ent a $^3$He surface to the $H_\downarrow$. At our current experimental temperature range the thermal response of the HSC is sluggish compared with pure $^4$He because of the substantially higher vapor pressure. Lower temperatures will relieve this problem.

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# Origin of Low-Temperature Tunneling States in Glasses

Morrel H. Cohen
*The James Franck Institute and Department of Physics, The University of Chicago, Chicago, Illinois 60637*

and

G. S. Grest
*Department of Physics, Purdue University, West Lafayette, Indiana 47907*

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The low-temperature tunneling levels observed in glasses are discussed in terms of the free-volume model. As the system falls out of thermodynamic equilibrium near its glass transition temperature $T_g$, liquid clusters are frozen in. This Letter proposes that voids are formed within the liquid clusters as they in turn freeze at lower temperatures. Approximately $10^{-4}$ such centers form per atom, 1% of which contribute to the heat capacity below 1 K.

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Anderson, Halperin, and Varma[1] and Phillips[2] proposed to explain the linear temperature dependence of the specific heats of glasses at low-temperature via tunneling centers. They assumed that in any glassy system a certain number of atoms, or groups of atoms, has accessible two nearly equivalent equilibrium configurations corresponding to the minima of asymmetric double-well potentials and tunnels between them. The model explains many other experimental observations.[3-6] Nevertheless, there is no successful microscopic description of a tunneling center. Instead, tunneling is treated via a model Hamiltonian for two-level systems representing the ground states in the two local energy wells. Here we explore the origin of the tunneling states.

The tunneling states are commonly associated with a small group of atoms undergoing a local rearrangement.[6] The number of atoms involved is assumed to be reasonably small to minimize the distance between states in configuration space. However, the larger the number of atoms, the easier it is to find two ground states of roughly equivalent energies. It is believed that this competition between accessibility and degeneracy determines the size of the tunneling states.[6] It is also suspected that these excitations are universal among all types of glass formers and an intrinsic feature of the glassy state.[7-9]

This universality is essential to any theoretical model which illuminates their origin. A model should also describe the relation of the tunneling states to the glass transition at $T_g$ where the system falls out of complete thermodynamic equilibrium[10] and is trapped in a region of configuration space far removed from its crystalline ground state. The residual entropy of the glass is a measure of the number of other energetically equivalent regions into which the glass could have been trapped. Most of those states are mutually inaccessible because they are distant in configuration space, but mutually accessible nearly degenerate states presumably[1,2] exist. These would be the desired tunneling states. Behaviors at $T \cong 0$ and $T \cong T_g$ are thus critically related. How the glassy state is formed directly affects the tunneling states; both should be describable within the same theory.

Here we show how the free-volume model can account for both the glass transition and tunneling states. The basic ideas employed do not depend on any specific details of the free-volume model and apply outside the context of any particular model.

We[11,12] have developed a free-volume model of the thermodynamic and kinetic behavior of dense liquids and glasses. Our results for the viscosity and heat capacity are in both qualitative and quantitative agreement with experiment. We propose to describe here the tunneling states within our generalized free-volume model. In this model the liquid-glass transition results from the reduction of the free volume of the amorphous phase near $T_g$. One associates a local volume $v$ of molecular scale with each molecule. The excess of $v$ over a critical value $v_c$ is regarded as free. Molecular transport occurs when voids of volume greater than the molecular volume $v_m$ form by the redistribution of free volume.[13]

At low temperatures and high density each molecule is restricted primarily to movement within a cell or cage defined by its nearest neighbors; the local volume is simply the cage volume.[11] The local free energy of a cell depends only on its volume, $f = f(v)$; the total free energy is[11]

$$F = N \int P(v)[f(v) + kT \ln P(v)]\,dv - TS_c, \qquad (1)$$

where $P(v)$ is the probability of volume $v$ and $S_c$ is the communal entropy. For $T$ near $T_g$, the contributions of curvature to $f(v)$ are small compared to $kT_g$ near its point of inflection; we can approximate $f(v)$ by[11]

$$f(v) = \begin{cases} f_0 + \frac{1}{2}\kappa(v - v_0)^2, & v \leqslant v_c \\ f_0 + \frac{1}{2}\kappa(v_c - v_0)^2 + \zeta(v - v_c), & v \geqslant v_c. \end{cases} \qquad (2)$$

