

State density of a system of anharmonic oscillators in a glass

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There are singularities in the energy distribution of the state density of a system of noninteracting anharmonic oscillators. These singularities can explain the low-frequency Raman peaks in glasses, the plateau on the temperature dependence of the thermal conductivity, and why the specific heat exceeds the Debye value.

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The concept of two-level systems in glasses at low temperatures had led to substantial progress in our understanding of the properties of glasses at these temperatures.¹ On the other hand, some important questions which arise in connection with this approach have yet to be explained theoretically. Up to what energy E (E is the distance between the two levels) is the model of a two-level system valid? (In other words, where is the third level?) What is the state density $n(E)$ at energies above a few degrees?

The properties of glasses (their specific heat, thermal conductivity, etc.²) exhibit a universal behavior not only at temperatures $T \lesssim 1$ K, where they can be described satisfactorily by the two-level model, but also at high T , up to several tens of degrees, where these properties are not explained by the two-level model.³ Of particular concern here are the plateau on the temperature dependence of the thermal conductivity at $T \sim 10$ – 20 K and the specific heat, which is higher than the Debye value. We are thus led to the question of identifying the universal factors which allow a consistent explanation of not only the existence of two-level systems in glasses but also the anomalous features which do not conform to the two-level concept. In this letter we attempt to resolve this question.

Our approach is to take into account the important role played by the anharmonicity of the local atomic potentials. Anharmonicity is anomalously influential in glasses in comparison with the situation in crystals because of fluctuations in the structural parameters, among which there are fluctuations which correspond to very small or even negative values of the local quasielastic constants. Of importance below is the circumstance that, according to Ref. 4, a local atomic potential can be regarded as effectively a single-mode potential and described by

$$V(x) = \epsilon [\eta (x/a)^2 + t(x/a)^3 + (x/a)^4] \quad \text{for } |\eta| \ll 1, |t| \ll 1, \quad (1)$$

where ϵ and a are the characteristic energy and radius of the atoms. The random quantities η and t vary from one object to another. In certain other values, potential (1) is a two-well potential; in the case of a high barrier between wells and a slight asymmetry, we have a two-level system with an energy gap E much smaller than the distances to other levels. This is the case if $E \ll \omega \sim \hbar \omega_D (\hbar \omega_D / \epsilon)^{1/3} \sim 30$, where ω_D is the Debye

frequency.⁴ At $T \ll \omega$, the models of Refs. 1 and 4 are essentially equivalent. Since we are interested in properties for which higher values of E are important (for example, the specific heat at $T \gtrsim 10$ K), we will go beyond the range of applicability of the two-level model, and we must deal with the need to examine the spectrum of a highly anisotropic oscillator, (1).

The spectrum of potential (1) is $E_n = \epsilon_n \hbar^{4/3} \epsilon^{1/3} / 2^{2/3} M^{2/3} a^{4/3} \sim \epsilon_n \omega$, where M is the mass of the atomic particle, and the ϵ_n are the eigenvalues of the equation

$$-\psi'' + (\alpha y^2 + \beta y^3 + y^4) \psi = \epsilon \psi, \quad (2)$$

$$\alpha = \eta / \eta_L, \quad \beta = t / \sqrt{\eta_L}, \quad \eta_L = (\hbar^2 / 2Ma^2 \epsilon)^{1/3} \sim (\hbar \omega_D / \epsilon)^{2/3} \sim 10^{-2}.$$

The ϵ_n spectrum of Eq. (2) obviously does not change upon the shift $V(y) \rightarrow V(y + \tilde{C})$, where \tilde{C} is a constant. We choose this constant in such a way that the term linear in y drops out of the potential $V(y + \tilde{C})$. Within an inconsequential constant we can then write $V(y + \tilde{C}) = \alpha' y^2 + \beta' y^3 + y^4$, where

$$\alpha' = \frac{1}{16} \sqrt{9\beta^2 - 32\alpha} (3\beta - \sqrt{9\beta^2 - 32\alpha}) \quad (\beta' = \frac{1}{2} (\sqrt{9\beta^2 - 32\alpha} - \beta)). \quad (3)$$

This result means that an arbitrary gap between levels, $\epsilon_n - \epsilon_m \equiv \epsilon_{nm}(\alpha, \beta)$, is invariant under transformations (3); i.e., $\epsilon_{nm}(\alpha, \beta) = \epsilon_{nm}(\alpha', \beta')$.

We are interested in the first gap between levels, which is an analytic function of α and β on the entire $\{\alpha, \beta\}$ plane. It is not difficult to show that the function $I = \alpha - 3\beta^2/8$ is invariant under transformations (3). We thus have $\epsilon_{21} = \epsilon_0 + \gamma(\alpha - 3/8\beta^2) + \dots$ near the point $\alpha = \beta = 0$. For the symmetric case ($\beta = 0$), numerical calculations have been carried out,⁵ and they lead to $\gamma > 0$. We may thus conclude that ϵ_{21} falls off along the β axis at $|\beta| \ll 1$. At $|\beta| \gg 1$, however, ϵ_{21} should increase with increasing $|\beta|$, since the spectrum of the lower levels in this case is described by the expression for a harmonic oscillator with an elastic coefficient proportional to β^2 . On the β axis we thus have points $C = (0, \pm \beta_0)$ at which $\epsilon_{21}(0, \beta)$ reaches a maximum.

