Intrinsic Quantum Excitations of Low Temperature Glasses

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Several puzzling regularities concerning the low temperature excitations of glasses are quantitatively explained by quantizing domain wall motions of the random first order glass transition theory. The density of excitations agrees with experiment and scales with the size of a dynamically coherent region at T_g, being about 200 molecules. The phonon coupling depends on the Lindemann ratio for vitrification yielding the observed universal relation $l/\lambda \simeq 150$ between phonon wavelength λ and mean free path l. Multilevel behavior is predicted to occur in the temperature range of the thermal conductivity plateau.

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Decades ago, measurements of the heat capacity and thermal conductivity of glasses at cryogenic temperatures revealed the presence of excitable degrees of freedom not present in perfect crystals [1]. These could be described as two level tunneling systems whose energies and tunneling matrix elements were randomly distributed [2,3]. Coupling the tunneling systems to phonons explained the thermal measurements and also predicted novel physical effects, such as the nonlinear absorption of sound and a phonon echo, which were later observed [4,5].

The nature of the tunneling entities has remained obscure. Thoughtful experimentalists and theorists have noticed puzzles when the model quantitatively confronts experimental data [6–8]. For example, the entropy contained in these excitations is much less than the residual entropy frozen in at the glass transition. Yet, the density of two level systems varies only modestly from material to material. There is also a mysterious nearly universal relation between the density of the two level systems and their coupling to phonons which can be deduced from the observation that the mean free path of phonons is about 150 times their wavelength at low temperature [7]. If the two level systems arise from the motions of highly localized specific configurations of atoms, as in impurity doped crystals, instead of such a universal relation we would expect significant variation with the glass's chemical composition. These facts lead Yu and Leggett [8], as well as others [9,10], to investigate the possibility that the experimentally observed excitations are really highly renormalized collective excitations of a system of microscopic tunneling entities that interact strongly through the exchange of phonons. While such a coupling seems to be present, manifesting itself in spectral diffusion of the two level entities [11], quantitative calculations based on the interacting model suggest that thermodynamic manifestations of the interaction should be confined to ultralow temperatures [10,12]. This scenario then has not yet explained the observations which called it forth.

Here we explore an alternative view of the quantum excitations of a glass. Rather than regarding the tunneling entities as extrinsic, we quantize the excitations that are responsible for the activated dynamical events which slow as the glass transition is approached. These excitations are mostly frozen in at the liquid glass transition. Many aspects of these activated motions can be understood using the random first order transition theory of glasses [13]. This theory starts from some exactly solvable mean field glass models showing one step replica symmetry breaking [14,15]. The picture of activated motions goes beyond mean field theory by considering entropic droplets [16]. The theory quantitatively explains for a wide range of substances both the barrier heights [17] and nonexponentiality of relaxations [18] observed near the glass transition. In this picture, a viscous liquid or glass consists of a mosaic of frustrated domain walls separating regions of energetically less frustrated material. Each mosaic cell resembles a local minimum of the free energy, an "inherent structure" if you will [19]. The typical size of the cells is nearly universal and does not vary much with the composition of the glass because it depends on the near universal value of the maximum vibrational amplitude sustainable by the glass — the Lindemann ratio. The mosaic length scale depends not on the molecular character of the glass but on its preparation time scale, logarithmically.

Large scale motions such as these domain wall movements have usually been discounted as a possible origin of the two level systems because tunneling amplitudes decrease with the number of independently moving entities and with the distance over which they move (see Refs. [20–22] for exceptions). We will show that occasionally in the amorphous solid such collective tunneling can occur with a significant amplitude owing to the extraordinary multiplicity of tunneling paths available for such an entity and to the possibility of achieving a sharp local resonance.

