Tunneling and interaction effects in two-level systems in glasses studied by atomistic simulations

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We use molecular dynamics simulations to characterize low-energy two-level systems (TLS) in glasses. We estimate that in silica glass, TLS parameters are broadly distributed in such a way that the tunnel splitting is in the 0.01–1 K range. We also observe simultaneous atomic jumps in different TLS below 30 K and suggest that this is evidence of strong interaction between TLS below this temperature scale.

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Experiments, accumulated in the past few decades, suggest that some properties of low-temperature glasses and amorphous solids do not depend on their chemical composition and microscopic structure, i.e., such properties are universal. For example, below 1–5 K many glasses show an additional (relative to crystals) linear-in-temperature contribution to heat capacity[1] of comparable magnitude. A particular universality is seen for many glasses having (almost) constant ratio of the phonon wavelength to its mean free path.[2] In order to explain low-temperature thermal and acoustic properties of glasses, the so-called standard model has proposed the existence of noninteracting two-level systems (TLS).[3] At low (~1 K) temperatures, two-level energy states, formed due to the quantum tunneling of an object between the two minima of double-well potential (DWP), were suggested to be the origin of anomalous thermal properties of glasses. Many properties, including linear-in-temperature specific heat, thermal conductivity, and many linear and nonlinear sound absorption properties, were consistently described in the framework of the standard model.[4] The standard model is a phenomenological theory which so far did not find a systematic theoretical justification. Namely, the microscopic origin of TLS in various glasses and, more importantly, the generic universality of low-temperature properties remain a deep open problem.

At the microscopic level, the main open question remains as to what is the nature of two-level systems in a glass. Previous molecular dynamics (MD) simulations have found that silica glass, a prototypical glass system, can support large cooperative atomic motions in DWP, which involve coupled displacements and rotations of several, on the order of ten, SiO_4 tetrahedra[5] [see Fig. 1(b)]. If M is the mass of an object in DWP, D is the value of jump, and V is the activation barrier, the tunnel splitting is[6]

$$\Delta = 2\hbar\omega\sqrt{\frac{2V}{\pi\hbar\omega}}\exp(-D\sqrt{2MV}/\hbar). \quad (1)$$

A natural question arises, given that a TLS object consists of several (up to ten) tetrahedra, some of which move large 0.6–0.8 Å distances,[5] whether such an object can actually tunnel and hence contribute to the anomalous low-temperature properties, as the standard model predicts. In order to apply Eq. (1), one needs to (1) reliably estimate the value of activation barrier V, and (2) find a suitable way to calculate the tunnel splitting in a situation where there is a field of atomic displacements, d_i, each corresponding to a different atomic mass m_i, rather than a single value of D.

The difficulty in the reliable estimation of tunnel splitting, the role of elastic interactions between TLS, and the absence of *direct* experimental confirmation of tunneling states have led to questioning of their existence altogether.[7] The nature of TLS (tunneling or otherwise) in the presence of strong elastic interactions between TLS is even less understood.[7] In this paper, we perform extensive MD simulations of silica glass to extract the microscopic parameters needed to calculate tunnel splitting. We estimate that these parameters are distributed in glass in such a way that some TLS can tunnel at ~1 K, whereas for others, $\Delta \ll 1$ K.

In addition, we address the question of interaction between TLS. Despite many successes of the standard model, an apparent shortcoming has become evident throughout the years. As formulated, the standard model assumes that TLS do not interact. Yet irradiation experiments have shown that TLS interact strongly through strain fields of the solid,[9] and that universal properties appear as a consequence of saturation from the strong interactions between bare defects. Another recent experiment indicated that, perhaps, nonlinear acoustic properties[10] cannot be understood in the framework of noninteracting TLS. A more general theory, as may be perceived, should take into account the interaction among TLS through strain fields, although quite different versions of such a theory were suggested. For many scenarios,[7,8] one of the difficulties is how to explain how strongly interacting TLS are responsible for the well-known nonlinear as well as linear universal properties of sound absorption. An important task for MD simulations is therefore to look for the evidence of interaction between TLS and attempt to estimate its strength. If, for example, the interaction is strong, TLS cannot be considered independent as originally proposed in the standard model, and a system may have qualitatively different properties. In this paper, we find that the effects of interaction between TLS can be seen at as high temperature as 30 K.

