

Role of Quantum Effects in the Glass Transition

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It is shown that quantum effects lead to a significant decrease of the glass transition temperature T_g with respect to the melting temperature T_m , so that the ratio T_g/T_m can be much smaller than the typical value of $2/3$ in materials where T_g is near or below ~ 60 K. Furthermore, it is demonstrated that the viscosity or structural relaxation time in such low temperature glass formers should exhibit highly unusual temperature dependence, namely a decrease of the apparent activation energy upon approaching T_g (instead of traditional increase).

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The glass transition is usually considered to be a high temperature phenomenon, wherein super-cooling of a liquid below its melting temperature T_m leads to the formation of a nonequilibrium amorphous solid at the so-called glass transition temperature T_g [1,2]. Quantum effects, on the other hand, are believed to play an important role only at very low temperatures where they are known to significantly affect the properties of glasses at temperatures below 10 K [3]. In this Letter we show that quantum effects such as tunneling can significantly broaden the super-cooled liquid regime in low temperature glass formers by decreasing the ratio T_g/T_m from its well known classical value of $2/3$ [4]. They can also lead to an unusual temperature dependence of the viscosity or structural relaxation time τ_α , wherein a *decrease* in apparent activation energy (defined as the slope of $\log\tau_\alpha$ vs $1/T$) can occur upon lowering the temperature of the liquid toward T_g . This trend is opposite to the behavior of the relaxation time in normal glass forming liquids where the apparent activation energy ubiquitously increases upon cooling.

It has been known for some time that quantum effects can play a role in melting of small clusters [5]. Moreover, recent simulations of Lennard-Jones systems suggest that quantum effects might play a role in the dynamics of glass forming liquids and can either slow down or accelerate the dynamics [6,7]. Simulations also suggested that quantum effects might play a role in diffusion of water molecules at ambient temperature [8,9]. Recently, a quantum effect on the thermally activated glide of dislocations was found [10]. It was shown that zero-point vibrations ease dislocation motion below typically half the Debye temperature. All these results raise an important question—can quantum effects play any role in the glass transition of real systems?

We present a simple quantitative analysis that indeed predicts a significant role of quantum effects in the glass transition of low- T_g liquids. This effect becomes important when the ratio of T_g to the Debye temperature θ_D is lower than ~ 0.5 . We start our analysis from a simple

consideration of the mean-squared atomic displacements (MSD) $u^2(T)$, which are known to play an important role in the solid-liquid transition. The Lindemann criterion of crystal melting states that the MSD at T_m is a universal portion of the average interatomic distance, about 0.12–0.15 [11]. In supercooled liquids, a few theories and experiments predict that the temperature dependence of τ_α is determined solely by the MSD [12–15]. Traditionally, only the thermally induced atomic displacements are considered in these works. However, zero-point vibrations of atoms that arise due to the quantum fluctuations also contribute to u^2 . In this paper we consider the role of this zero-point MSD in the glass transition, namely, in the value of T_g and in the temperature dependence of the structural relaxation time.

To estimate the relative amplitude of zero-point displacements, we focus on vibrational MSD. The latter can be represented as a sum of two terms, $u^2 = u_T^2 + u_0^2$, where u_T^2 corresponds to thermal fluctuations, and u_0^2 to quantum fluctuations, wherein [16]

$$u_T^2(T) = \frac{1}{M} \int \frac{g(\omega)}{\omega} n(\omega, T) d\omega \quad (1)$$

and

$$u_0^2 = \frac{1}{2M} \int \frac{g(\omega)}{\omega} d\omega. \quad (2)$$

Here, $g(\omega)$ is the vibrational density of states, M is molecular mass, and $n(\omega, T) = (\exp(\hbar\omega/k_B T) - 1)^{-1}$ is the temperature dependent Bose factor. In the Debye model $g(\omega) = 3\omega^2/\omega_D^3$, $u_0^2 = \frac{3\hbar}{4M\omega_D}$, and at high T , $u_T^2 \approx 3k_B T/M\omega_D^2$. Here, $\omega_D = c_D(6\pi^2\rho)^{1/3}$ is the Debye frequency, ρ is particle number density, $c_D = (\frac{3}{c_l^{-3} + 2c_t^{-3}})^{1/3}$ is the Debye sound velocity, and c_l and c_t are the longitudinal and transversal sound velocities, respectively. It can be seen from the above expressions for thermal and zero-point MSD that the fraction of the zero-point contribution to the

