Glass-Transition Temperature of Water: A Simulation Study

Nicolas Giovambattista,[1] C. Austen Angell,[2] Francesco Sciortino,[3] and H. Eugene Stanley[1]
[1]*Center for Polymer Studies and Department of Physics, Boston University, Boston, Massachusetts 02215, USA*
[2]*Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287, USA*
[3]*Dipartimento di Fisica, Istituto Nazionale per la Fisica della Materia,*
and INFM Center for Statistical Mechanics and Complexity, Università di Roma La Sapienza,
Piazzale A. Moro 2, I-00185 Roma, Italy
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We report a computer simulation study of the glass transition for water using the extended simple point charge potential. To mimic the difference between standard and hyperquenched glass, we generate glassy configurations with different cooling rates, and we calculate the temperature dependence of the specific heat on heating. The absence of crystallization phenomena allows us, for properly annealed samples, to detect in the specific heat the simultaneous presence of a weak prepeak ("shadow transition") and an intense glass transition peak at higher temperature. Our results support the viewpoint that the glass transition temperature is higher than the conventionally accepted value 136 K. We also compare our simulation results with the Tool-Narayanaswamy-Moynihan phenomenological model.

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Much recent research has focused on the properties of glassy water, the most common form of water in the Universe. Water can exist in more than one distinct amorphous form [1,2]. The conversion between different glass structures, the different routes producing glass structures, and the relation between the liquid and the glass phases are under active debate. A particularly relevant aspect of this debate concerns the identification of the glass transition temperature T_g at ambient pressure and the magnitude of the associated jump of the specific heat. Extrapolation of T_g in binary aqueous solutions, in the limit of vanishing solute concentration, provides the estimate $T_g \approx 136$ K [3]. Early differential scanning calorimetry (DSC) studies report conflicting results. Some experiments detect the glass transition [4] but others do not [5]. An exothermal peak in the specific heat of properly annealed hyperquenched water supports the estimate $T_g \approx 136$ K [6], with a specific heat jump of 1.6–1.9 J/mol/K. This T_g value [7,8] has been recently debated [9–11]. It has been suggested [11] that the small peak measured in Ref. [6] is a prepeak typical of annealed hyperquenched samples preceding the true glass transition located at $T_g \approx 165$ K. Assigning $T_g \approx 165$ K would explain some of the puzzles related to the glass transition in water [8,9,11]. The $T_g \approx 165$ K proposal can not be experimentally tested due to the homogeneous nucleation of the crystal phase at $T_\times \approx 150$ K.

Here we report a numerical study of the temperature dependence of the specific heat obtained upon *heating* different glass configurations across the glass-to-liquid transition for the extended simple point charge (SPC/E) model for water. We analyze the effects both of the cooling rate and of annealing ("aging") before heating the glass since both effects are important for determining T_g [12,13]. Both of these effects have been studied extensively in many materials [14,15]. Numerical studies are particularly suited since crystallization does not take place on the time scale probed in simulations. We show that both the shadow and the glass transition peaks can be resolved in the same heating scan. Finally, we compare the simulation results with the Tool-Narayanaswamy-Moynihan (TNM) phenomenological model [14,16,17].

We perform *NVT* molecular dynamics (MD) simulations for a system of $N = 216$ molecules, with periodic boundary conditions. Interactions are cutoff at a distance of $r = 2.5\sigma$, where σ is the length parameter defined in the SPC/E potential, and the reaction field method is implemented. We average quantities over 32 independent trajectories at fixed density $\rho = 1$ g/cm^3. During cooling or heating, T is continuously changed by $\delta T = q\delta t$, where q is the cooling/heating rate, and $\delta t = 1$ fs is the elementary integration time step. The specific heat is measured only during heating the glass configurations. We perform (i) cooling scans at constant cooling rate down to $T = 0$ K, starting from equilibrium liquid configurations at $T = 300$ K, (ii) heating scans at constant heating rate, starting from $T = 0$ K glass configurations, and (iii) aging at constant $T_{\rm age} = 100$ K, where significant aging effects are observed. We study two cooling rates $q_c = -3 \times 10^{10}$ K/s and $q_c = -10^{13}$ K/s, to mimic, respectively, the standard and hyperquenched cooling rates [18], and one heating rate $q_h = +3 \times 10^{10}$ K/s. Slow experimental scan rates are typically ≈ 0.3 K/s, while the slowest simulation scan rate compatible with present computational facilities is 10^{11} times faster ($\approx 3 \times 10^{10}$ K/s). Hence, the temperature at which the system will lose equilibrium on cooling will be significantly higher in simulations than in experiment. The key fact that the structural relaxation time becomes longer than the experimental (or simulation) time is the same

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for experiments and simulations. Therefore, as shown below, while the T_g estimates differ, the T dependence and the phenomenology do not depend significantly on the scan rate. In hyperquench experiments, a cooling rate $10^{5.5}$ times faster than the slow or "standard" rate is usually achieved, while in the present simulations the faster quench rate is approximately 300 times faster than the slower quench rate.

