 K are out of equilibrium, it does not severely effect our estimates because the value of S_{ex}(150 K) is already extremely small, and further equilibration at the T would only reduce S_{ex} closer to zero. This would result in a slightly more pronounced inflection on S_{ex} than we have anticipated here.

6. Conclusion

We have presented evidence from simulations supporting the use of Adam–Gibbs equation to interpret the dynamics of supercooled liquids. In the case of liquid water, experimental data, when combined with the Adam–Gibbs equation, suggest that water undergoes an unusual fragile-to-strong crossover, which may prove important in technological uses of vitreous water, such as biopreservation. Additionally, we have reviewed results supporting the conjecture that T_g may be significantly higher than previously expected.

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