The density of excitations available through collective tunneling can be calculated using an argument based on the classical density of states of systems with one step broken replica symmetry [23]. The result depends only on the glass transition temperature T_g and the mosaic size, and explains the magnitude of the heat capacity. The coupling of these tunneling excitations to phonons is set by T_g itself, again because of the universal Lindemann ratio. For resonant scattering, the material dependent factors cancel to yield the observed relation between phonon wavelength and mean free path. Our arguments show that tunneling will appear to be two state like over the wide range of temperatures where echo experiments have been performed, but that the two state character breaks down at higher temperatures where a plateau in the thermal conductivity is observed [24] and where single molecule experiments already give evidence for deviations from two-stateness [25].

First, a simple argument for the density of excitations to set the stage. The motions above the glass transition temperature T_g are rearrangements of finite sized cooperative regions from one local free energy minimum to another [17]. The free energy cost to create a new minimum as a function of the droplet radius is $F(r) = 4\pi\sigma(r)r^2 - \frac{4\pi}{3}r^3 T\tilde{s}_c$. Here $\sigma(r) \equiv \sigma_0 a^{1/2} r^{3/2}$ is a radius dependent surface tension whose form follows from a renormalization group calculation and is caused by the wetting of the interface between two particular low energy configurations by other possible arrangements. σ_0 is surface tension at the molecular length scale a. $\tilde{s}_c$ is the configurational entropy per unit volume, which favors creating other minima. In terms of the number of particles in the droplet $N \equiv \frac{4\pi}{3}(r/a)^3$, we have $F(N) = \gamma\sqrt{N} - Ts_c N$, where $\gamma \equiv 2\sqrt{3\pi}\,\sigma_0 a^2$, and $s_c(T)$ is configurational entropy per particle. An approximate density functional calculation [17] gives $\gamma = \frac{3}{2}\sqrt{3\pi}\,k_B T \ln(\alpha_L a^2/\pi e)$, where $\alpha_L a^2 \sim 10^2$, the inverse square of the Lindemann ratio, hardly varies from substance to substance. The maximum of the free energy $F^{\ddagger} \equiv \gamma^2/4Ts_c$ is reached at $N_0 = (\gamma/2Ts_c)^2$ giving the typical motional barrier. T_g is set by the quenching time for the glass $\tau = \tau_0 e^{F^{\ddagger}/k_B T_g}$, where τ_0 is a molecular time scale. At T_g the system breaks up into a mosaic of regions of size ξ, where $F(N^*) = 0$, giving $N^* \simeq 190$ and $\xi \equiv N^{*1/3}a$. ξ only logarithmically depends on τ and is about $\simeq$ 5.7 molecular radii, for quenching times of hours, independent of molecular composition.

Each mosaic cell resembles a finite size mean field system at T_K, i.e., where the entropy vanishes. The density of minima $n(\epsilon)$ for any system experiencing an entropy crisis is $n(\epsilon)d\epsilon = \frac{d\epsilon}{k_B T_g} e^{\epsilon/k_B T_g}$. The proportionality constant $1/k_B T_g$ guarantees that there is only one absolute ground state: $\int_{-\infty}^{0} d\epsilon\, n(\epsilon) = 1$. The total density of states in the sample per unit volume is therefore $N(\epsilon) \simeq \frac{1}{k_B T_g \xi^3} e^{\epsilon/k_B T_g}$. We do not distinguish between the energy and the *free* energy of basins because the zero point vibrational entropy varies little from basin to basin. At low energies, one thus gets for the conventional density of excitations $\bar{P} = \frac{1}{k_B T_g \xi^3}$. For silica with $T_g \simeq 1500$ K and $a \simeq 3.5$ Å, this gives $\simeq 6 \times 10^{45}\ \mathrm{J^{-1}\,m^{-3}}$, a value typical for many glasses [24]. Apart from the T_g variation, which has been noted experimentally (see, e.g., [26]), the density is seen to be nearly universal for glasses made with the same quenching rate. By integrating the flat distribution $\bar{P}$ up to T_g one finds that the low level excitations accessible at cryogenic temperatures would account for less than $(a/\xi)^3 \simeq 1\%$ of the residual entropy at T_g.

