Microscopic Description of Tunneling Systems in a Structural Model Glass

A. Heuer and R. J. Silbey
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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We present a quantitative method which systematically finds tunneling systems in glasses and hence allows a microscopic check of the standard tunneling model. We apply this method to a two-component model amorphous alloy. The major assumptions of the standard tunneling model are qualitatively verified. Small quantitative differences in the distribution of the tunneling matrix elements explain why the experimental temperature dependence of the specific heat is superlinear and the thermal conductivity is subquadratic. Connections to the soft-potential model and recent strong-coupling models are discussed.

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At low temperatures ($T < 1$ K) glasses possess properties markedly different from the behavior of crystals, e.g., the temperature dependence of the specific heat $C(T) \propto T^{1.1-1.3}$ and the thermal conductivity $\kappa(T) \propto T^{1.8-1.95}$ [1-3]. The main characteristics of the low-temperature properties of glasses have been explained by a phenomenological tunneling model which we call the standard tunneling model (STM) [1,2]. In the STM it is assumed that localized excitations with very low energies E exist in glasses. They are regarded as excitations in such double well potentials (DWP's) which by chance happen to be nearly symmetric. It is generally assumed that the existence of DWP's is due to the disorder in glasses so that a local rearrangement of atoms might switch the system between two adjacent local energy minima. For given T, DWP's with E of the order of k_BT dominate the physical properties. In such DWP's a transition between the two minima is possible via tunneling. Therefore we will refer to them as tunneling systems (TS's) which are characterized by an asymmetry Δ and a tunneling matrix element Δ_0.

In the STM it is assumed that the distribution of TS's is given by

$$P(\Delta,\Delta_0)=P_0/\Delta_0\,, \tag{1}$$

which corresponds to the least biased distribution. The form of $P(\Delta,\Delta_0)$ implies that the distribution of the excitation energy $E=(\Delta^2+\Delta_0^2)^{1/2}$ is independent of E. Except for small systematic deviations the temperature behavior of $C(T)$, $\kappa(T)$ and further physical quantities like, e.g., the absorption of sound are correctly predicted. Experimentally it turns out that for most glasses P_0 is in the range $(0.5\text{–}3)\times 10^{45}\ \mathrm{J}^{-1}\mathrm{m}^{-3}$ [4].

At the present time no microscopic justification of the STM exists. Furthermore in recent years the validity of the STM has been questioned and alternative models have been proposed [5-7]. They are based on the assumption that the interaction between TS's, which is mediated by phonons, is much stronger than the intrinsic energies of the individual TS's. This assumption could be checked, if it were possible to estimate, from a microscopic picture, the density of TS's, hence the value of P_0, and the deformation potential γ. By γ the coupling between TS's and acoustic phonons is described.

In this Letter we present a simulation procedure which is able to describe the low-energy excitations in a glass on a microscopic level. Some previous attempts to detect numerically DWP's were based on the assumption that a TS is described by the motion of a single atom [8,9]. We show that this assumption is unrealistic. More realistic DWP's were found in simulations by Weber and Stillinger [10]. Since they chose a rather time-consuming method to detect DWP's, they only reported a few DWP's.

Let the glass consist of N atoms with masses m_i and position vectors $\mathbf{r}_i$ $(1 \le i \le N)$ so that its total Hamiltonian reads

$$H_{\text{total}}=\sum_i \frac{m_i}{2}\left(\frac{d}{dt}\mathbf{r}_i\right)^2+E_{\text{pot}}(\mathbf{r}_1,\ldots,\mathbf{r}_N)\,. \tag{2}$$

In a first step a glass configuration $\{\mathbf{r}_{i,L}\}$ is constructed which corresponds to a local minimum of the potential energy. This is achieved by quenching an equilibrated computer liquid [10]. In a second step it is checked whether a second local energy minimum $\{\mathbf{r}_{i,R}\}$ exists which is adjacent to the original one. As a measure for the distance between two configurations we choose the mass-weighted Euclidian distance

$$\operatorname{dist}(\{\mathbf{r}_{i,1}\},\{\mathbf{r}_{i,2}\}) \equiv \left[\sum_i \frac{m_i}{\tilde{m}}(\mathbf{r}_{i,1}-\mathbf{r}_{i,2})^2\right]^{1/2}, \tag{3}$$