total MSD in the Debye model depends only on the ratio $\frac{T}{\theta_D}$ (where $k_B\theta_D = \hbar\omega_D$). Analysis of the ratio $\frac{u^2(T)}{u_0^2}$ in the Debye model (Fig. 1) suggests that thermal and zero-point contributions to the total MSD become comparable at $\frac{T}{\theta_D} \sim 0.5$. Thus, one can expect a significant influence of quantum effects on the glass transition when $T_g/\theta_D < 0.5$.

We note that the relative importance of the quantum effects at a temperature T is quantified by the dimensionless parameter Λ^* , which is the ratio of the thermal wavelength $\frac{\hbar}{\sqrt{k_BMT}}$ to the particle size a . As the thermal wavelength increases, Λ^* increases and the significance of quantum behavior also increases. Λ^* is related to the de Boer parameter Λ as $\Lambda^* = (\epsilon/k_B T)\Lambda$ where ϵ is the well depth of the pair potential [5]. Λ is useful for comparing the degree of the quantum character of different liquids at a given temperature. It can be shown that under some assumptions (Debye model of vibrational density of states and the Lindemann criterion applied to the glass transition) $\Lambda^* = \frac{\gamma}{3} \frac{\theta_D}{\sqrt{T_g T}}$, where $\gamma = (u^2(T_g)/a^2)^{1/2} \approx 0.12-0.15$ is the Lindemann parameter [11]. In particular, at the glass transition $\Lambda^*(T_g) = (\gamma/3)\theta_D/T_g \approx 0.05\theta_D/T_g \approx 0.2\frac{u_0^2}{u^2(T_g)}$. Then the condition $\theta_D/T_g > 2$ or $\frac{u_0^2}{u^2(T_g)} > 0.5$ roughly corresponds to $\Lambda^*(T_g) > 0.1$. This estimate agrees with the simulation data [Fig. 2(a) in Ref. [6]] predicting sizable quantum effects in diffusion of a supercooled liquid in this range of Λ^* .

It is known that glasses and supercooled liquids have an excess of low frequency vibrational modes in comparison to the Debye model known as the so-called boson peak [17]. Although these vibrations constitute only 5–10% of the total $g(\omega)$, they may contribute a larger fraction to the MSD because of the factor $1/\omega$ in Eqs. (1) and (2). In

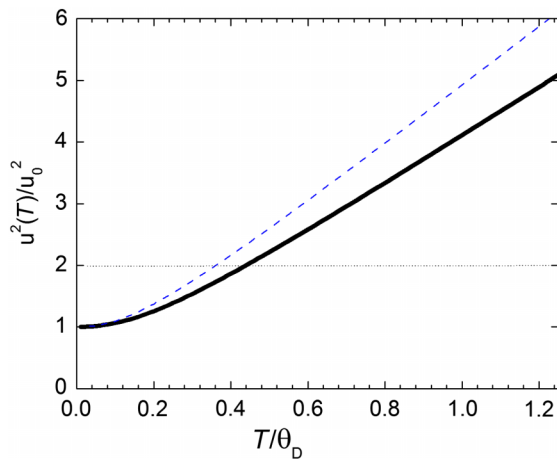


FIG. 1 (color online). The ratio of the MSD to its zero-point part in the Debye model (solid line) and in the Debye model + boson peak (dashed line). The dotted horizontal line marks the value when thermal MSD is equal to zero-point MSD.

addition, at $T > \theta_D$, $n(\omega) \sim T/\omega$, which contributes an additional factor $1/\omega$ for the thermal MSD, so in this temperature range the relative contribution to MSD from the boson peak may be even more significant. Thus, the presence of the boson peak partially reduces the relative fraction of the zero-point MSD. A simple model of the boson peak, in which it is presented by a log-normal function, shows that in the prototypical glass former glycerol the condition $u_0^2 = 0.5u^2$ is reached at about 20% lower temperature than in the Debye model without the boson peak vibrations (Fig. 1). In what follows we will neglect this difference. However, we discuss the effects of the boson peak in more detail in the Supplemental Material, Ref. [18].