A more complete argument demonstrates that resonant tunneling consisting of small displacements of atoms within a region of size on the order ξ, as illustrated in Fig. 1, can indeed occur and gives the same excitation density as the simpler argument. We first examine the existence of resonant levels. Consider a region from the system quenched below T_g which forms a particular local minimum. An excitation corresponds to introducing a different minimum structure, encompassing N molecules. The internal energy will be on average $\Delta c_p(T_g - T_K)N \simeq T_g s_c N$, where Δc_p is the configurational heat capacity. On top of the internal energy, there is a contribution from an interface energy $\gamma\sqrt{N}$ due to the mismatch with the configuration of the surrounding material. The distribution of excitation energies of those "droplet" configurations should be Gaussian [15], giving for the number of states higher in energy by E than the original one $\Omega_N(E) \sim \exp\{s_c N - \{[E - (T_g s_c N + \gamma\sqrt{N})]^2/2\delta E^2 N\}\}$. δE^2 is the variance in energy per particle at the glass transition temperature. s_c is the residual entropy that would be frozen at T_g [17]. The entropy crisis for the bulk fixes the glass transition temperature by $\delta E^2 = 2s_c T_K^2$. The number of states at small excitation energies grows with the excited region's size. Yet below a critical size the domain wall energy prevents resonance. The number of nearly resonant levels becomes on the order one only for $N = (\gamma/T_g s_c)^2 \Rightarrow N = N^*$, as before. Again, excitation energies are distributed according to an exponential $e^{E/k_B T_g}$, giving the same $\bar{P}$. The multiplicity of nearly isoenergetic, i.e., resonant configurations intrinsically follows from the nonequilibrium freezing at T_g.

The enormous multiplicity of states at T_g not only allows resonance but also yields myriads of possible tunneling paths from the initial configuration to the resonant one with a droplet of size N^* embedded in it. Each path is a connected sequence of dropletlike configurations involving rearrangements of a region containing a growing number

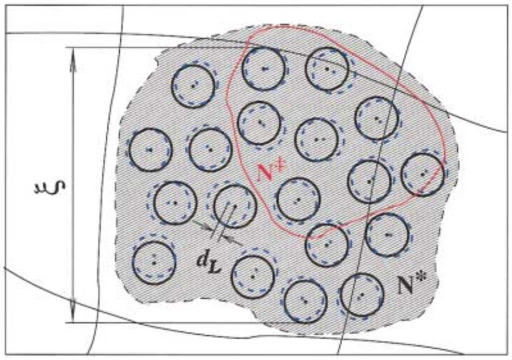

FIG. 1 (color). A schematic of a tunneling center is shown. ξ is its typical size. d_L is a typical displacement of the order of the Lindemann distance. Red contour illustrates a transition state size.

