Origin of the $T^{1+\alpha}$ dependence of the heat capacity of glasses at low temperature

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We address the issue of the experimentally observed deviation of the heat capacity of glasses from linearity at low temperatures $T \sim 1$ K. The energy spectrum of an anharmonic oscillator in a double-well potential is calculated, using parameters from recent molecular dynamics simulations of two-level systems in silica glass. A model that accounts for the contribution of more than two lowest-energy levels of a single anharmonic oscillator to the heat capacity at $T \sim 1$ K is proposed and is shown to describe the experimentally observed $\propto T^{1.3}$ behavior of the heat capacity of silica glass.

All glasses show anomalous behavior of the heat capacity C at low temperatures ~ 1 K, seen as an additional contribution to the Debye law[1] (Fig. 1). This contribution is explained in the model of two-level tunneling-states,[3] which assumes that certain objects in the glass move in double-well potentials (DWP's), giving rise to two-level tunneling states. It has been difficult to identify the existence of DWP's in glasses using atomistic simulations, which has contributed to the growth of a literature doubting their existence. Recently, we performed molecular dynamics (MD) simulations of silica glass[4,5] and have found that it can maintain large-amplitude reorientations of several tens of connected SiO$_4$ tetrahedra. We suggested that these motions are those giving rise to the two-level tunneling states of Ref. 3.

In this work we use the insights into the nature of DWP's in silica glass gained in Refs. 4 and 5, including the size of participating objects, barrier height, and hopping frequency, to address another issue related to the observed anomalous heat capacity at low temperature. In the model of two-level tunneling states,[3] the heat capacity for a single tunneling state, C_0, is calculated assuming that at low temperature the dynamics in the two-level system (TLS) includes only transitions between the two lowest-energy levels E_1 and E_2. Since topological disorder in the glass results in the presence of DWP's with different parameters, and hence different values of E_1, E_2, the heat capacity is derived by averaging C_0 with the density of two-level states:

$$C = \int C_0(\Delta E) n(\Delta E) d(\Delta E) = \frac{\pi^2}{6} k_B^2 n(0) T, \qquad (1)$$

where $\Delta E = E_2 - E_1$, and $n(0)$ is the density of states at $\Delta E \sim 1$ K, which is assumed to be approximately constant in the range of ΔE.[3] According to Eq. (1), the contribution to the heat capacity due to two-level tunneling states is linear with temperature. However, experimentally the dependence of C on T at low temperature shows a deviation from linearity as $\propto T^{1+\alpha}$, where for silica glass, $\alpha = 0.3$ (see Fig. 1). No generally accepted explanation exists so far for this deviation.[2]

In this paper we show that deviation from linearity may be explained if the dynamics of the object in DWP's in glass involves transitions between more than two lowest-energy

levels at $T \sim 1$ K. We start by numerically finding the energy spectrum of a single anharmonic oscillator, using the range of model parameters from our recent MD simulation of DWP's in silica glass, as well as from experimental data.[4,5] The low-lying part of calculated spectrum of symmetric anharmonic oscillators is a set of close pairs of energy levels. Using this property of the spectrum, we analytically derive the expression for the energy and show that our model predicts the observed $\propto T^{1.3}$ behavior of the heat capacity.

We start by noting that the difference between the two lowest-energy levels of the object in a DWP constructed from the superposition of two harmonic wells is given by

$$\Delta E = 2\hbar\omega \sqrt{\frac{2V}{\pi\hbar\omega}} \exp(-d\sqrt{2MV}/\hbar), \qquad (2)$$

where M is the mass of the object, ω is the oscillation angular frequency for one harmonic well, V is the barrier height, and $2d$ is the separation between two minima, such that $V = \frac{1}{2} M\omega^2 d^2$ (see, for example, Ref. 6). Expression (2) is derived in the approximation $d\sqrt{2MV}/\hbar \gg 1$, and hence ΔE is very sensitive to the object's mass M. As mentioned earlier,
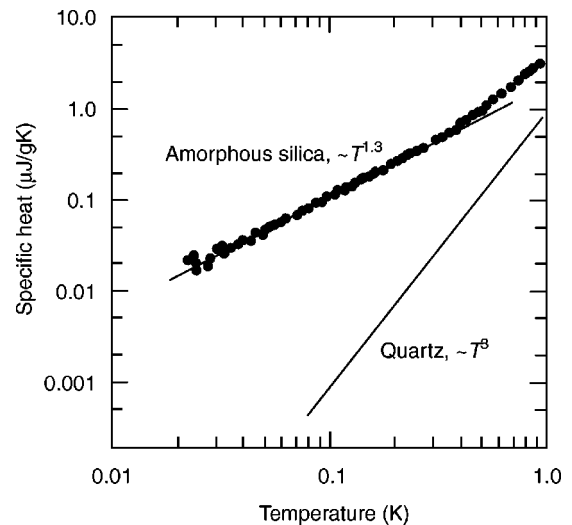