Figure 1 shows the specific heat $C_V(T)$ calculated by differentiating the temperature dependence of the total energy of the system on heating at the rate $q_h = +3 \times 10^{10}$ K/s. The glass configurations are obtained by cooling equilibrium $T = 300$ K liquid configurations at the standard cooling rate $q_c = -3 \times 10^{10}$ K/s. Following the usual experimental protocol, we estimate T_g from the intersection of the two dashed lines in Fig. 1. The resulting value, $T_g = 188$ K, is slightly below the lowest T at which equilibrium simulations can be performed for SPC/E [19–21]. The $C_V(T)$ rise of ≈ 55 J/mol/K is more than an order of magnitude larger than the experimentally measured rise of $\approx$ 1.6–1.9 J/mol/K [12]. For $T \gtrsim 240$ K, $C_V(T)$ coincides with equilibrium data for the SPC/E potential. Indeed, the equilibrium relaxation time of the system for $T \gtrsim 240$ K is $\lesssim 20$ ps, smaller than the characteristic scan time 1 K$/q_h \approx 30$ ps.

We compare in Figs. 2(a) and 2(b) the behavior of $C_V(T)$ on heating two different glasses, the *standard glass* obtained with the cooling rate $q_c = -3 \times 10^{10}$ K/s and the *hyperquenched glass* obtained with the faster rate $q_c = -10^{13}$ K/s. For the hyperquenched glass, $C_V(T)$ develops a valley for $T < T_g$, in agreement with DSC heating scan experiments[11,22–24] [indeed, the plots of $C_V(T)$ in Fig. 2(a) for the heating of the standard and hyperquenched glasses with no aging are remarkably similar to those observed in Fig. 1 of Ref. [23] and the inset of Fig. 1 of Ref. [24]]. The presence of a valley can be related to the descent of the system on the potential energy landscape upon heating with a rate slower than the cooling rate [25].

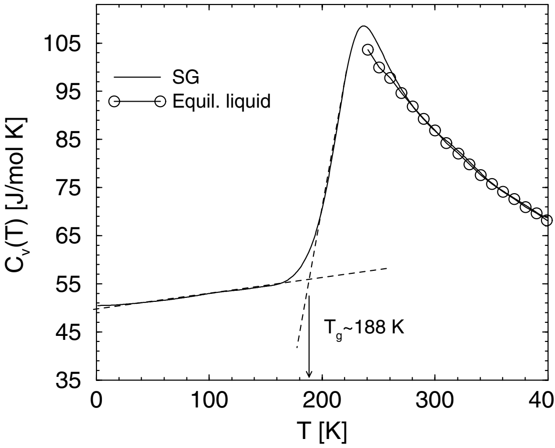

FIG. 1. Specific heat from MD simulations calculated by differentiating the total energy during heating of the standard glass (SG). Circles denote equilibrium values of $C_V(T)$ in the liquid state.

Figures 2(a) and 2(b) show $C_V(T)$ for the heating scan of the hyperquenched glass which has been annealed at