Those cells with $v > v_c$ we call liquidlike and those with $v < v_c$, solidlike. The fraction of the liquidlike cells is $p$. Only liquidlike cells have a free volume $v_f$,

$$v_f \equiv v - v_c, \quad v > v_c. \qquad (3)$$

From the linearity of $f(v)$ for $v > v_c$, the local free energy $\sum_i f(v_i)$ contributed by liquidlike cells depends only on the average $v_i$ among the liquidlike cells. Thus the free energy is unchanged by any free exchange of free volume among the liquidlike cells. Such an exchange takes place only between liquidlike cells which are nearest neighbors and which have a sufficiently large number, $\geqslant z$, of other liquidlike nearest-neighbors that the volumes of any neighboring solidlike cells are not constrained to change simultaneously. A new type of percolation problem is defined in which a liquidlike cell is in a liquidlike cluster only if it has $z$ neighbors which are also liquidlike.[11]

Atoms diffuse when a fluctuation in cellular volume of atomic size $v_m$ or greater occurs.[13] This arises from redistribution of the free volume only within a given cluster. The total free volume within a cluster of size $\nu$ must, therefore, be greater than $v_m$ for diffusion to occur,[11]

$$\sum_{i=1}^{\nu}(v_i - v_c) > v_m, \quad v_i > v_c. \qquad (4)$$

For diffusive motion to occur within a given cluster, it size $\nu$ must be at least $v_m/\overline{v}_f$, $\overline{v}_f$ being the average free volume within a liquidlike cluster,

$$\nu \geqslant \nu_m = v_m/\overline{v}_f. \qquad (5)$$

A cluster for which (5) holds is a liquid cluster; each atom or molecule within it moves in time through the entire cluster. Each molecule finds accessible the configuration space of every other molecule in the cluster, which generates the communal entropy.

Liquid clusters of size $\nu > \nu_m$ are frozen in at $T \lesssim T_g$ because of the finite cooling rate required to avoid crystallization. In those clusters, large (~atomic size) displacements can occur for $T \lesssim T_g$ by the coupling of translational motion and density fluctuations. For temperatures near $T_g$, the curvature in $f(v)$ is negligible, and the local free energy is independent of the relevant configuration coordinates. However, when $T \ll T_g$, this curvature becomes significant and gives rise to local energy minima separated by saddlepoint barriers on the order of $kT_g$ in size. The energy scale is set by $kT_g$ since it is near $T_g$ that the system falls out of equilibrium, freezing in potential variations of at most this size. This is quite general and does not depend on the free-volume model. As freezing proceeds, the system moves into one of its many total-free-energy minima. The most probable pattern is a freezing inward into the cluster from the interface with the solidlike or glassy regions with no significant relaxation between the clusters and the solidlike environment.[12] The excess volume $\Delta v_\nu = \nu[(v_c - v_0) + \bar{v}_f]$ stays within the cluster. $\nu\bar{v}_f$ is the free volume which is still freely redistributed at $T < T_g$; $\nu(v_c - v_0)$ is the thermal expansion of each cell required to reach the liquidlike range. Some fraction of $\nu(v_c - v_0)$ becomes available for redistribution as the cluster freezes into the minimum.

The freezing of a liquid into a glass requires atomic movement, which occurs by the concentration of the free volume into ephemeral voids of the size $v_m$.[11,13] This process can be regarded as a diffusion of the void away from the interface into the interior where it becomes trapped as the freezing is completed. For each $\nu_m = v_m/\bar{v}_f$ atoms one void of volume somewhat greater than $v_m$ forms.