In this work, we use the silica glass as a case study. We

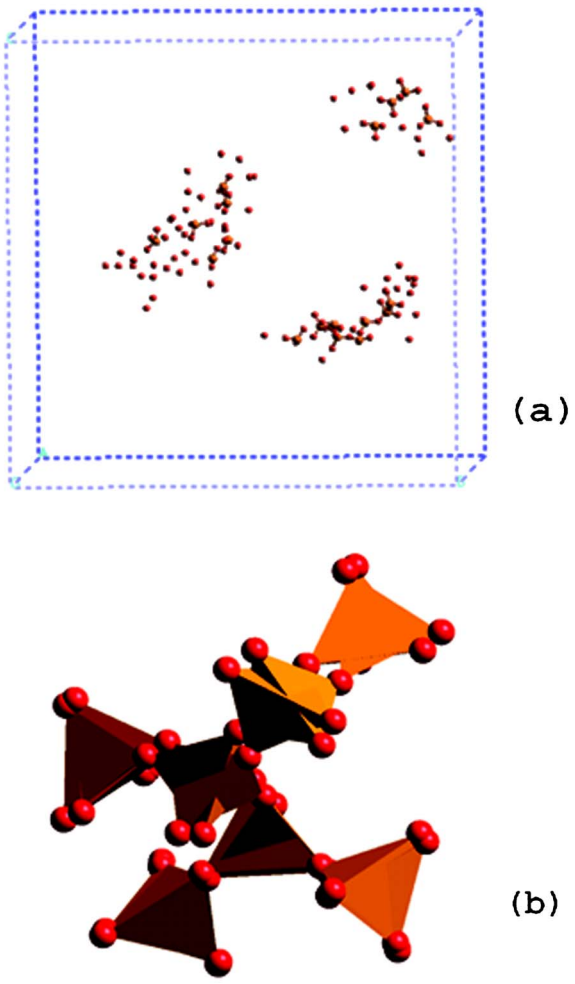

FIG. 1. (Color online) An example of two-level systems in the MD simulation (a), and jump motion in a single TLS (b). Initial and final configurations are superimposed in (b) to highlight the amplitude of atomic jumps.

work with several different glass structures containing fully connected 4096 tetrahedra, and use the highly successful Tsuneyuki interatomic potential.[11] Other details, using simulation method, preparation of glass structures, etc. are given in earlier publications.[5]

We begin by estimating an activation barrier V. The classical MD simulations allow the observation of the rattling of atoms in local minima as well as rare thermally activated hopping of several tetrahedra; therefore, corresponding rattling and hopping frequencies can be estimated directly (see Figs. 2 and 3). The rattling oscillation frequency, ν_0, in one potential well, and ν, the frequency of hopping between two minima, are related as

$$\nu = \nu_0 \exp(-V/kT). \quad (2)$$

In previous MD simulations, only one or two events were observed due to the reduced ability to simulate longer time scales.[5] More recently, this obstacle has been overcome, and we can observe enough hopping events in order to calculate V from Eq. (2).

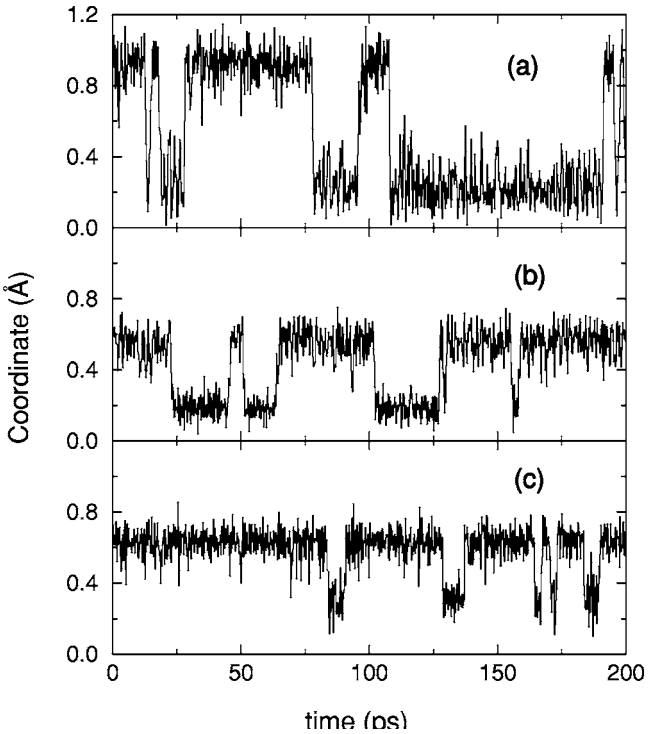

FIG. 2. Typical trajectories of central atoms in different TLS, showing larger ~0.6–0.8 Å (a) and (b) and smaller ~0.3–0.4 Å (c) jumps. For convenience in comparison, the coordinates of atoms are shifted by constant values. The simulation temperature is 50 K.