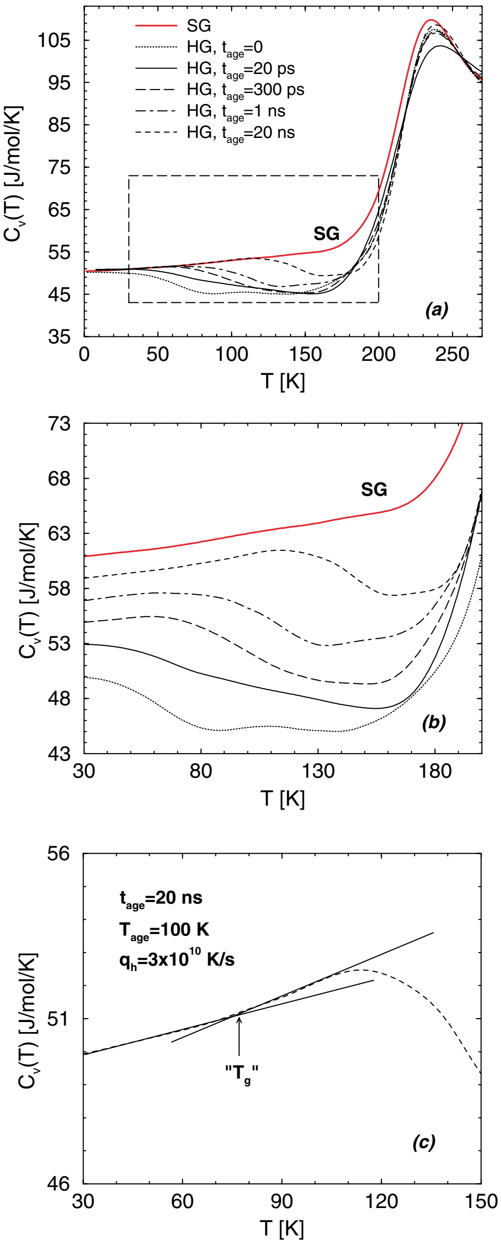

FIG. 2 (color online). (a) T dependence of C_V for heating scans of the standard glass (SG) and the hyperquenched glass (HG). Also shown are the heating scans of the HG that has been annealed at $T_{\mathrm{age}} = 100$ K for four different aging times t_{age}. (b) Magnification of (a). Curves are shifted, for clarity, by 3 J/mol/K (for $t_{\mathrm{age}} = 20$ ps), 5 J/mol/K (for $t_{\mathrm{age}} = 300$ ps), 7 J/mol/K (for $t_{\mathrm{age}} = 1$ ns), 9 J/mol/K (for $t_{\mathrm{age}} = 20$ ns), and 11 J/mol/K (for SG). (c) Magnification of $C_V(T)$ for the hyperquenched glass annealed at $T_{\mathrm{age}} = 100$ K for $t_{\mathrm{age}} = 20$ ns to highlight the weak prepeak at $T \approx 113$ K. The straight lines show a possible construction that, in the absence of the peak at $T \approx 220$ K, could be interpreted as the glass transition temperature "T_g".

$T_{\rm age} = 100$ K for different aging times $0 < t_{\rm age} \leq 20$ ns. This annealing procedure is intended to mimic the experimental annealing procedure [26]. Note that aging reduces the valley in $C_V(T)$ and that, as $t_{\rm age}$ increases, $C_V(T)$ evolves toward the standard glass value (Fig. 1). Inspection of the curves for large $t_{\rm age}$ [Fig. 2(c)] shows that a small prepeak appears at $T \approx 113$ K. If the standard protocol (Fig. 1) for the identification of the glass transition in the specific heat is applied, we obtain $T_g \approx 75$ K [Fig. 2(c)]. The amplitude of the prepeak in $C_V(T)$ at $T \approx 113$ K is of the order of 1–2.5 J/mol/K and is reminiscent of the experimental value 1.6–1.9 J/mol/K obtained in DSC measurements of hyperquenched water after annealing [12]. In the present case, in which crystallization does not interfere with the heating scan, there is no ambiguity in associating this peak with a precursor of the true glass transition, which takes place at a much higher T. To prove that the weak C_V prepeak is outside the noise level, we show in Fig. 3 the T dependence of $\Delta E \equiv E - 6RT$, where E is the total energy per molecule and R is the gas constant. The term $6RT$ is the contribution to E expected for a glass of rigid molecules in the harmonic approximation for the potential energy. The derivative of ΔE with respect to T gives $C_V(T)$ minus the factor $6R$. Therefore, the maximum in ΔE in Fig. 3 confirms that the prepeak in $C_V(T)$ is outside the noise level.

Results presented in Figs. 2 and 3 are consistent with recent anneal-and-scan experiments [11] on hyperquenched inorganic glass, which does not crystallize on heating. Our simulations thus suggest that the measured specific heat peak (Ref. [7]), which has been used to identify T_g, is a prepeak associated with the use of a hyperquenched sample combined with the annealing procedure.

Next, we discuss the possibility of modeling the simulation results using the TNM approach [14,22,26], which is able to model the experimental heating scan of the specific heat for glasses generated with standard cooling rates (although it fails when applied to hyperquenched glasses [23]). The TNM model assumes the response function of the system can be represented by a stretched exponential function with stretching parameter β. It also assumes that the relaxation time τ depends not only on the bath temperature T but also on a fictive temperature T_f which accounts for the out-of-equilibrium condition. Narayanaswamy proposed that τ is related to T_f by

$$\tau(T, T_f) = A \exp\left[\frac{x\Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_f}\right], \qquad (1)$$

where $0 \leq x \leq 1$, Δh^* and A are constants, and R is the ideal gas constant [27]. An alternative relation [28] is offered by the generalization of the Adam-Gibbs expression, which connects, in equilibrium, τ to the configurational entropy S_c. The resulting Adam-Gibbs-Scherer (AGS) expression is

$$\tau(T, T_f) = A' \exp\left[\frac{E_A}{S_c(T_f)T}\right], \qquad (2)$$

where

$$S_c(T) = \int_{T_K}^{T} \frac{\Delta C}{T} dT, \qquad (3)$$

T_K is the Kauzmann temperature, E_A is a constant, and ΔC is the difference between the specific heats of the liquid and the glass. The TNM model requires β as a fitting parameter; additionally, it requires the parameters $(A, x, \Delta h^*)$ for the Narayanaswamy expression or (A', E_A, T_K) for the AGS expression.