with $\tilde{m} \equiv \sum_i m_i/N$. It is important to keep the center of mass of the glass fixed. Finding the $\{\mathbf{r}_{i,R}\}$ by a gradient method requires a starting point which is already in the neighborhood of this minimum. We assume that the atomic rearrangements which correspond to a specific DWP are mainly described by the movement of one atom and its n nearest neighbors ($n \approx 10\text{–}20$). Based on this assumption, which is subsequently checked self-consistently, we realize this step in the following way: (a) selection of one atom and its n nearest neighbors, (b) search for the energy minimum $\{\mathbf{r}_{i,0}\}$ in this subspace with the restriction $\operatorname{dist}(\{\mathbf{r}_{i,0}\},\{\mathbf{r}_{i,L}\})=d_0$ for a given value of d_0 of the order of the expected distance between

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the two energy minima, and (c) relaxation of the whole glass. Using this procedure the probability is rather large that in the rare cases in which an adjacent energy minimum is present, $\{\mathbf{r}_{i,0}\}$ is close to $\{\mathbf{r}_{i,R}\}$ so that the gradient method in (c) is able to reach this minimum. It is convenient to use a simulated annealing method in step (b) [11]. We define $d \equiv \text{dist}(\{\mathbf{r}_{i,L}\},\{\mathbf{r}_{i,R}\})$. In a first approximation the reaction path between $\{\mathbf{r}_{i,L}\}$ and $\{\mathbf{r}_{i,R}\}$ is described by the configurations $\{\mathbf{r}_{i,\text{rp}}(x)\}$ with $\mathbf{r}_{i,\text{rp}}(x) = \mathbf{r}_{i,L} + (x/d)(\mathbf{r}_{i,R} - \mathbf{r}_{i,L})$ where x is a variable describing the position along the reaction path. Since we are only interested in the dynamics along the reaction path we may neglect the other degrees of freedom in H_{total}, yielding

$$H_{\text{DWP}} = \frac{\bar{m}}{2}\left(\frac{d}{dt}x\right)^2 + \tilde{E}_{\text{pot}}(x)\,, \tag{4}$$

where $\tilde{E}_{\text{pot}}(x)$ describes a DWP with minima at $x=0$ and $x=d$. Note that the mass, entering H_{DWP}, does not depend on the microscopic structure of the DWP. Apart from d the DWP is characterized by its asymmetry Δ and its potential height V (the energy difference between the barrier and the upper well). A better approximation of the reaction path is the shortest path between $\{\mathbf{r}_{i,L}\}$ and $\{\mathbf{r}_{i,R}\}$ which crosses the saddle point between both configurations, yielding modified values for V and d. A numerical procedure for the determination of the saddle point is given by Weber and Stillinger [10] and has been implemented in our routine.

We treat the same system that Weber and Stillinger analyzed: an amorphous nickel phosphorus mixture near the eutectic composition of 80% ^{62}Ni and 20% ^{31}P [10]. The pair potential between two atoms a distance r apart is described by

$$V_{ij}(r) = \begin{cases} A_{ij}[(a_{ij}r)^{-12} - 1]\exp[(a_{ij}r - a)^{-1}], & 0 < a_{ij}r \le a, \\ 0, \quad a_{ij}r \ge a, & \end{cases} \tag{5}$$

with $a = 1.652\sigma$, where $\sigma = 2.2$ Å is the unit length. Here i or $j=1$ designates Ni, while i or $j=2$ designates P. Realistic values for A and a are $A_{11} = 8200$ K, $a_{11} = 1.0$ (Ni-Ni), $A_{12} = 1.5A_{11}$, $a_{12} = 1.05$ (Ni-P), and $A_{22} = 0.5A_{11}$, $a_{22} = 1.13$ (P-P). The mass density ρ_0, as deduced from the experimental value, is $\rho_0 = 8348$ kg/m^3. The value of $\bar{m}$ is 9×10^{-26} kg. We choose $N = 150$ atoms and implement periodic boundary conditions. The simulations were performed on a RS6000 workstation. In what follows we denote the set of all DWP's with the properties $0.1\sigma < d < 1.0\sigma$, $V < 600$ K, $|\Delta| < 800$ K by $\mathcal{D}_0$. We choose $d_0 = 0.4\sigma$, $n = 16$ and systematically vary the initial atom in step (a). It turns out that, by the above routine, a particular DWP $\in \mathcal{D}_0$ is found on average 8 times, with variations between 1 and 20. It rarely happens that a DWP $\in \mathcal{D}_0$ is only detected once or twice. Furthermore, for DWP's $\in \mathcal{D}_0$ there are hardly any correlations between their potential parameters and the frequency with which they are found. Therefore we may conclude that most of the DWP's $\in \mathcal{D}_0$ are detected and the few which are not detected are equally distributed in $\mathcal{D}_0$.