FIG. 1. Specific heat of silica glass and quartz as a function of temperature (from Ref. 2).

we have seen that the object moving in DWP's in silica glass consists of several tens of connected SiO_4 tetrahedra,[4,5] giving a mass that is larger by an order of magnitude than is usually assumed. Larger values of M lead to a substantial decrease of ΔE, and the energy levels that are next to the first pair are expected to lower, so that they start getting excited at ~1 K and hence contribute to the heat capacity. To demonstrate this, we need to derive the energy spectrum of anharmonic oscillators explicitly.

An alternative Hamiltonian that describes an object moving in a DWP is

$$H = -\frac{\hbar^2}{2M}\frac{d^2}{dq^2} + M\omega^2 q^2 + A\exp(-\gamma q^2), \qquad (3)$$

where q is the coordinate, M is the object's mass, ω is the angular frequency of oscillation in the harmonic well when $A=0$, and A and γ are parameters that determine the form of the DWP. The matrix elements of Hamiltonian (3) using harmonic oscillator basis functions are

$$H_{mn} = \delta_{mn}\hbar\omega\left(n + \frac{1}{2}\right) + AV_{mn},$$

$$V_{mn} = \frac{1}{\sqrt{\pi 2^{n+m}n!m!}}\int e^{-(1+\hbar\gamma/M\omega)x^2}H_n(x)H_m(x)dx,$$

where $H_n(x)$ are Hermite polynomials.[7] The integral of V_{mn} exists in analytical form as a function of $\xi = 1 + \hbar\gamma/M\omega$. Note that the reason for choosing the DWP in the form of Eq. (3) is that it is essentially harmonic at higher values of energy. Using harmonic oscillator basis functions, the anharmonicity in Eq. (3) becomes a vanishing perturbation at higher energy values, which results in good convergency of energy values as the size of the Hamiltonian matrix increases.

We introduce the barrier height V and a requirement that the energy minima of DWP's be separated by a certain distance d, thus reducing the model parameters to M, V and ν, where $\nu = \omega/2\pi$. The range of these parameters can be chosen using our recent MD simulations of silica glass,[4,5] in which the motions in DWP's involve several tens of connected SiO_4 tetrahedra, with typical values of atomic jumps from one minimum to another of about 1 Å, giving us the range of values M and d. We choose the upper limit of V at 0.05 eV, consistent with our estimations from MD.[4,5] The upper limit of ν may be estimated by noting that the motion in DWP's, being a soft potential, does not involve any distortions of SiO_4 tetrahedra. The mode that can propagate without SiO_4 units having to distort is called a rigid unit mode (RUM), and we have previously found that the structure of silica glass is essentially RUM floppy.[4,5] From a comparison of calculated and experimental dynamic structure factors in silica glass, we have found that the frequencies of the RUM's spread from zero up to the boson peak at ~1 THz.[5] Values of ν are determined by the superposition of RUM's with different frequencies ν_i, leading to the appearance of modes with frequencies that start from $\min|\nu_i - \nu_j|$.
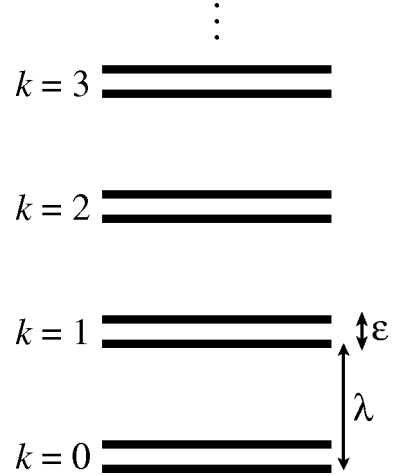

FIG. 2. Schematic representation of the low-lying part of the energy spectrum $\{E_k\}$ of symmetric anharmonic oscillators.