The number $N_T$ of these voids present at low $T$ is[14]

$$N_T \sim \tilde{N} P_z(p_{\text{froz}})/\nu_m + \tilde{N}\left[\sum_{\nu=\nu_m}^{2\nu_m - 1} C_{\nu z}(p_{\text{froz}}) + 2\sum_{\nu=2\nu_m}^{3\nu_m - 1} C_{\nu z}(p_{\text{froz}}) + \cdots\right], \tag{6}$$

where $\tilde{N} = p a_z(p) N$ is the total number of atoms in clusters, $a_z(p) \leq 1$, $P_z(p)$ is the probability of being on the infinite cluster, $C_{\nu z}(p)$ is the cluster distribution and $p_{\text{froz}}$ is the fraction of liquidlike cells frozen at $T \lesssim T_g$. Although the quantities $a_z(p)$, $P_z(p)$, and $C_{\nu z}(p)$ have not yet been determined theoretically, we can estimate useful upper bounds on $\nu_m$ and $N_T$. Our best fits[11] to the measured viscosity data for six glass formers give $\nu_m \approx 30$ at $T_g$. That is, for each 20–40 atoms within a cluster, we expect to find a void of the size $\sim v_m$. Having chosen the percolation threshold value of $p_c = 0.15$, we found that $p_{\text{froz}} \sim 0.2$ was a typical result from our relaxation studies[12] of the specific heat near $T_g$. If we set $a_z(p_{\text{froz}}) \sim 0.1$ and $p_z(p_{\text{froz}}) \sim 0.1$, we find $N_T/N \sim 10^{-4}$. A more precise estimate must await a study of the cluster distribution function $C_{\nu z}(p)$. Our relaxation theory[12] indicates that $p_{\text{froz}}$ and therefore $N_T$ should be essentially independent of the cooling rates used to produce the glass.

We assert that these voids are the tunneling centers. Any one of the neighboring atoms can move into the void, but, in contrast to the crystal, the void itself, and the configuration of the surrounding atoms, is irregular. Such motion can be expected to be substantially easier for one particular atom. That atom then tunnels into the void by *multiparticle tunneling* along a suitable one-dimensional path. Ignoring path curvature, we have for the effective Hamiltonian,

$$\begin{aligned} H &= \frac{p^2}{2\mu} + V_0(x) + \sum_\lambda \tfrac{1}{2}\hbar\omega_\lambda(x) + \left(\Phi_0(x), \frac{p^2}{2\mu}\Phi_0(x)\right) \\ &= p^2/2\mu + V(x), \end{aligned} \tag{7}$$

provided the tunneling energy separations are much smaller than the mean phonon frequency $\omega_\lambda(x)$. Here $\mu$ is the mass of the atom, $V_0(x)$ is the equilibrium potential energy, $\Phi_0(x)$ is the ground-state eigenfunction for all the remaining degrees of freedom $\lambda$, and the integration in the last term is over those degrees of freedom.[15] $V(x)$ is of the general form assumed in Ref. 1. There is tunneling between the two minima, with a tunneling energy

$$\Delta_0 = \hbar\omega_0 e^{-\Lambda} \tag{8}$$

and energy

$$E = \pm(\Delta^2 + \Delta_0^2)^{1/2}, \tag{9}$$

relative to the mean energy $\frac{1}{2}\hbar\omega_0$ above the lower minimum. Here $\Delta$ is the splitting of the lowest two energy levels. An estimate of $\Lambda$ for the symmetric well case can be obtained by using the triangular barrier approximation, which gives

$$\Lambda = (d/\hbar)[2\mu(V - \tfrac{1}{2}\hbar\omega_0)]^{1/2}, \tag{10}$$

where $d$ is the separation in $x$ of the two minima. Because the liquid clusters freeze in at $T \lesssim T_g$, the energy scale of $\Delta$ is set by $T_g$. Either of the two can be the lower so that $\Delta$ has a roughly Gaussian distribution around zero with a rms value for which $T_g$ sets the scale. $|\Delta|$ can be represented as distributed over a rectangular distribution of width $\lesssim T_g$. Since $\omega_0$ is a typical vibrational frequency, it will be on the same scale. $V$ is also governed by the same scale. Values of $V$ so close to $\frac{1}{2}\hbar\omega_0$ that $\Lambda$ is small enough for $\Delta_0^2 \simeq \Delta^2$ accord-