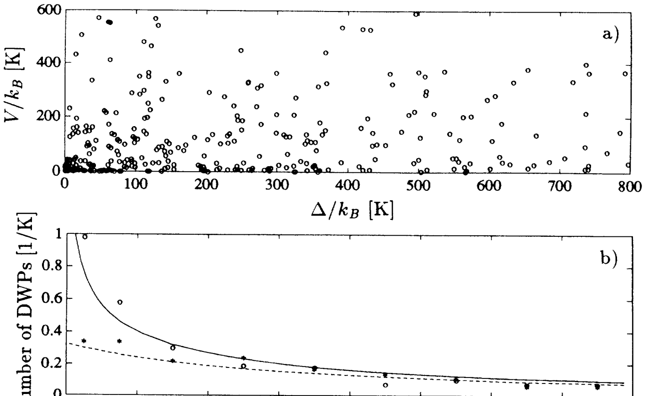

FIG. 1. (a) Distribution of the 310 detected simulated DWP's $\in \mathcal{D}_0$ with respect to the asymmetry Δ and the potential height V. (b) Distribution of the 310 detected simulated DWP's with respect to Δ for different regions of V [$V/k_B \le 100$ K (o), $V/k_B > 100$ K (*)] as compared to the distribution derived from the DWP's $\in \mathcal{D}_0$ generated from the p_i (straight line and dashed line, respectively).

We analyzed $n_a = 220$ different glass configurations by the above method. We found 310 DWP's $\in \mathcal{D}_0$ which on average corresponds to one DWP $\in \mathcal{D}_0$ per 106 atoms. Their distribution with respect to Δ and V is shown in Fig. 1(a). Small values of Δ and V occur more frequently than large values of Δ and V and furthermore Δ and V are strongly correlated.

The participation number p, which is a measure of the size of the cluster of atoms which participate in the motion between the two minima, may be defined by $p = d^2/d^2_{\text{max}}$, where d_{max} denotes the maximum distance any single atom moves. In Fig. 2 we show the distribution of p. We see that for the large majority of DWP's p is smaller than 8. It turns out that the character of this distribution does not change significantly if we vary n between 10 and 20. Simulations on glasses with $N = 64$ yield approximately the same distribution function. Changes occur only for values of N as small as 32. Therefore we may conclude that neither the choice of n nor the fact that we "only" simulate glasses with $N = 150$ atoms has significant consequences for the nature of the DWP's. In the analysis of soft potentials, rather than DWP's, Laird and Schober determined participation numbers of the order of 20 [12].

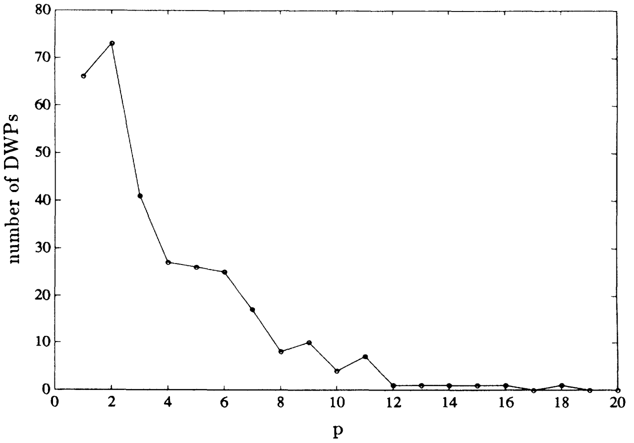

FIG. 2. Distribution of the participation number p for the 310 detected simulated DWP's $\in \mathcal{D}_0$.