To show that C is a stationary point of the function $\epsilon_{21}(\alpha, \beta)$, we note that the point C is mapped into itself under transformations (3). This result means that the expansion

$$\epsilon_{21}(\alpha, \beta) = \epsilon_{21}(0, \beta_0) + b_1 \alpha + b_2 (\beta - \beta_0)^2 + b_3 \alpha^2 + b_4 \alpha (\beta - \beta_0)$$

near this point must be invariant under transformations (3). This circumstance imposes some restrictions on the coefficients: $b_1 = 0$, $b_4 = -(8/3)(b_2/\beta_0)$. Since $b_2 > 0$, C is a minimum at $b_3 > (16/9)(b_2/\beta_0^2)$, while it is a saddle point at $b_3 < (16/9)(b_2/\beta_0^2)$. A more detailed analysis, for which we do not have room here, shows that when a minimum is reached at the point C it is not possible to draw a topologically consistent pattern of constant-energy lines $\epsilon_{21}(\alpha, \beta) = \text{const}$ in the $\{\alpha, \beta\}$ plane. We therefore assume that the point C is a saddle point (Fig. 1).

Because of the saddle point, the state density¹⁾ $n_{21}(E) = \langle \delta[E - E_{21}(\eta, t)] \rangle_{\eta, t}$ has a van Hove singularity for the first gap between levels: This singularity diverges logar-

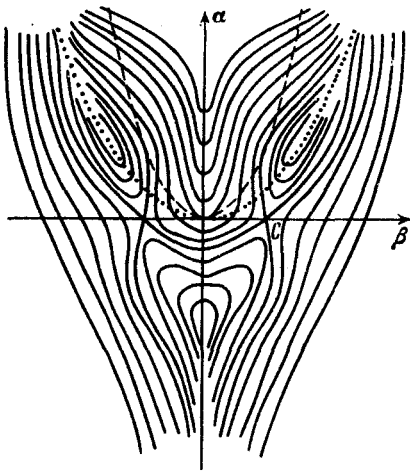


FIG. 1. Schematic contour diagram of curves of $\epsilon_{21}(\alpha, \beta) = \text{const}$. Here C is a saddle point. The region of single-well potentials is on and within the parabola $\alpha = (9/32)\beta^2$, shown by the dashed curve, and also on the β axis. The other points in the plane correspond to two-well potentials. Symmetric two-well potentials also occur along the parabola $\alpha = (1/4)\beta^2$, shown by the dotted curve, in the $\alpha < 0$ plane.

ithmically at the energy E corresponding to the point C . In magnitude this energy is on the order of w .

Analyzing potential (1), and using some corresponding arguments, we can show that the state density $n_{31}(E)$ for the gap between the first and third levels is zero up to an energy on the order of w , where there is a finite discontinuity in the state density.

The behavior $n_{21}(E)$ at $E \gg w$ is determined by potentials (1) of a harmonic type with $\eta \gg \eta_L$ or $|t| \gg \sqrt{\eta_L}$; the typical value is $\eta_L \sim 10^{-2}$ [see (2)]. Since the distribution functions of the random quantities η and t vary significantly over characteristic distances $\Delta\eta \gtrsim 10^{-1} \gg \eta_L$, we may assume that the behavior $n_{21}(E) \sim E$ (which corresponds to $\nu, t^2 \lesssim \Delta\eta$) holds essentially all the way up to energies on the order of $\hbar\omega_D/3$.

We believe that the features observed in the thermal properties of glasses—the plateau on the temperature dependence of the thermal conductivity and the peaks in the reduced specific heat $C(T)/T^3$ at $T \sim 10$ K (Ref. 2)—are in fact caused by the singularities in $n_{21}(E)$ which we have just found.²⁾ The existence of a harmonic region, $n_{21}(E) \sim E$, on the other hand, combined with the sharp decay at $E \sim w$, gives rise to Raman-scattering peaks at low frequencies, $\omega_0 \gtrsim w/\hbar$, as can be shown. Such peaks have in fact been observed in many glasses.² They correspond in position and shape to the IR absorption peaks,⁶ as would follow naturally from our arguments.

In summary, this new approach seems to permit a consistent explanation of the observed properties of glasses both in the region in which the two-level model is applicable and at higher T . This approach brings out a new universal aspect of glasses: a singularity in the state density of the vibrational spectrum at a characteristic energy $E \sim w \sim 30$ K. A more detailed study of these questions by numerical calculations will be reported separately.

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¹The average over the random quantities η and t is carried out with distribution functions discussed in Ref. 4. An important aspect of these distribution functions is that they may be assumed constant at $|\eta| \lesssim \eta_L$ and $|t| \lesssim \sqrt{\eta_L}$.

²Our calculations show that the contribution of phonons with energies $\hbar\omega \gg w$ to the thermal conductivity which stems from the resonant scattering of these phonons by quasilocal harmonic modes is independent of the temperature at $T \gg w$. The anharmonic modes with $\epsilon_{21} \ll w$ make a contribution to the thermal conductivity at $T \gg w$ which increases linearly with the temperature. The peaks in the state density should give rise to a plateau in the thermal conductivity at $T \sim w/3$ because of the resonant scattering of phonons in these states.

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