One of the most interesting questions is how the quantum effects influence the temperature dependence of the structural relaxation. Structural relaxation in most glass forming liquids exhibits non-Arrhenius behavior with a monotonic increase of the apparent activation energy (the slope of $\log\tau_\alpha$ vs $1/T$) upon approaching T_g ; i.e., $\log\tau_\alpha$ vs $1/T$ is a convex curve. It is known that quantum effects lead to a decrease of the activation barriers, e.g., via the Wigner correction to the classical rate [19]. This might lead to an unusual temperature dependence of the relaxation time at low enough T . To estimate this effect, we consider a simple model. Multiple experimental, theoretical, and simulation studies demonstrated that the temperature dependence of τ_α can be related to the temperature dependent MSD as $\tau_\alpha \propto \exp[\text{const}/u^2(T)]$ [12–14]. The most recent analysis [15] suggested that a universal expression for $\log\tau_\alpha$ can be obtained, such that

$$\log\tau_\alpha = a_0 + a_1 u_g^2/u^2(T) + a_2 (u_g^2/u^2(T))^2, \quad (3)$$

with $a_0 = -11.922$, $a_1 = 1.622$, and $a_2 = 12.3$ (assuming $\log\tau_\alpha(T_g) = 2$). In Eq. (3) the third term in the right-hand side arises by taking the average of the local α -relaxation time $\tau_{\alpha\text{loc}} \propto \exp[\text{const}/u^2(T)_{\text{loc}}]$ over a Gaussian distribution of local mean-square displacements $u^2(T)_{\text{loc}}$ due to spatial heterogeneities [15]. The connection of the viscosity or structural relaxation time to MSD [Eq. (3)], was originally derived based on a thermal activation mechanism of relaxation. The quantum tunneling gives additional contribution to the structural relaxation. It can be shown (Supplemental Material, Ref. [18]) that considering $u^2(T)$ in Eq. (3) as the *total* MSD, including contribution of zero-point vibrations, takes roughly into account the quantum tunneling effect.

Let's estimate a possible influence of zero-point vibrations on T_g . In the classical case $u^2(T_{g\text{class}}) = bT_{g\text{class}}$ where the factor b is determined by the elastic properties of the glass. Assuming that MSD at T_g for the given material should be a constant, the addition of zero-point vibrations should lead to a depression of T_g so that

$$u_0^2 + bT_g = bT_{g\text{class}}. \quad (4)$$

Assuming the usual classical relation between $T_{g\text{class}}$ and the melting temperature T_m , $T_{g\text{class}} \sim AT_m$, where $A \approx 2/3$, Eq. (4) can be rewritten as $u_0^2/b + T_g = AT_m$. In the Debye model of vibrations $u_0^2/b = \theta_D/4$. This leads to a simple relationship between T_g and T_m of the system:

$$\frac{T_g}{T_m} = \frac{A}{1 + \frac{B}{T_g}} \approx \frac{A}{1 + \frac{\theta_D}{4T_g}}, \quad (5)$$

where $B = \frac{u_0^2}{b}$. In real systems the parameter B might depend on the strength of the Boson peak and some other parameters. The Eq. (5) predicts that quantum effects should lead to a significant decrease of the ratio T_g/T_m with decreasing T_g/θ_D .