For each set of (M,V,ν), we numerically diagonalize H_{mn}. We find that in the range of model parameters considered, the values of the lowest-energy levels converge well with increasing size of H_{mn}. We are interested in whether the range of parameters (M,V,ν) requires that more than the two lowest-energy levels give a contribution to the heat capacity at ~1 K. This would be true if

$$\lambda = E_3 - E_1 \approx k_B T_0, \qquad (4)$$

where E_1 and E_3 are first and third energy levels, and T_0 ~1 K. By varying the values of (M,V) at a given value of ν we have found that the condition (4) can be satisfied within the range of parameters described above, with the value of ν up to ~0.1 THz. The latter value of ν is consistent with the one we derive from constructing the profile of the potential energy over the jump event.

We find that within the considered range of model parameters, the structure of the low-lying part of the energy spectrum can be well approximated as a set of close pairs of levels, with the energy difference within a pair ϵ significantly smaller than the distance between different pairs λ, $\epsilon \ll \lambda$ (see Fig. 2). Such a structure of the energy spectrum of symmetric anharmonic oscillators was noted in Ref. 7. It is also consistent with the structure of the spectrum derived using the potential of two superimposed harmonic wells, if the object's mass is large.[6] The latter condition is given as $d\sqrt{M\omega/\hbar} \geq 4$ (Ref. 6) and is well satisfied for values of M,V,ν in the considered range.

We now derive the energy of the glass arising from the spectrum of energy levels shown schematically in Fig. 2, assuming that λ~1 K:

$$E = \int E_0(\{E_k\})n(\{E_k\})dE_1 \cdots dE_N, \qquad (5)$$

where E_0 is the energy of a single anharmonic oscillator, and $n(\{E_k\})$ is the density of states of the configuration $\{E_1, \ldots, E_N\}$.

As was noted above, within the range of considered model parameters, the low-lying part of the energy spectrum

can be represented in terms of ϵ and λ (see Fig. 2). Thus E_0 becomes a function of ϵ and λ only, and the energy can be written as

$$E = \int E_0(\epsilon, \lambda, N) n(\epsilon, \lambda) d\epsilon \, d\lambda, \qquad (6)$$

where $n(\epsilon, \lambda)$ is the density of states that yields the energy spectrum with the structure shown in Fig. 2 and parameters ϵ and λ. For N pairs of energy levels in the spectrum, the partition function is

$$Z = \sum_{k=0}^{N-1} \exp(-\beta k \lambda)[1 + \exp(-\beta \epsilon)]$$

$$= [1 + \exp(-\beta \epsilon)] \frac{1 - \exp(-N\beta\lambda)}{1 - \exp(-\beta\lambda)}, \qquad (7)$$

where $\beta = 1/k_B T$. Formally the summation in Eq. (7) should be extended to infinity, but in what follows we preserve N as a parameter for reasons that become apparent later. E_0 is given as

$$E_0 = E_{01}(\epsilon, \beta) + E_{02}(\lambda, \beta, N), \qquad (8)$$

where

$$E_{01}(\epsilon, \beta) = \frac{\epsilon}{\exp(\beta\epsilon) + 1} \qquad (9)$$

and

$$E_{02}(\lambda, \beta, N) = \frac{\lambda}{\exp(\beta\lambda) - 1} - \frac{N\lambda}{\exp(N\beta\lambda) - 1}. \qquad (10)$$

Since E_0 can be written as a sum of two terms, each of them separately dependent on ϵ and λ, the integration (6) is easily performed as it splits into two separate terms:

$$E = \int E_{01}(\epsilon, \beta) n(\epsilon) d\epsilon + \int E_{02}(\lambda, \beta, N) n(\lambda) d\lambda. \quad (11)$$

