

Amorphous materials at low temperatures: why are they so similar?

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In addition to the well-known qualitative similarity of behavior of a wide range of amorphous materials, one dimensionless quantity, the reduced attenuation of transverse ultrasound, shows a *quantitative* universality whose explanation in terms of the standard “tunnelling two-level system” model would seem to require a totally unbelievable degree of chance coincidence. In addition, while the height of the “plateau” in the thermal conductivity is material-specific, the higher-temperature behavior is consistent with universal behavior. I sketch the outlines of a scenario which holds out hope of understanding these observations.

Amorphous (non-crystalline) matter comes in a wide variety of forms – ordinary window glass and its relatives, commercial fluoride glasses, amorphous semiconductors, metallic glasses, amorphous polymers, biological materials, The chemical composition and the physical structure of these materials at a microscopic level could hardly be more different; essentially, the only thing they have in common is the property of *not* being crystalline. And yet, as is well known, at temperatures below about 1 K the behavior of almost all amorphous materials is qualitatively similar [1]. Common features include a nearly linear specific heat, a thermal conductivity roughly proportional to T^2 , complicated noise and relaxation properties and (at least in dielectric materials) a series of characteristic nonlinear acoustic properties such as phonon echoes. It is noteworthy that at least some of these features are shared by some compositionally or otherwise disordered crystals such as KBr–KCN solutions [2], charge density wave systems [3] and high-temperature superconductors [4], and even by at least one nominally pure crystal [5]. Moreover, some properties such as the thermal conductivity show qualitatively and perhaps quantitatively universal features even outside the low-temperature regime (cf. below).

In the light of this situation it seems artificial to maintain the long-standing textbook fiction that perfect crystals are the paradigm of solid-state systems and amorphous matter a sort of minor and regrettable exception to the general rule. Rather, one should perhaps coin the slogan: Glassy behavior is the norm, crystalline the anomaly!

There is no space here to review all or even most of the characteristic properties of glasses, so let me just mention briefly a few which are relevant to the thesis of this talk. I will confine myself here to amorphous dielectrics, i.e., exclude both metallic glasses and disordered crystals. It is instructive to start with what may be in the true sense of the words “the exception which proves the rule” – the one characteristic of glasses below 1 K which is not even qualitatively universal, namely the thermal expansion coefficient or, what is equivalent, the Grüneisen parameter Γ . This shows wild variations between materials: it can have either sign, is often strongly temperature-dependent below 1 K and in some cases attains very large negative values. An important clue is that Γ is extremely sensitive to the context x of polar impurities; moreover the data [6] appear compatible with the conjecture that at sufficiently low T and large x , Γ will

approach the value +1 which would be obtained for a pure system of electric dipoles of fixed strength. This suggests that in the low-temperature limit the thermal expansion may be completely dominated by the interactions of the polar impurities; and this in turn might lead us to wonder whether some, at least, of the residual differences in the behavior of different amorphous materials might be simply attributable to differences in the content of such impurities (as is known to be the case for the specific heat of different SiO₂ samples) [7].

Two other properties of interest are the specific heat and thermal conductivity. As is well known, the specific heat appears to be time-dependent below ~1 K and it is therefore difficult to extract a "true" (infinite-time) value; in so far as such can be defined, it is usually believed to be proportional to $T^{1+\beta}$, where β lies in the range 0.1–0.3 and is material-dependent. It should be noted that the data could almost certainly be fit as well with the formula $c_v \sim T / [\ln(T_0/T)]^\alpha$, with α a universal number close to 1 and T_0 material-dependent. At higher temperatures it is conventional to discuss the specific heat by plotting c_v/T^3 versus T , in which case one often gets the so-called "bump" around 3–10 K. Actually, it may be more informative to subtract off the "Debye" (phonon) specific heat c_D (a procedure which is well defined in the low-temperature limit but more speculative elsewhere) and plot $(c_v - c_D)/T$ versus T : if this is done, the graphs for most amorphous materials look similar, with a nearly flat part below 1 K (cf. above) and a steep rise around 1–10 K followed by a flattening off towards a value of the order of 100 times the low-temperature one.

The thermal conductivity κ is the most intriguing of all the widely measured properties of glass. Below 1 K it is, like the specific heat, qualitatively universal, behaving roughly as $T^{2-\beta'}$, where β' is close but not identical to the specific-heat exponent β . Around 1–10 K there is always a "plateau", where κ is approximately constant over about a decade in temperature, and at higher temperatures a region where κ is again very roughly proportional to T^n but with n now closer to 1.

Even more striking is the *quantitative* universality discovered by Freeman and Anderson [8] by plotting the quantity κ/K versus T/θ_D , where θ_D is the Debye temperature^{#1} and K a quantity proportional to θ_D^2/v , v being an appropriately averaged speed of sound. When this is done they show that the graphs for the six different amorphous dielectrics examined (the oxide glasses SiO₂ and B₂O₃ and the polymers PB, PET, PS and PMMA) are essentially indistinguishable both for $T/\theta_D \leq 10^{-2}$ (i.e., roughly, below 1 K) and also for $10^{-1} < T/\theta_D < 10$; it is only in the plateau region ($10^{-2} \leq T/\theta_D \leq 10^{-1}$) that the curves diverge appreciably. Further work [9] has confirmed that these statements remain true for other dielectric glasses. Moreover, even for metallic glasses, the coincidence, though not quite as dramatic as for the dielectrics, is still striking.