We were unable to find enough experimental data on θ_D for low-temperature supercooled liquids to check the relation (5) between T_g/T_m and θ_D/T_g . However, we note that variations of θ_D in different materials are small relative to changes of T_g or T_m . For example, atomic θ_D is about 260 K [20] for B_2O_3 ($T_g = 526$ K), 492 K [20] for silica ($T_g = 1420$ K), 317 K [21] for glycerol ($T_g = 186$ K), 207 K [22] for ortho-terphenyl ($T_g = 243$ K), and 254 K [23] for 1-butanol ($T_g = 111$ K). This follows also from the classical relation between T_m and θ_D given by the Lindemann criterion of melting. At the melting point the thermal MSD, $3\hbar^2 T_m / M k_B \theta_D^2$, is a fixed fraction of a^2 , so $T_m \propto \theta_D^2$; i.e., θ_D varies slower than T_m . Thus in rough approximation we can consider the parameter B in Eq. (5) as only weakly material dependent, $B = \alpha \bar{\theta}_D$ where $\bar{\theta}_D$ is a typical Debye temperature of molecular liquids and α is a dimensionless constant.

Analysis of the literature data in molecular and hydrogen-bonding glass formers indeed reveals the predicted strong decrease in the T_g/T_m ratio for materials with T_g below ~ 60 – 80 K (Fig. 2). It can be seen in Fig. 2 that in materials with T_g above ~ 100 K, the T_g/T_m ratio retains the classical value in the range ~ 0.5 – 0.8 , but it drops to much lower values for materials with T_g below 50 K. Moreover, Eq. (5) provides a reasonable qualitative description for the behavior of T_g/T_m (Fig. 2) with best fit parameters $A \approx 0.8$ and $B \cong \alpha \bar{\theta}_D \approx 65$ K which corresponds to a reasonable value of $\bar{\theta}_D$ for $\alpha = 0.3$ – 0.5 . These results suggest that quantum effects can indeed play a significant role in reducing the glass transition temperature in low- T_g materials.

Using Eq. (3) with $u^2(T)$ calculated in the framework of the Debye model including zero-point MSD, we have calculated the relative influence of quantum effects on the temperature variations of τ_α [Fig. 3(a)]. At relatively high T_g ($T_g/\theta_D = 2$), when quantum effects are negligible (Fig. 1), Eq. (3) predicts normal behavior for $\log \tau_\alpha$ vs $1/T$, i.e., a monotonic increase of the slope (apparent activation energy) with decreasing temperature. However, unusual behavior is predicted for low- T_g materials. Surprisingly,

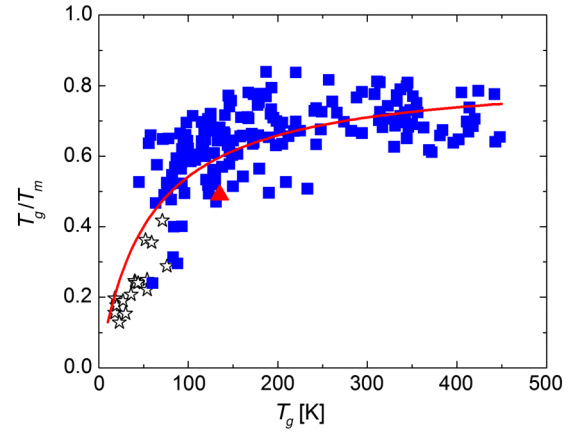


FIG. 2 (color online). The dependence of the ratio T_g/T_m on T_g in molecular and hydrogen-bonding glass formers (symbols). The triangle presents water. The line is the fit by the expression (5). All the materials, respective data, and sources of the data are listed in the Supplemental Material, Ref. [18]. Stars correspond to the estimates of T_g from Ref. [1] of the Supplemental Material.

one can observe a clear decrease in the apparent activation energy upon approaching T_g when the ratio T_g/θ_D is approximately 0.2–0.3 [Fig. 3(a)].

