Glass-Transition Temperature of Water: A Simulation Study

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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 \( T_g \approx 136 \text{ K} \) [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 \( T_g \approx 136 \text{ K} \) [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 \( T_g \approx 165 \text{ K} \). Assigning \( T_g \approx 165 \text{ K} \) would explain some of the puzzles related to the glass transition in water [8,9,11]. The \( T_g \approx 165 \text{ K} \) proposal cannot be experimentally tested due to the homogeneous nucleation of the crystal phase at \( T_N \approx 150 \text{ K} \).

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 \( \sigma \) 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 \( \rho = 1 \text{ g/cm}^3 \). During cooling or heating, \( T \) is continuously changed by \( \Delta T = q \Delta t \), where \( q \) is the cooling/heating rate, and \( \Delta t = 1 \text{ fs} \) 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 \( T = 0 \text{ K} \), starting from equilibrium liquid configurations at \( T = 300 \text{ K} \), (ii) heating scans at constant heating rate, starting from \( T = 0 \text{ K} \) glass configurations, and (iii) aging at constant \( T_{age} = 100 \text{ K} \), where significant aging effects are observed. We study two cooling rates \( q_c = -3 \times 10^{10} \text{ K/s} \) and \( q_c = -10^{13} \text{ K/s} \), to mimic, respectively, the standard and hyperquenched cooling rates [18], and one heating rate \( q_h = +3 \times 10^{10} \text{ K/s} \). Slow experimental scan rates are typically \( =0.3 \text{ K/s} \), while the slowest simulation scan rate compatible with present computational facilities is \( =10^{11} \text{ times faster} \). 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.
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 $\approx 55$ 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 $T \approx 240$ K, $C_V(T)$ coincides with equilibrium data for the SPC/E potential. Indeed, the equilibrium relaxation time of the system for $T \approx 240$ K is $\approx 20$ ps, smaller than the characteristic scan time $1$ K/$q_h = 30$ 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].

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

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.

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 $T_{age} = 100$ K for four different aging times $t_{age}$. (b) Magnification of (a). Curves are shifted, for clarity, by $3$ J/mol/K (for $t_{age} = 20$ ps), $5$ J/mol/K (for $t_{age} = 300$ ps), $7$ J/mol/K (for $t_{age} = 1$ ns), $9$ J/mol/K (for $t_{age} = 20$ ns), and $11$ J/mol/K (for SG). (c) Magnification of $C_V(T)$ for the hyperquenched glass annealed at $T_{age} = 100$ K for $t_{age} = 20$ 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 “$T_g$”.
transition in the specific heat is applied, we obtain
standard protocol (Fig. 1) for the identification of the glass
of the true glass transition, which takes place at a much
after annealing [12]. In the present case, in which crys-
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tained in DSC measurements of hyperquenched water
Inspection of the curves for large $t_{\text{age}}$ [Fig. 2(c)] shows
that a small prepeak appears at $T = 113$ K. If the stan-
dard 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 $T = 113$ K is of the order of 1–2.5 J/mol/K and is remi-
niscent of the experimental value 1.6–1.9 J/mol/K ob-
tained in DSC measurements of hyperquenched water
after annealing [12]. In the present case, in which crys-
tallization 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
$\Delta E$ with respect to $T$ gives $C_V(T)$ minus the factor $6R$.
Therefore, the maximum in $\Delta E$ 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 hyper-
quenched inorganic glass, which does not crystallize
on heating. Our simulations thus suggest that the mea-
sured 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 simu-
lation 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 $\beta$. It also
assumes that the relaxation time $\tau$ 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 $\tau$ is related to $T_f$ by

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

where $0 \leq x \leq 1$, $\Delta h^*$ 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 expres-
sion, which connects, in equilibrium, $\tau$ to the configura-
tional entropy $S_c$. The resulting Adam-Gibbs-Scherer
(AGS) expression is

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

where

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

$T_K$ is the Kauzmann temperature, $E_A$ is a constant, and
$\Delta C$ is the difference between the specific heats of the
liquid and the glass. The TNM model requires $\beta$ 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 $\tau$. 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 dif-
fferences 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 acces-
sible 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 $\Delta E = E - 6RT$, 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 $\Delta E$ instead of $E$ amplifies the very weak signal, whose derivative is responsible for the weak peak in $C_V$ shown in Fig. 2(c).](image-url)
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 ‘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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[18] For experiments that compare the behavior of normal and hyperquenched glasses, it is useful [9] to define a ‘standard scan’ as one in which the cooling rate at which the glass is formed and the heating rate at which its glass transition is studied are the same and yield an ‘onset heating’ $T_g$ (and also fictive temperature $T_f$), at which the enthalpy relaxation time is the standard glass transition value 100 s [C.A. Angell, Chem. Rev. 102, 2627 (2002)]. In laboratory studies, this is obtained for a cooling/heating rate $q = \pm 0.33$ K/s. In our simulations, a useful standard scan is one with $q = \pm 3 \times 10^2$ K/s, being the slowest rate at which data can be acquired in reasonable computing times. The $T_g$ endotherm then has a form typical of the general experimental phenomenon. The relaxation time (obtained from the intermediate scattering function) at $T = 190$ K, i.e., just above $T_g$, is $3 \times 10^{-7}$ s [19]. Our fastest quench rate is $q_c = -10^{15}$ K/s. Being only $10^{15}$ faster than the standard cooling rate, this restricts the strength of the shadow transition that we are able to see relative to experiment, where the fastest and slowest cooling rates differ by a factor of $\approx 10^{15}$.
[27] In fact, Eq. (1) corresponds to Narayanaswamy’s original equation rewritten by Moynihan et al. [14], who introduced the parameter $x$.