Figure 4 compares our MD results during the heating scan of the standard and hyperquenched glass with the predictions of the TNM model using both the Narayanaswamy and AGS expressions for τ. A detailed analysis will be presented elsewhere; here we show that both expressions give satisfactory results only for the standard glass [Fig. 4(a)]. The quality of the fit for the hyperquenched glass is unsatisfactory, as observed in the analysis of experimental data for hyperquenched samples [23], suggesting that in the hyperquenched experiments the aging sample cannot be connected to a liquid at a fictive temperature T_f [25]. It also suggests that the application of the TNM approach for testing the shadow glass transition must be viewed with caution [10].

In summary, we show by a numerical protocol that the complex phenomenology of the glass transition can be reproduced in simulations, notwithstanding the large differences in cooling rates. The TNM model, which describes the experimental specific heat for the standard cooling rate, also describes the corresponding simulation results. One advantage of simulations is to shed light on phenomena that occur outside the experimentally accessible region [30]. Our simulations show that the glass transition is characterized by a large specific heat peak, and when hyperquenched samples are annealed, the glass

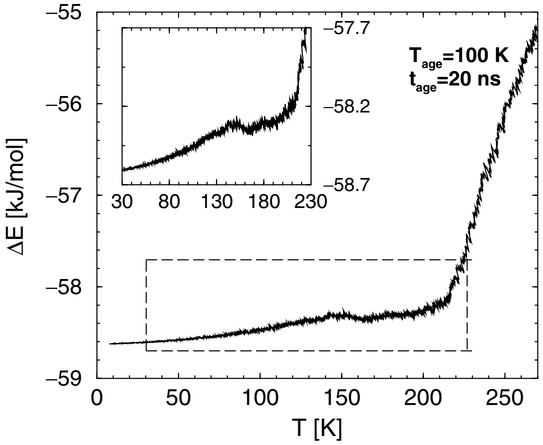

FIG. 3. T dependence of $\Delta E \equiv E - 6RT$, where E is the total energy per molecule, R is the gas constant, and $6RT$ is the total energy of a glass of rigid molecules in the harmonic approximation, contributing a constant $6R$ to C_V. Using ΔE instead of E amplifies the very weak signal, whose derivative is responsible for the weak peak in C_V shown in Fig. 2(c).

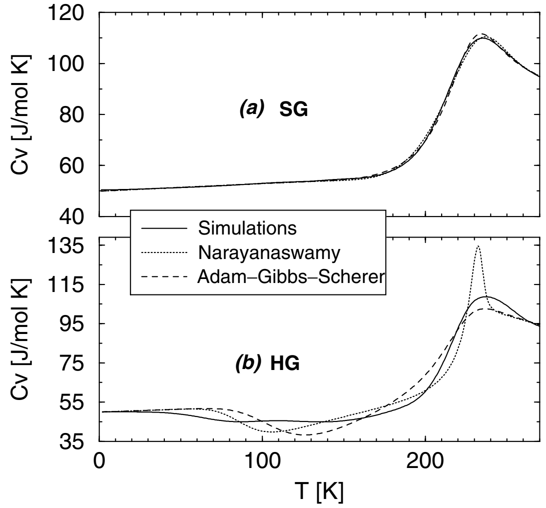

FIG. 4. Heating scans from the (a) standard glass (SG) and (b) hyperquenched glass (HG). Our simulations are compared with the predictions of the TNM model using both the Narayanaswamy expression (fitting parameters for the SG are $\ln(A/ns) = -22.36$, $\beta = 0.525$, $x = 0.635$, and $\Delta h^*/R = 4632$ K) and the Adam-Gibbs-Scherer expression (fitting parameters for the SG are $\ln(A/ns) = -9.86$, $\beta = 0.519$, and $E_A = 27\,626$ kJ/mol; we use S_c from Ref. [29] and hence we do not require T_K). We see that the TNM model describes the behavior of $C_V(T)$ for the SG but fails for the HG.

peak is anticipated at lower T by a prepeak with a much lower amplitude. Our work supports the recent reinterpretation of experimental data [11], which identifies 136 K as the temperature of the prepeak and suggests ≈ 165 K as the "true" glass transition temperature. We stress how similar the highly nonlinear transition phenomenon studied here is to the typical experimental glass transition, notwithstanding the fact that the present study is made above such significant temperatures as the mode coupling temperature and the crossover temperature at which the liquid dynamics are thought to change character [31]. This encourages optimism that problems in glass science can be studied using MD methods, despite the enormous time scale gap.

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