The fragility index m has been widely used to characterize the steepness of $\log \tau_\alpha$ vs T_g/T at T_g [24], such that

$$m = \left. \frac{\partial \log \tau_\alpha}{\partial (T_g/T)} \right|_{T=T_g}. \quad (6)$$

Fragility for most of nonpolymeric materials usually varies in the range $m \sim 20$ – 100 , and reaches ~ 150 – 180 in some polymers [25]. Equation (3) predicts fragility $m \sim 24$ for the high T_g materials. This number is reasonable for the so-called “strong” systems where vibrational contribution dominates $u^2(T)$ [26]. However, for materials with $T_g/\theta_D = 0.2$ and 0.3 , Eq. (3) predicts a drop in the fragility index to unusually low values $m \sim 10$ and ~ 16 , respectively [Fig. 3(a)]. To the best of our knowledge, bulk supercooled liquids with such low fragility have not yet been discovered. We emphasize once again that the shape of the $\log \tau_\alpha$ vs T_g/T curve for systems with small ratios T_g/θ_D turns from convex to concave; i.e., the apparent activation energy (the slope of $\log \tau_\alpha$ vs $1/T$) starts decreasing upon approaching T_g (Fig. 3).

To verify how general this prediction is, we consider another example that does not involve the Debye model. We analyze the experimental data for $\log \tau_\alpha$ [27] and $u^2(T)$ [22] of the fragile (i.e., with highly non-Arrhenius behavior in the supercooled region) glass former ortho-terphenyl (OTP). We emphasize that we don’t expect any quantum effects in OTP, we use these data to present a hypothetical fragile liquid. $\log \tau_\alpha$ calculated using experimental data for $u^2(T)$ in OTP [22] [inset, Fig. 3(b)] and Eq. (3) agrees well with the experimental results for $\log \tau_\alpha$ [Fig. 3(b)].

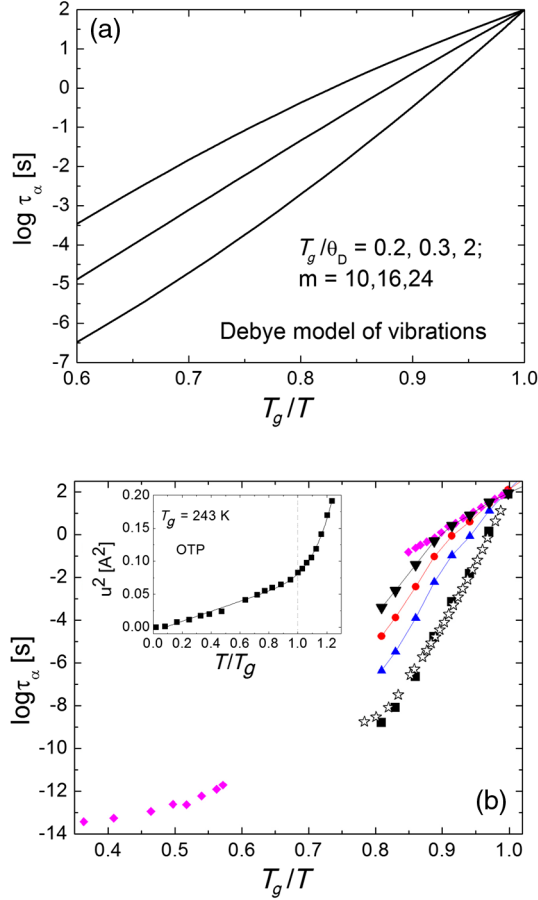


FIG. 3 (color online). (a) $\log \tau_\alpha$ estimated according to the universal Eq. (3) 15 in the Debye model for various ratios T_g/θ_D . (b) Stars: experimental data for $\log \tau_\alpha$ of orthoterphenyl 27 (fragility $m = 70$); squares: $\log \tau_\alpha$ obtained from the experimental data for u^2 of OTP 22 (see inset) using the Eq. (3). Down triangles, circles, and up triangles: $\log \tau_\alpha$ of a model system obtained by artificial increase of zero-point contribution u_0^2 in the total MSD $u^2(T)$ of OTP with $u_0^2 = 0.8u^2(T_g)$, $0.7u^2(T_g)$, and $0.5u^2(T_g)$, respectively. Corresponding fragilities are 19, 22, and 33. Diamonds: viscosity of water [29] shifted by an arbitrary parameter.