At low temperature, $k_B T \sim \epsilon$, only the first term in Eq. (11) is significant, since $\epsilon \ll \lambda$ (note that this condition has not been used until now) and, as will be shown later, the integrand in the second term in Eq. (11) is significant only when $k_B T \sim \lambda$. The integration over ϵ can be done by extending the range of ϵ from zero to infinity, since the dependence of E_{01} on ϵ in Eq. (9) is well centered around $\tilde{\epsilon} \approx 1.3 k_B T$. For this reason the behavior of $n(\epsilon)$ is not important in the range beyond $\tilde{\epsilon}$. As the line of argument in Ref. 3, we assume that $n(\epsilon)$ is approximately constant for the contributing states. Because $\tilde{\epsilon} < \Delta E \sim 1$ K, we can set $n(\tilde{\epsilon}) \approx n(0)$, where $n(0)$ is the density of states introduced in Eq. (1). The energy at $k_B T \sim \epsilon$ is

$$E_\epsilon = \int_0^\infty E_{01}(\epsilon, \beta) n(\epsilon) d\epsilon = \frac{\pi^2}{12} n(0) k_B^2 T^2. \qquad (12)$$

The resultant heat capacity is identical to Eq. (1) and corresponds to the case when only the lowest-energy pair is accessible to the system.
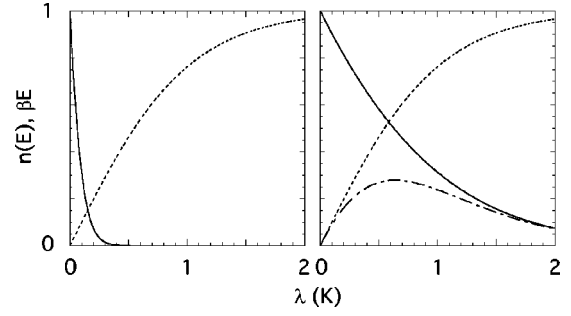

FIG. 3. Left shows a $n(\lambda)$ (dashed line) and $E_{02}(\lambda, \beta, N=\infty)$ (solid line) for low temperature (high β). The product is vanishingly small, leading to a negligible contribution to the energy, Eq. (11). The right side shows the same $n(\lambda)$ (dashed line), but with $E_{02}(\lambda, \beta, N=\infty)$ at a temperature of around 0.5 K (solid line). The product of the two is very similar to $E_{02}(\lambda, \beta, N=2)$ at the same temperature (chain curve).

As $k_B T$ becomes comparable with λ, the contribution from the second term in Eq. (11) becomes significant. To evaluate the integral over λ, we note that, similar to E_{01}, E_{02} has a well-defined maximum for finite N. Indeed, $E_{02}(\lambda, \beta, N=2) = E_{01}(\lambda, \beta)$, and the peak position decreases slowly with N, remaining around $\lambda \approx k_B T$ for several N. Thus for finite N the integration over λ in Eq. (11) can be carried out in the same manner as over ϵ above. For $N=\infty$, E_{02} has its maximum value of 1 at $\lambda=0$. On the other hand, we find from the calculated energy spectra of Eq. (3) that all sets of physical model parameters give $n(\lambda) \rightarrow 0$ for $\lambda < \tilde{\lambda} \approx 1$ K and give $n(\lambda)$ constant for $\lambda > \tilde{\lambda}$. Qualitatively this may be understood by noting that the value of ω^2 in Eq. (3) has a natural lower limit. This imposes the limit on the separation between different energy pairs and hence λ (in the case of harmonic oscillators, the corresponding level separation is simply proportional to ω), thus suppressing the states with small values of λ. That $n(\lambda) \rightarrow 0$ when $\lambda < \tilde{\lambda}$ means that the product $E_{02}(\lambda, \beta, N=\infty) n(\lambda)$ in Eq. (11) is centered around $\tilde{\lambda}$. Therefore for $N=\infty$ the integration over λ can also be carried out in the same way as over ϵ. Note that $\tilde{\lambda} \approx 1$ K corresponds to the system with effective two energy pairs contributing at 1 K. Thus we can write $E_{02}(\lambda, \beta, N=\infty) n(\lambda) = E_{02}(\lambda, \beta, N=2) n(\tilde{\lambda})$. From calculations we find $n(\tilde{\lambda}) \approx n(\tilde{\epsilon})$, and the energy at $k_B T \sim \lambda$ is then given as

$$E = E_\epsilon + \int_0^\infty E_{02}(\lambda, \beta, 2) n(\tilde{\lambda}) d\lambda = \frac{\pi^2}{6} n(0) k_B^2 T^2. \quad (13)$$

