

A glimmer into Glasses

1. Two-level systems in evaporated amorphous silicon.

Authors: D.R. Queen, X. Liu, J. Karel, H.C. Jacks, T.H. Metcalf, F. Hellman
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2. Suppression of tunneling two-level systems in ultrastable glasses of indomethacin.

Authors: T. Prez-Castaeda, C. Rodriguez-Tinoco, J. Rodriguez-Viejo, M.A. Ramos
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Recommended with a Commentary by Chandra Varma, University of California, Riverside.

A firm realization that glasses are fundamentally different from crystalline materials, not only near the transition from the liquid state to the solid state, came through the measurements [1] of the specific heat and thermal conductivity of a variety of glasses at low temperatures in the 1970's. The low temperature specific heat C_p was found well represented as $\propto T$ and the thermal conductivity $\kappa \propto T^2$. This was immediately followed by a phenomenological explanation [2, 3] in terms of the two level tunneling model (TLM), which besides explaining these facts suggested that the internal relaxation coefficient $Q(\omega, T) \equiv 2\pi^2(\ell/\lambda)$ should be independent of ω and T . Here ℓ is the phonon mean path and λ is the wave-length of sound. This, and several other ramifications of the model were soon found.

However, troubling issues remain, even at the phenomenological level. First, the universality [4][5] of the phenomena - the coefficient of the linear specific heat is the same to within an order of magnitude in a wide variety of glasses, ranging from silica to molecular glasses and Q is the same to within a factor of only 2. In the simplest TLM model Q is $\propto n_0\gamma^2/\rho v^2$, where n_0 is the same density of states of the two level systems which gives the coefficient of the linear in T specific heat, γ is a typical coupling constant of the TL's to the phonons and ρ is the density. This adds to the universality mystery. Second, the parameters employed in the simplest TLM are not transferable between the specific heat and the thermal conductivity or ultrasound relaxation in a given substance by rather large factors. Some satisfaction is provided by the fact that the TL's which appear in specific heat must be weakly coupled to the phonons compared to those that contribute to the anomalous κ or Q [6]. Third, the measured T^3 specific heat is larger than that given by the elastic constants - the original TLM has nothing to say about this. Finally, what are these two level tunneling states anyway.

It is clear that the TL's are motion of atoms or group of atoms not representable by anharmonic phonons, for example the local degrees of freedom in the liquid state. In fact an

original motivation for the model comes from ancient knowledge that glasses have extensive ground state entropy so that the *total* entropy would appear to be larger than that of the same substance forming a crystal. The paradox is resolved only if the excess entropy comes from the difference in the latent heat of the liquid to crystalline solid transition compared to an equivalent quantity in the liquid to glass transition. The excess low temperature measured entropy may be thought of as the leaking of the ground state entropy to finite temperatures; this naturally gives the observed increase (logarithmically) with increase in time of measurement. In fact the observed linear in T entropy is only a small fraction of the ground state entropy. The density of states n_0 in silica glasses is only about $10^{-3}/T_m$ per SiO_2 molecule, where T_m is the melting temperature, about $10^3 K$, while the ground state entropy in the same units is $O(1)$.

Some recent clever measurements, in the highlighted papers above and in the references in them, have shed light on the origin of the anomalous properties of glasses by changing their magnitude in a given substance through different ways of preparing the glass. The first paper prepares amorphous Si by vapor deposition at various deposition temperatures and characterizes the glassy state by a variety of ways, and measures their specific heat, sound velocities, but not yet their internal friction coefficient. Increase in deposition temperature leads to a glass with a larger density. This is accompanied by a dramatic reduction of the linear in T heat capacity and in the excess T^3 specific heat. Also, a dramatic reduction of the temperature dependence of the sound velocity, which implies a dramatic reduction in Q . Some of the results are summarized in the figure 1, which also has some earlier (inconclusive) measurements on other materials. A three order change in the linear in T heat capacity with a 15% change in density in amorphous Si is eye-popping. The change in the so called excess T^3 specific heat with density is identical to that of the linear in T heat capacity.