We simulate glass structures at five different temperatures in the 10–100 K range. We identify TLS in glass structure as clusters of atoms which experience large jumps. Figure 1(a) shows three representative TLS in the MD simulation box. In each of them, we find, as in the previous studies,[5] large-amplitude atomic jumps, which correspond to (nearly) rigid rotations and displacements of several connected SiO_4 tetrahedra [see Figure 2(b)] (the animations of TLS motion can be found at www.esc.cam.ac.uk/~kot/glass.html).

In each TLS, we identify "active" atoms as those for which the difference between the average positions before and after jump exceeds the double of the amplitude of ther-

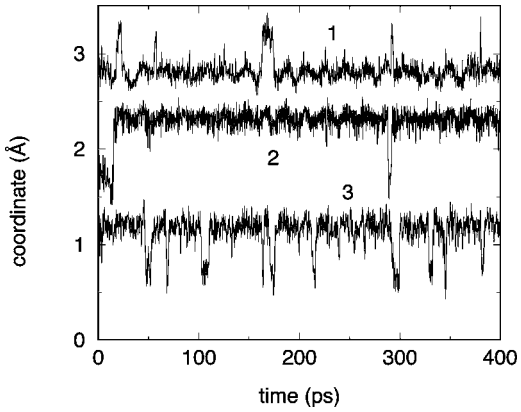

FIG. 3. Atomic coordinates of central atoms from three different TLS. For convinience in comparison, the coordinates of atoms are shifted by constant values. The simulation temperature is 30 K.

mal vibrations. In each TLS, we call an atom with the largest atomic jump a "central" atom. In Figs. 2 and 3, we show representative trajectories of central atoms from several different TLS in the simulation at two different temperatures, 30 and 50 K. In each TLS, the trajectories of other atoms follow the pattern of the central atoms, i.e., show jumps at the same moments of time, albeit with smaller amplitudes. We find that jumps of central atoms in different TLS are distributed in the range 0.3–0.8 Å (see Fig. 2).

Since jump motion is generally irregular (see Figs. 2 and 3), we define the average jump period τ in a given TLS as the total simulation time divided by half the number of transitions between two minima. It follows from Eq. (2) that $\tau=\tau_0\exp(V/kT)$, where $\tau_0=0.7$ ps is the average period of oscillation in one well. Next, we average τ over different TLS to sample different trajectories of atomic jumps. This gives $\tau=43$ ps and 107 ps for simulations at 50 and 30 K, respectively, and the average value of barrier $V\approx 178$ K. We note that V is calculated from the hopping frequency ω in one TLS. If TLS interact (which is indeed the case, as will be shown below), ω can differ as compared to the case of an isolated TLS. In this sense, the calculated values of V and hence Δ are "renormalized" (from their values in a single isolated TLS) to effectively account for the interaction between TLS. We also note that although the current system size does not allow us to simulate enough TLS to calculate the distribution of barriers in different TLS, the calculated value of V is consistent with the maximum of distribution found from the analysis of the potential energy landscape of silica.[12]

Next, we consider how to calculate tunnel splitting of an object that consists of atoms with different masses, each jumping different distance [see Figure 1(b)]. One way of doing this is to calculate the effective mass M_e,

$$M_e=\sum_i m_i(d_i/D)^2, \tag{3}$$

where D is displacement of the central atom, and m_i and d_i are masses and displacements of all other atoms in a TLS. Tunnel splitting is then calculated from Eq. (1) by using the values of M_e and D. Basing on the results of Ref. 13, Eq. (3) has been recently employed to calculate tunneling probability of cooperative motion of atoms in metals.[14] We note that this involves certain assumptions that result in Eq. (3) being an approximation (in particular, it is interesting to clarify to what extent it accounts for various effects of TLS-phonon coupling).

For a given TLS, we use Eq. (3) to calculate M_e by summing over active atoms (defined above) in that TLS. For several different TLS that have D in the range 0.3–0.8 Å, we find that the range of M_e is 100–400 amu, corresponding to approximately one to five coupled SiO_4 tetrahedra. This number is consistent with the participation ratio calculated from the analysis of silica potential energy landscape.[12] We note, however, that the landscape analysis results in a different insight about the nature of TLS: it finds that TLS move along one-dimensional chains.[12] On the other hand, in the present and earlier MD simulations,[5] we find that TLS are best viewed as three-dimensional clusters [see Figure 1(b)].