The main point is illustrated in Fig. 3. At low temperature, the product of $E_{02}(\lambda, \beta, N=\infty)$ and $n(\lambda)$ is small for all λ, so that the contribution to the energy, Eq. (11), is negligible. In this limit, the TLS model[3] is a good approximation. At higher temperatures, the product of $E_{02}(\lambda, \beta, N=\infty)$ and $n(\lambda)$ is peaked at a nonzero value of λ and could be said to resemble the form of $E_{02}(\lambda, \beta, N=2)$ at the same temperature (or indeed, if appropriate, the same function for slightly
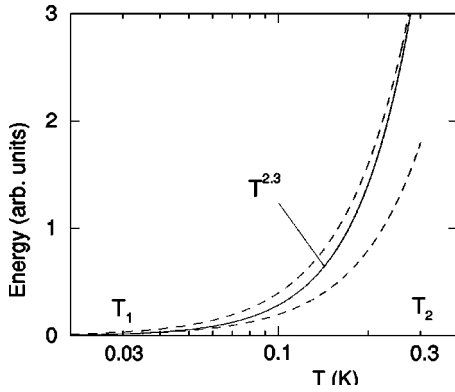
FIG. 4. Energy as a function of temperature (solid line) varying as $T^{2.3}$, shown as a crossover between two parabolas χT^2 and $2\chi T^2$ (dashed lines) in the range $T_1 = 0.03$ K and $T_2 = 0.3$ K.

higher values of N). Thus the energy function crosses over from the TLS function to something resembling the state with N pairs of energy levels.

Based on Eqs. (12) and (13), the observed deviation of the heat capacity from linearity can be described as follows. As the temperature increases from ϵ to λ, the energy deviates from the parabola $E = \chi T^2$ to $E = 2\chi T^2$, where $\chi = (\pi^2/12)n(0)k_B^2$. This is shown schematically in Fig. 4. In the crossover regime between $T_1 \sim \epsilon$ and $T_2 \sim \lambda$ we might expect to find the energy $\propto T^{2+\alpha}$. We have $(T_2/T_1)^{2+\alpha} = 2(T_2/T_1)^2$ or $\alpha = \log 2/\log(T_2/T_1)$. From Fig. 1, $T_2/T_1 \approx 10$ and we obtain $\alpha = 0.3$ (see Fig. 4). The resultant form $E \propto T^{2.3}$ leads to the heat capacity varying as $\propto T^{1.3}$. This is exactly as is seen in Fig. 1, and thus we conclude that the proposed model correctly describes the experimentally observed behavior of heat capacity. This argument has been

supported by numerical calculations using a form of $n(\lambda)$ that gives $n(\lambda)E_{02}(\lambda,\beta,N=\infty) \sim E_{02}(\lambda,\beta,N=2)$ at 0.5 K, resulting in a crossover from $E \propto T^2$ to $E \propto T^{2.3}$ at $T \sim 0.1$ K.

Before concluding, we discuss what effect the asymmetry of DWP's may have on our model. Generally, the asymmetry changes the structure of energy levels, Fig. 2, with the separation between two lowest-energy pairs equal to

$$\Delta E = \sqrt{\epsilon^2 + \Delta_0^2}, \tag{14}$$

where Δ_0 is the potential asymmetry, and ϵ is the tunneling contribution. Due to isotropic atomic arrangements in glass, the density of states $n(\Delta_0)$ with asymmetry between Δ_0 and $\Delta_0 + d\Delta_0$ is equal for positive and negative Δ_0. Together with the condition that $n(\Delta_0)$ be a monotonous function which decreases as $|\Delta_0|$ increases, since $|\Delta_0|$ is limited by its maximum value in glass, this means that there is a nonzero number of states with $\Delta_0 \sim 0$. Since $\epsilon \ll 1$ K, the typical values of ϵ are below 0.1 K, and the values of asymmetry up to 0.1 K would not have a significant effect on the value of separation between two lowest-energy levels (14), as well as on the overall structure of energy spectrum in Fig. 2 and, hence, on our model.

In summary, we have addressed the issue of the nonlinearity of the heat capacity of glasses at low temperature ~ 1 K. We have shown that within the range of parameters that describe the DWP's in silica glass, more than two lowest-energy levels need to be taken into account when calculating the heat capacity at ~ 1 K. We have proposed a model that accounts for the contribution of higher-energy levels and describes the experimentally observed $\propto T^{1.3}$ behavior of the heat capacity.

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