This agreement justifies the use of Eq. (3). As the next step, we artificially increased the contribution of zero-point MSD to the total $u^2(T)$. We considered three cases: (i) $u_0^2 = 0.8u^2(T_g)$; (ii) $u_0^2 = 0.7u^2(T_g)$, and (iii) $u_0^2 = 0.5u^2(T_g)$. So obtained $u^2(T)$ together with Eq. (3) were used to estimate $\log \tau_\alpha$ vs T_g/T [Fig. 3(b)]. The same unusual behavior is also observed in this approximation. Quantum effects lead to a significant decrease of the fragility index. Moreover, calculated $\log \tau_\alpha$ shows a kind of fragile-to-strong crossover behavior [28], i.e., decreasing slope of $\log \tau_\alpha$ vs T_g/T dependence with decreasing temperature. Most importantly, this analysis reveals the same decrease in the apparent activation energy upon approaching T_g [Fig. 3(b)]. Thus, regardless of the model approximation, our analysis predicts that quantum effects will lead

to unusual temperature dependence of structural relaxation time upon approaching T_g .

We are not aware of any glass forming systems that show the predicted behavior, but we did not find any relaxation data for the low- T_g materials. However, the predicted behavior (Fig. 3) might provide new explanation for anomalous behavior expected for the supercooled water [28,29]. It is known [28,29] that high temperature relaxation behavior of bulk water cannot be extrapolated to the glass transition region ($T_g \sim 136$ K [29,30]). The apparent activation energy of the water relaxation time should decrease upon approaching T_g [29]. There are many papers speculating about possible Fragile-to-Strong crossover in supercooled water as the mechanism that might lead to the reduction of the activation energy [31–33]. Here we note that water can be a good candidate for observation of the quantum effects in the glass transition because it has a very light molecule. Computer simulations already showed that molecular diffusion in liquid water can be enhanced by a factor of about 1.5 due to quantum effects [8], although recent paper [9] predicts this factor less by $\sim 20\%$. Figure 2 shows that water, with its $T_g/T_m \sim 0.5$, actually appears in the range where quantum effects might be measurable close to T_g . Using the density of vibrational states for low-density ice measured at 115 K [34] and Eqs. (1) and (2), we estimate the zero-point MSD amplitude in water at $T = 136$ K as $u_0^2 \sim 0.4$ of the total MSD. Thus, quantum fluctuations indeed might significantly affect dynamics of water at T_g .

In Fig. 3(b) we compare water viscosity data from Ref. [29] (shifted by a constant value vertically in order to superimpose with the relaxation time data) and relaxation time of the OTP and hypothetical model fragile system described above. At high temperatures (no quantum effects), OTP and water have similar temperature dependence in the Angell plot [29], but close to T_g water has much lower fragility than OTP. One can see that behavior of water in the vicinity of T_g coincides with that of the hypothetical model system that is based on adding artificial zero-point MSD to the total $u^2(T)$ of OTP [Eq. (3)] with the amplitude $u_0^2 \sim 0.8u^2(T_g)$. There are many measurements of relaxation in confined water [30,35,36]. These data also show behavior qualitatively similar to the one predicted in the Fig. 3. In particular, unusually low fragility $m \approx 14$ was reported for confined water in Ref. [36]. Thus the quantum effects might play a role in the unusual behavior in water.

The presented analysis suggests that quantum effects such as tunneling may significantly influence the temperature dependence of the structural relaxation time in low- T_g glass-forming materials. Quantum effects should lead to unusual temperature variations of structural relaxation. The rate of these variations (the slope of $\log \tau_\alpha$ vs $1/T$) should decrease upon approaching T_g , while it only increases in most glass formers. In other words, while all

usual glass forming liquids show only convex behavior of $\log\tau_\alpha$ vs $1/T$, quantum effects will lead to a crossover from convex to concave behavior of $\log\tau_\alpha$ upon approaching T_g (Fig. 3). As a result, the glass transition range becomes significantly broader, and the ratio T_g/T_m decreases significantly. The latter indeed has been observed experimentally (Fig. 2). However, we are not aware of direct experimental evidence of the herein predicted temperature variations of structural relaxation time (Fig. 3). Studies of low- T_g glass forming liquids will provide direct tests of the proposed scenario.

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