$N < N^*$ particles. The tunneling amplitude will be a sum over all these paths, much like the partition sum for a random directed polymer [27] with the weight of each path being the exponential of its action in units of $\hbar$. If $\hbar$ is large, the path sum will be dominated by a large number of paths. These would go through a nearly continuum of paths as shown in Fig. 2. This situation would correspond with a "quantum melted glass" [28]. On the other hand, for small $\hbar$, the smallest action path only will contribute giving a tunneling element $e^{-S_{\min}/\hbar}$. This action varies from one resonant pair to another and will be exponentially distributed over a range scaling with $k_B T_g$, giving a power law distribution for the tunneling amplitude. Finding the precise statistics of the lowest action path from the direct polymer analogy is quite complex since the tunneling distribution depends on detailed (correlated) statistics of the energy variations all along the tunneling paths. We obtain a sensible approximation by recognizing that the action will be crudely proportional to the largest barrier encountered as the virtual tunneling droplet grows, as would be true for an inverted oscillator potential. To find the statistics of this barrier at any value of N we must find the distribution of the lowest energy droplet state at N (notice we neglect correlations here). This distribution is of the same form as the one in $\Omega_N(E)$, except the variance is twice larger now because the energies of both the initial and the transition states may fluctuate since the system can choose where to begin to tunnel: $\Omega_N(V) \sim \exp\{s_c N - \{[V - (T_g s_c N + \gamma\sqrt{N})]^2/4\delta E^2 N\}\}$. Generally, where a resonant state exists the tunneling path will start by rearranging high energy local configurations into ones with internal energies near E_K. The lowest barrier likely to be encountered occurs when $\Omega_N(V_{mp}) \simeq 1$, as usual in the extreme value statistics, giving $V_{mp} = \gamma\sqrt{N} - (2\sqrt{2} - 1)T_g s_c N$. V as a function of N is shown as a solid black line in Fig. 2. The maximum value of V_{mp} is proportional to the activation barrier at T_g, $F^\ddagger$ but smaller due to the fluctuation of the initial energy: $V_{\max} = F^\ddagger/(2\sqrt{2} - 1) \simeq 26 T_g s_c$. The maximum occurs at $N^\ddagger \equiv N_0/(2\sqrt{2} - 1)^2 \sim 14$. This is small enough that we can expect system dependent corrections. There will generally be states below V_{mp} which can allow tunneling as in the green line shown in Fig. 2. The distribution of barriers (and therefore actions) below $V_{\max}$ follows from $\Omega_N(V)$ giving an exponential distribution proportional to $\Omega(V^\ddagger) \sim \exp\{-18 s_c + \frac{V^\ddagger}{\sqrt{2}T_g}\}$. The chances to be able to tunnel to a state of precisely the minimum resonant size is suppressed by a factor $e^{-18 s_c}$. But to find a state which is simultaneously resonant and within easy tunneling requires encompassing a region with only 18 additional molecules, less than a single layer. Hence, any region of size $\simeq$200 molecules will have a nearly resonant tunneling state within range T_g. Tunneling involves simultaneous motion of all the atoms in the droplet, and might have a high effective mass or even be damped owing due to the complex rearrangements involved. It is hard to rule out the latter possibility, but the actual effective mass is low since moving a domain wall over a molecular distance a in an (imaginary) tunneling time τ involves displacing individual atoms only a Lindemann length d_L. The kinetic energy associated with this motion is $M_w(a/\tau)^2 = N_w m(d_L/\tau)^2$, where $N_w \simeq (\xi/a)^2$ is the number of molecules in the wall and m is the molecular mass. Thus the mass of the wall M_w is only $m(\xi/a)^2(d_L/a)^2$. Using $(\xi/a) \simeq 5.8$ and $(d_L/a)^2 \simeq 0.01$ gives $M_w \simeq m/3$. Computational studies of similar multiparticle tunneling events [20,21] are consistent with the low mass obtained here. As we shall see below, $(d_L/a)^2 \simeq k_B T_g/\rho c_s^2 a^3$, where ρ is mass density and c_s is the speed of sound. This gives $M_w \simeq (\xi/a)^2 k_B T_g/c_s^2$. It follows that the frequency of motion at the barrier top $\omega^\ddagger = -\partial^2 V/\partial r^2/M_w \simeq 1.6(a/\xi)\omega_D$, expressing V as a function of droplet's radius $r \equiv a(3N/4\pi)^{1/3}$.

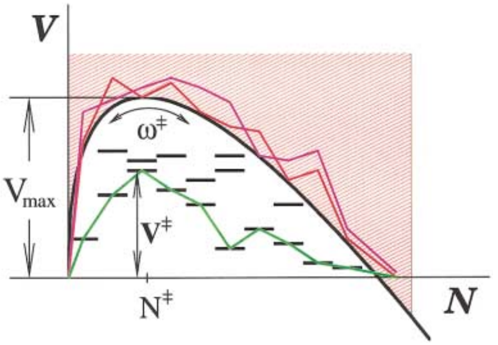

FIG. 2 (color). The black solid line shows the barrier along the most probable path. Thick horizontal lines at low energies and the shaded area at energies above the threshold represent energy levels available at size N. The red and purple lines demonstrate generic paths, and the green line shows the actual (lowest barrier) path, which would be followed if $\hbar\omega^\ddagger < k_B T/2\pi$.