For each TLS, we use its D and the corresponding M_e to calculate Δ according to Eq. (1). Using $V=178$ K, we obtain the range of Δ between 0.01 K and 0.8 K. This simulation gives, therefore, an interesting result: it identifies TLS with smaller D ($D\approx 0.3$–0.4 Å), and M_e that give $\Delta\approx 1$ K. This means that the tunneling of these TLS is the dominant process at 1 K, as originally assumed in the standard model. TLS with larger D and M_e, on the other hand, are passive in terms of contributing to anomalous thermal properties at 1 K. A future study, of course, should calculate the distribution of D and M_e in different TLS.

We now address the issue of interaction between TLS. There is no general recipe of how to calculate the interaction energy from the MD simulations. However, if, as assumed, TLS interact through the strain fields,[7] the interaction depends on the "alignment" of strain induced by the motion of one TLS and the path along the jump (reaction path) of another TLS. If strong enough, the interaction can be observed in the MD simulation as simultaneous jumps of atoms in different TLS. Simultaneous jumps are expected to be more pronounced at low temperature, since large thermal motion destroys coherence of jumps in time at high temperatures. Hence an estimate of the interaction energy can be obtained from the typical temperature at which correlated atomic jumps in different TLS start to appear.

At 50 K, we observe only one simultaneous jump in two TLS shown in Figs. 2(b) and 2(c) during the simulation period, at 130 ps. At 30 K, we observe more simultaneous jumps. In Fig. 3, we show the atomic coordinates of three central atoms at 30 K, each taken from different TLS. It is seen that TLS 1 and 2 experience simultaneous jumps at 20 ps and 290 ps, TLS 1 and 3 at 170, 290, and 380 ps, and TLS 2 and 3 at 290 ps. All three TLS jump at 290 ps.

The degree of correlation between two TLS, f_{ij}, can be quantified as $n_{\mathrm{cor}}/min(n_i,n_j)$, where n_i and n_j are the numbers of jumps in each TLS, and n_{cor} is the number of simultaneous jumps. As defined, f varies from 0 to 1 from the case of absence of simultaneous jumps to the case when all jumps are simultaneous. From Fig. 3 we find that f is in the range 0.7–1 for different pairs of TLS, suggesting that the correlation is significant.

We note that the frequency of hopping events is low enough (especially the frequency of events in TLS 1 and 2, see Fig. 3), so that jump simultaneity is noncoincidental. In principle, this frequency may be reduced even further by reducing the simulation temperature; however, this encounters the problem that at low temperature hopping events are not excited during the time scale of MD simulations, as discussed below. We further note that there is a tradeoff in defining an optimal simulation temperature at which simultaneous jumps are best seen. On one hand, at high ($\geqslant$50 K) simulation temperature, we observe enough jumps to study their correlation in time, but the temperature appears to be high enough to destroy jump simultaneity. On the other hand, one could hope to see more simultaneous jumps at lower ($\leqslant$20 K) temperature. However, at 10 and 20 K, we do not observe hopping events during the simulation period of up to 0.5 ns. This is consistent with the estimation that if $V=178$ K, the average hopping period, $\tau_0\exp(V/kT)\approx 5.1$ ns at 20 K, which exceeds the time scale currently available in our MD simulations.

The scale of interaction energy found above (30–50 K) is consistent with an estimate based on general grounds. A crude estimate compares elastic dipolar interactions $[\gamma^2/(\rho c^2)](1/R^3)$ between coarse-grained subvolumes of the size R and the elastic excitation energy of subvolume (or phonon energy) $\hbar c/R$,[7] where $\gamma \sim 1$ eV is the deformation coupling constant, ρ and c are the density and sound velocity correspondingly. The crossover length scale and energy scale are $\xi \sim \gamma/\sqrt{\rho h c^3} \sim 10^{-7}$ cm and $E_\xi \sim (\hbar c)/\xi \sim 50$ K, using typical values of $\rho = 1$ g/cm^3 and $c = 5 \times 10^5$ cm/s. Roughly the same length scale ξ is associated with medium-range order and the onset of strong scattering for phonons (Ioffe-Mott crossover), while the energy scale E_ξ is of the order of the boson peak.[15]