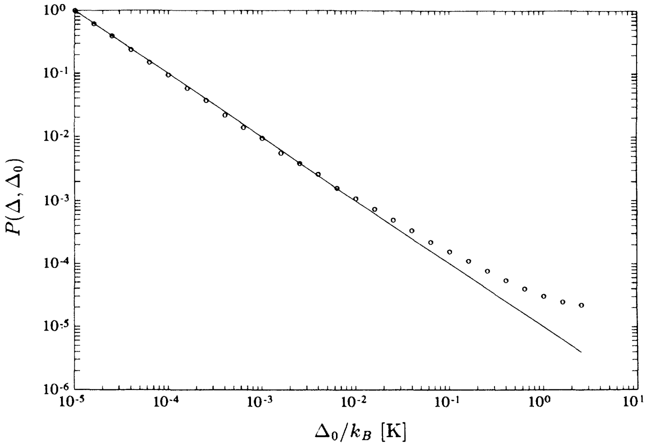

FIG. 3. Distribution of $P(\Delta,\Delta_0)$ as derived from the DWP's generated from the p_i. The straight line corresponds to the prediction of the STM. $P(\Delta,\Delta_0) \propto 1/\Delta_0$. $P(\Delta,\Delta_0)$ has been normalized such that $P(\Delta,\Delta_0 = k_B 10^{-5}\ \text{K}) = 1$.

Among the 310 DWP's only one DWP has a value of $E < 1$ K. Since the number of low-energy excitations is supposed to be very small this does not come as a surprise. A detection of a thousand DWP's in this energy range, which is the minimum basis for a careful statistical analysis of the TS distribution function, requires an increase of the product $n_a N$, and hence of the CPU time, by a factor of at least 1000. This immediately excludes such a procedure. Because of the strong statistical correlations between V, Δ, and d it is not obvious how to extract information about DWP's with $E < 1$ K from our set of DWP's. However, there does exist a way to get this information. We describe each DWP by the fourth-order polynomial $\tilde{E}_{\text{pot}}(x) = w_2 x^2 + w_3 x^3 + w_4 x^4$ such that the three parameters Δ, V, and d are correctly reproduced. Selecting both minima of a DWP as $x = 0$ we obtain two triplets (w_2, w_3, w_4) per DWP. Hence this procedure yields a set of 620 triplets $\{(w_2, w_3, w_4)\}$. Discretizing each w_i axis this set corresponds to a discrete distribution function $p_{\text{total}}(w_2, w_3, w_4)$. Anticipating that the $\{w_i\}$ are statistically independent we first determine functions $p_i(w_i)$, such that the variance $\chi_1 \equiv \langle [p_{\text{total}}(w_2, w_3, w_4) - p_2(w_2) p_3(w_3) p_4(w_4)]^2 \rangle$ is a minimum. The brackets denote the sum over the discretized w_i axes. Then we randomly generate 620 new triplets $(w_2, w_3, w_4) \in \mathcal{D}_0$, each with probability $p_2(w_2) p_3(w_3) p_4(w_4)$, and perform the same statistical analysis. This new set of triplets yields a variance χ_2. Since by construction the generated set of triplets is based on independent distribution functions $p_i(w_i)$ the ratio of χ_1/χ_2 is a good measure for the statistical independence of the $\{w_i\}$ in our original set. Only in the case of statistical independence $\chi_1 \approx \chi_2$, otherwise χ_1 is significantly larger. In our case it turns out that $\chi_1 \approx \chi_2$, which proves the statistical independence. In the same way we can show that a different choice of the polynomial $\tilde{E}_{\text{pot}}(x) = u_0(u_2 x^2 + u_3 x^3 + x^4)$ does not lead to independent distribution functions. Our result is further confirmed by comparing the original distribution of DWP's with the distribution of generated DWP's in the (V, Δ, d) space. In Fig. 1(b) the results for the (V, Δ) plane are presented. Taking into account the statistical errors of the original distribution, it is reasonably well approximated by the generated distribution.