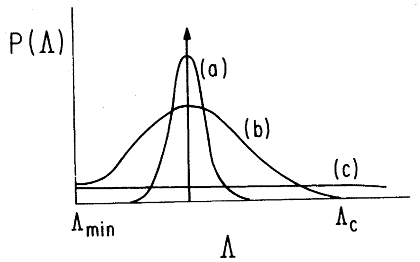

FIG. 1. Probability distribution $P(\Lambda)$ vs $\Lambda$.

ing to Eq. (10) are, therefore, improbable. Consequently, we almost always have $\Delta_0 \ll |\Delta|$, and the density of states for the tunneling levels is given by the distribution of $|\Delta|$.

At low $T$, the values of $|\Delta|$ important for the specific heat are $\sim kT \ll kT_g$. We can restrict ourselves to the case $\Delta = 0$ in estimating $\Lambda$ and use Eq. (10). In estimating $\Lambda$ we are thus dealing with a void containing two energetically equivalent positions for a given atom. If it were a vacancy in a crystal, the value of $\Lambda$ so calculated would have a delta function distribution. The disorder in the glass smears this distribution, as shown in Fig. 1. For there to be a two-level system, there is a $\Lambda_{\rm min} \sim 5$–$10$[1,4] for each barrier shape. Since ultrasonic experiments are insensitive to large $\Lambda$,[4,6] there is an effective cutoff $\Lambda_{\rm max}{}^{ua} \simeq \Lambda_{\rm min} + 1$. $P(\Lambda)$ is found to be essentially constant[5] between $\Lambda_{\rm min}$ and $\Lambda_{\rm max}{}^{ua}$. From the fast and slow specific-heat measurements,[4,5] we know that $P(\Lambda) \simeq 0$ for $\Lambda > \Lambda_{\rm max}$ and $\Lambda_{\rm max} < \Lambda_c = 15$–$20$. Therefore, all tunneling levels contribute to $C_p$, and we can expect distribution (b) in Fig. 1 to occur. Loponen *et al.*[16] set limits on the relaxation times $T_1$ for the coupling of the phonon system to the tunneling center systems by faster heat-capacity measurements. From their data we infer that $5\ \mu{\rm sec} \leqslant T_1 \leqslant 5$ msec, which corresponds to $\Lambda_{\rm min} \simeq 12$ and $\Lambda_{\rm max} \simeq 17$, consistent with the previous estimates and Fig. 1(b).

Since all $\Lambda$ contribute to $C_p$, we can calculate the fraction of the centers $\overline{N}_T$ contributing to $C_p$ at 1 K to be $(1\ {\rm K})/|\Delta|_{\rm max}$ of the total $N_T$. Assuming $\Delta_{\rm max} \sim 100$ K, we find $\overline{N}_T/N \sim 10^{-6}$, in good agreement with the data.[6] We are unable to estimate the $\Lambda$ value for the peak in $P(\Lambda)$ or $\Lambda_{\rm max}$ which involves solving a multiparticle tunneling problem without knowing details of the configuration.

The essential point of our free-volume picture is the flatness of the free energy as a function of the cellular volume on the scale of $kT$ for $T \gtrsim T_g$. It is this feature only which we invoke to explain the existence of tunneling levels. A free energy flat in localized regions of the configuration space on a scale of $kT_g$ simply cannot be regarded as flat any longer at much lower temperatures. Instead $kT_g$ becomes the bound to the magnitudes of the variations, i.e., maxima, minima, and saddle points (enhanced somewhat by thermal contraction) of importance for tunneling at low temperatures. In this view, tunneling is a continuation of diffusion. This view is independent of the particular set of configuration coordinates convenient for any particular material and thus portrays tunneling as a general phenomenon, universal in the same way that diffusion, viscosity, and the glass transition are universal.

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