The appearance of correlated jumps in different TLS at 30 K suggests that interaction energy is large enough to be taken into account by the models that consider low-temperature universal behavior of glasses. Taking the density of TLS extracted from the specific heat measurements $P = 10^{33}$ (erg cm^3)$^{-1}$,[4] we can estimate crudely an average distance, r_{av}, between TLS which are distributed in the energy window, δE, of 10 K. This estimate, $P = [\delta E (4\pi/3) r_{\mathrm{av}}^3]^{-1}$, gives a typical distance of 63 Å which is close to the value of 30–40 Å we found in our simulations. Given that the interaction energy from the simulation is 30 K, and that interactions depend on distance in the dipolar manner, the larger distance in the experiment still results in interaction energy that is significant at low temperature.

A possible consequence of strong interactions between TLS is that the low-energy degrees of freedom should be viewed as collective modes rather than local independent tunneling systems (it should be noted that in the presence of strong interactions, the energy spectrum becomes strongly mixed, and the question whether the low-energy excitations are two-level tunneling states loses its precise meaning). One example of such a picture is a phenomenological theory which ascribes anomalous low-energy states to collective modes.[16] Due to the presence and interaction between TLS, glass network is not stiff on short length scales since the strain can relax by the TLS motion; hence, the shear modulus can be significantly smaller on short length scales. Such an assumption is sufficient to show that the collective states associated with interacting defects contribute to sound absorption, as well as to linear-in-temperature specific heat.

To conclude, the present simulation has allowed us to (1) estimate that microscopic parameters of TLS are distributed in glass in such a way that some TLS tunnel at ~ 1 K (and hence may be relevant low-energy states), whereas others do not; and (2) to find an evidence of interaction between TLS that cannot be neglected at low temperature. This should be considered in constructing microscopic theories of low-energy excitations in glasses.

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[1] R. C. Zeller and R. O. Pohl, Phys. Rev. B **4**, 2029 (1971).
[2] R. O. Pohl, X. Liu, and E. J. Thompson, Rev. Mod. Phys. **74**, 991 (2002).
[3] P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. **25**, 1 (1972); W. A. Philips, J. Low Temp. Phys. **7**, 351 (1972).
[4] W. A. Phillips, Rep. Prog. Phys. **50**, 1657 (1987).
[5] K. Trachenko, M. T. Dove, K. D. Harmonds, M. J. Harris, and V. Heine, Phys. Rev. Lett. **81**, 3431 (1998); K. Trachenko *et al.*, J. Phys.: Condens. Matter **12**, 8041 (2000); K. Trachenko, M. T. Dove, and V. Heine, Phys. Rev. B **65**, 092201 (2002); K. Trachenko and M. T. Dove, J. Phys.: Condens. Matter **14**, 7449 (2002).
[6] E. Merzbacher, *Quantum Mechanics* (Wiley, New York, 1970).
[7] A. J. Leggett, Physica B **169**, 322 (1991); C. C. Yu and A. J. Leggett, Comments Condens. Matter Phys. **14**, 231 (1988).
[8] M. W. Klein, B. Fischer, A. C. Anderson, and P. J. Anthony, Phys. Rev. B **18**, 5887 (1978); A. L. Burin and Yu. M. Kagan, JETP **82**, 159 (1996).
[9] R. Berman, P. G. Klemens, and F. E. Simon, Nature (London) **166**, 864 (1950); X. Liu, P. D. Vo, R. D. Pohl, F. Schiettekatte, and S. Roorde, Phys. Rev. Lett. **81**, 3171 (1998).
[10] R. Konig, M. A. Ramos, I. Usheror-Marshak, J. Arcas-Goijarro, A. Hernando-Maneru, and P. Esquinazi, Phys. Rev. B **65**, 180201 (2002).
[11] S. Tsuneyuki, M. Tsukada, H. Aoki, and Y. Matsui, Phys. Rev. Lett. **61**, 869 (1988).
[12] J. Reinisch and A. Heuer, Phys. Rev. Lett. **95**, 155502 (2005).
[13] J. P. Sethna, Phys. Rev. B **24**, 698 (1981).
[14] T. Vegge, J. P. Sethna, S. A. Cheong, K. W. Jacobsen, C. R. Myers, and D. C. Ralph, Phys. Rev. Lett. **86**, 1546 (2001).
[15] S. R. Elliott, Nature (London) **354**, 445 (1991).
[16] M. Turlakov, Phys. Rev. Lett. **93**, 035501 (2004).