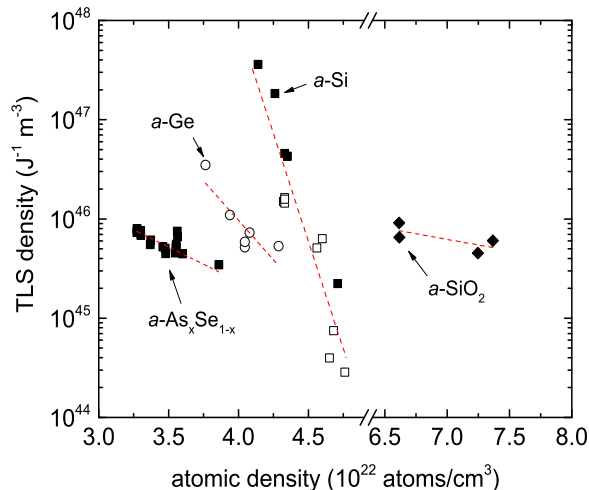


Figure 1: The effective density of two level states deduced from the measured coefficient of the linear in T specific heat as a function of the density in amorphous Si prepared by vapor deposition at various temperatures, and for some other materials - taken from Ref. 1 above.

In the second paper listed above, glasses are made of vapor deposited molecules of indomethacin ($C_{19}H_{16}ClNO_4$, also used as a non-steroidal anti-inflammatory) at various deposition temperature. The linear in T specific heat is unobservable when the deposition temperature is about $0.85 T_g$. T_g is the glass formation temperature when cooled very slowly. Such molecules have surface mobility even below T_g allowing formation of denser glasses. For the same deposition temperature, slower rate of cooling leads to a lower linear in T heat capacity as well as a much larger entropy released near the glass transition temperature. This is in the direction of consistency with the conjecture made above about the zero-point entropy and the latent heats of solidification.

The correlation of the excess low temperature entropy with the density brings to mind an approach to the analytical and numerical theoretical study [7] of glasses (as well as colloids, foams, sand, etc.) from quite a different end. This is the theory of jamming in random material with hard-core or quasi-hard-core interactions. The basic idea is that such substances are close to marginal stability, where the number of degrees of freedom per "molecule" are close to the number of constraints. Define δz_c as the degrees of freedom that are the excess of those at marginal stability, called the isostatic condition. The excess must then appear as local modes with distribution of frequencies close to 0. Calculations do indeed show a large uniform density of states, increasing near marginality, but it is accompanied with a hole in the low frequency limit. The excess is also accompanied by larger volume per "molecule" because the excess of the packing fraction ϕ over that at the isostatic condition (for hard sphere realizations of the model) is found to go as $(\phi - \phi_c) \propto (\delta z)^\zeta$, with $\zeta \approx 2$. This in an impressionistic way relates the observations in the two papers above to the theory of jamming near criticality.

The theory of jamming is effectively at $T = 0$. But it is a classical theory; indeed it has been appropriately used to study properties like viscosity near melting. To understand the low temperature properties of glasses, one needs to generalize it to a critical theory of quantum jamming. How TLs or equivalents might emerge as the effective low energy degrees of freedom of such a theory or its generalizations is not too clear. But it is an interesting and important problem. It might lead us to a theory for the near universality of the low temperature glass anomalies. The hint that the glassy state is *close* to zero temperature criticality is already found in the sound velocity measurements which imply a $\log T$ contribution to the compressibility. In the meantime, it might be worthwhile plotting the data to provide exponents of the variation of properties such as the specific heat and internal friction coefficients as a function of deviations from density at which the anomalies disappear. But the problem is un-likely to be specified only by the asymptotic behavior; a look at the figure shows a very large range of anomalous behavior around the possible marginal state.

References

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