In the last decade the soft-potential model has been developed in a number of publications [13,14]. This model assumes that the DWP's can be parametrized as $\tilde{E}_{\text{pot}}(x) = u_0(u_2 x^2 + u_3 x^3 + x^4)$ with a fixed value of u_0 and independently distributed values of u_2 and u_3. Assuming reasonable distribution functions for u_2 and u_3 several low-temperature properties of glasses could be well explained. We believe that our approach can serve as a microscopic foundation for a generalized soft-potential model, based on three distribution functions instead of two. Since we chose a microscopic approach, our distribution functions have a microscopic foundation and are thus not postulated within the framework of a phenomenological model. Microscopic determinations of distribution functions within the soft-potential model were until now restricted to the analysis of normal modes of two coupled SiO_4 tetrahedra [15].

From the $p_i(w_i)$, a large number of DWP's can be generated. The corresponding values of Δ_0 can be determined from solving the Schrödinger equation for H_{DWP}. Since the minima of the DWP's describe local energy minima of the whole glass, the resulting tunneling matrix elements are already renormalized. Based on this set of DWP's we may check the statistical assumptions of the STM. In agreement with the STM it turns out that for $|\Delta|/k_B < 4$ K the distribution function $P(\Delta,\Delta_0)$ is independent of Δ. The dependence of $P(\Delta,\Delta_0)$ on Δ_0 is shown in Fig. 3. For $\Delta_0/k_B < 0.01$ K we obtain $P(\Delta,\Delta_0) \propto 1/\Delta_0^{\epsilon}$ with $\epsilon = 1$ in agreement with the STM.

For $0.05 < \Delta_0/k_B < 1$ K the value of ϵ is approximately $\frac{3}{4}$ which leads in a first approximation to $C(T) \propto T^{5/4}$ and $\kappa(T) \propto T^{7/4}$. This demonstrates that this small departure from the prediction of the STM is fully consistent with experimental results. A detailed analysis will be given in a subsequent paper. For $\Delta_0/k_B > 1$ K a strong decrease of ϵ can be observed. This indicates that Δ_0/k_B approaches the crossover temperature T_0, for which the temperature dependence of $C(T)$ and $\kappa(T)$ changes dramatically. Typically T_0 is of the order of a few kelvin [14]. Qualitatively, the decrease of ϵ is directly connected to the fact that the number of DWP's with small values of V is very large [see Fig. 1(a)]. Therefore the observed behavior of $P(\Delta,\Delta_0)$ can be qualitatively explained without using details of our statistical analysis.

On average, generation of 405 DWP's $\in \mathcal{D}_0$ is necessary to obtain one DWP with $E < 1$ K. Together with our above result which connected the number of DWP's $\in \mathcal{D}_0$ with the total number of atoms we are able to determine the effective density of TS's which formally is defined as

$$n_{\mathrm{eff}}(E) = \int_0^E d\Delta \int_0^E d\Delta_0 \frac{\Delta_0^2}{E^2} \delta[E - (\Delta^2 + \Delta_0^2)^{1/2}] P(\Delta,\Delta_0) . \tag{6}$$

Within the STM we have $n_{\mathrm{eff}}(E) = P_0$. For $E/k_B = 1$ K we obtain $n_{\mathrm{eff}} = 1.6 \times 10^{46}$ $\mathrm{J^{-1} m^{-3}}$ which is a factor of 4–20 larger than typical values known from literature [4]. This result is robust against variations of the parameters of our statistical procedure, e.g., the size of $\mathcal{D}_0$ and against variations of the cutoff parameter in Eq. (5). Actually, n_{eff} has been experimentally determined to be approximately 2×10^{46} $\mathrm{J^{-1} m^{-3}}$ for NiP [16]. Because of the additional interaction with electrons it is not clear how reliable this value is.

In summary, for a structural model glass we have microscopically identified the DWP's which were postulated in the STM. Qualitatively all statistical assumptions of the STM have been justified. The small quantitative deviations from the STM are fully consistent with experimental observations. Assuming a typical value for the deformation potential γ of the order of 1 eV [4] our value of n_{eff} implies that our model glass is correctly described by the weak-coupling picture. We believe that our method has a wide range of applications and will help to answer the question how the structure of a glass influences the low-temperature properties, as well as be extended to explain the physics of glasses at temperatures above 1 K without adjustable parameters.

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