Since the tunneling matrix element Δ for a path with barrier $V^\ddagger$ is proportional to $e^{-\pi V^\ddagger/\hbar\omega^\ddagger}$, we obtain a rather flat distribution for the tunneling exponent $\log\Delta$, as is generally used to fit experiments.

We now determine the size of the coupling of the domain motions to the elastic (single polarization) strain field $\nabla\phi$, which has potential energy density $\rho c_s^2(\nabla\phi)^2/2$. At low temperature the phonon wavelengths are long, so one can describe the interaction with a standard pointlike term $\sigma_z^i \mathbf{g}\nabla\phi$, where σ_z is an operator of the tunneling degree of freedom. The tunneling entities first come into existence at a temperature T_A, somewhat higher than T_g, where mechanical stability of local minima to thermal vibrations is achieved [13]. The phonon energies at the microscopic scale and their coupling to the defects will be comparable and on the order of T_g, giving $\rho c_s^2 \langle(\nabla\phi)^2\rangle a^3 \simeq \langle \mathbf{g}\nabla\phi\sigma\rangle \simeq k_B T_g$. This sets the coupling g at the molecular scale $g \simeq \sqrt{\rho c_s^2 a^3 k_B T_g}$. The coupling to the extended defects is weakly dependent on their size. To see this, in the continuum limit, we separate the total elastic deformation tensor u_{ij} into contributions ϕ_{ij} and $\pm d_{ij}/2$ due to phonon displacement and the tunneling motion, respectively. The difference in energy between the defect configurations in the presence of a (longitudinal) phonon is then $\rho c_s^2 \phi_{ii} \int d^3\mathbf{r}\, d_{ii}$, where the integration covers the droplet. The coupling is therefore proportional to a surface integral $\int d\mathbf{s}\, d(\mathbf{r})$, where $d(\mathbf{r})$ are the tunneling displacements at the edge of the droplet. These are random and of order $(a/\xi)d_L$ because the *inelastic* displacements decrease from $\sim d_L$ in the center of the droplet to zero outside. The integral is of order $a^2\sqrt{N^{*2/3}}(a/\xi)d_L$; therefore $g \simeq \rho c_s^2 a^3 d_L$. Using $d_L/a \simeq \nabla\phi$ at T_g, one still gets $g \simeq \sqrt{\rho c_s^2 a^3 k_B T_g}$.

The resonant scattering from the tunneling of mosaic cells gives $l_{mfp}^{-1}(\omega) = \pi \frac{\bar{P} g^2}{\rho c_s^3} \omega \tanh(\frac{\hbar\omega}{2k_B T})$ as the inverse mean free path of a phonon with frequency ω [24,29]. Thus, $\lambda_{dB}/l_{mfp} \simeq 3\bar{P} g^2/\rho c_s^2$. Combining $\bar{P} \simeq 1/k_B T_g \xi^3$ with the expression for the coupling constant, one obtains $l_{mfp}/\lambda_{dB} \simeq (\xi/a)^3 \simeq 10^2$. This ratio depends only on ξ/a, independent of molecular composition. It is a geometrical factor reflecting the relatively low concentration of cooperative regions in a supercooled liquid frozen on quenching, an almost universal number within the random first order glass transition theory [17].

At high temperatures the domain wall motion will become noticeably multilevel. Ignoring damping, at a temperature $T' \simeq \hbar\omega^{\ddagger}/2\pi k_B \simeq (a/\xi)T_D/2\pi$, the wall motion will typically be classical. This temperature lies within the plateau in thermal conductivity [7]. Damping, which becomes considerable also at these temperatures, should lower this estimate, as also will the fluctuations in barrier height. A multilevel system will more effectively scatter phonons, which would cause the plateau. Consistent with this, single molecule studies of spectral diffusion of dyes in polymer glasses at these temperatures reveal spectral trails that wander [25], as expected for domain walls in crystalline materials [30]. Multilevel behavior at these temperatures is also implicated by studies on noise spectra in amorphous metals [31].

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