The work of Zaitlin and Anderson [10] has shown that for SiO₂ below ~30 K the heat is carried predominantly by phonons. If we believe that this is generally true of amorphous materials over the whole of the relevant temperature range, then the observation of Freeman and Anderson is telling us something strikingly simple [8]: namely, that both below about 1 K and above the plateau the ratio of mean free path l to wavelength λ of the phonons which dominate the thermal conductivity is nearly universal, being approximately 1 for the latter and 150 for the former. Only in the plateau region is it appreciably material-dependent. I return below to the direct experimental evidence for λ in the low-temperature regime. Note that the factor of 150 which differentiates κ in the low- and high-temperature regimes is of the same order as the factor (~100) by which the "linear" term (as defined above) in the non-phonon specific heat differs in the two regimes: i.e., κ is roughly inversely proportional to c_v .

At present there exists no model of the properties of glasses in general above ~1 K which can be said to command general acceptance (cf. the

^{#1} This was taken as an adjustable parameter as described in ref. [8]. Note however that the low- T fit is *independent* of θ_D to the extent that $\beta' \cong 0$, and the high- T fit is only weakly sensitive to it.

paper by J.P. Sethna in these proceedings). In the “low-temperature” regime below ~ 1 K, on the other hand, there exists a very well-developed model which is widely believed to explain most, if not all, of the experimental data, namely the “tunnelling two-level system” (TLS) model [11]. The crucial assumptions of this model are: (i) Because of the random nature of the structure, there exist single atoms, or groups of atoms, which have available to them two possible configurations which are nearly degenerate in energy, and moreover can tunnel between these two configurations with appreciable probability. (ii) The distribution of asymmetries, barrier heights, etc., is such that the probability of the resulting “tunnelling two-level system” (TLS) having an energy splitting E is approximately independent of E . (iii) The density of TLS is sufficiently low that they may be treated as mutually noninteracting except for those phenomena which vanish in the absence of interaction. The independent parameters of the model are the density of TLS as a function of E , and their couplings (or more precisely the distribution of their couplings) to longitudinal and transverse phonons and, where relevant, to electric fields. For certain purposes it may also be necessary to know the distribution of barrier heights, etc., explicitly. All these parameters are usually taken as phenomenological inputs to the theory.

The TLS model has had apparently impressive successes [12] not just in explaining many of the characteristic features of glassy behavior below 1 K (linear specific heat, logarithmic ultrasound velocity shift, T^2 thermal conductivity, etc.) but also in predicting the qualitatively novel (for a solid) series of nonlinear effects mentioned above. In the eyes of most physicists working in this area, these successes have established the model firmly as the effectively unique explanation of glassy properties below 1 K.

If I believed that the TLS model were the truth, or more precisely that it were the whole truth, about amorphous materials at low temperatures, there would be no reason for me to be giving this talk. So what is wrong with it? I think the point can be made most dramatically by

going back to that figure of 150 which we deduced, above, from the thermal conductivity for the ultrasonic attenuation per unit wavelength of phonons in the MHz–GHz range below 1 K. Let us ask: just how quantitatively universal is this number? (If we are looking for evidence of universality, it is clearly more promising to look at dimensionless numbers rather than quantities like the specific heat.) The ultrasonic attenuation per unit wavelength can, of course, be measured directly, or alternatively it can be related, given very general assumptions, by a Kramer–Kronig relation to the coefficient α of $\ln T$ in the ultrasound velocity shift $\Delta c/c$: see, e.g., ref [12]. For definiteness we discuss explicitly the quantity α , which is what is usually directly measured. To make the point most forcefully, let us make a minimal selection of the data: we consider transverse sound only and confine ourselves to genuinely amorphous dielectrics. (It may, of course, be objected that it is well known that we can get apparently irrefutable statistical evidence for astrological influences by confining ourselves to a sufficiently small group such as racing drivers. However, in the present case the exclusion of metallic glasses and disordered crystals still leaves us with over 50% of the raw data, and in the case of the former, at least, there are good physical reasons for the exclusion.) Now, in the TLS model α is given by the formula

$$\alpha = \frac{\gamma_t^2 (dn/d\varepsilon)}{\rho c_t^2}, \quad (1)$$

where ρ is the mass density, c_t the speed of transverse sound, $dn/d\varepsilon$ the density of states of TLS per unit energy and γ_t the TLS-transverse phonon coupling constant. In the model as usually understood, *these four parameters are completely independent inputs*.

In table 1 I list the values of ρ , c_t , γ_t and α for *all* the amorphous dielectrics for which I have been able to find complete data in the literature [13, 14]. α , ρ and c_t are directly measured, while γ_t is inferred using the TLS model from the relaxation data in the standard way (see refs. [13, 14]). There is no point in quoting a separate

Table 1
Parameters relevant to transverse sound propagation in amorphous dielectrics.

Material	ρ	c_1	γ_1	α
α -SiO ₂	2.2	3.8	.65	2.9
BK-7	2.51	3.8	.65	3.3
SF-4	4.78	2.24	.48	2.75
SF-57	5.52	2.22	.61	2.98
SF-59	6.26	1.92	.5	2.78
PMMA	1.18	1.57	.31	3.7
SC-5	1.14	1.56	—	4.1
SC-8	1.1	1.6	.2	2.6
V-52	4.8	2.25	.52	4.9
BALNA	4.28	2.3	.45	4.8
LAT	5.25	2.8	.65	3.7

Ultrasound-related properties of amorphous dielectrics. ρ , c_1 and γ_1 are in arbitrary units, α in units of 10^{-4} . Data from refs. [14].

value of $dn/d\varepsilon$ since for all but two cases^{#2} this is not independently measured but is inferred from the other data using eq. (1). The truly remarkable thing about this table is that while the “independent” inputs ρ , c_1^2 and r_1^2 fluctuate among the 11 materials by factors of ~ 6 , 6 and 10 respectively, the maximum fluctuation in α is a factor of 1.8! To ascribe this to random coincidence would seem to strain credulity.

I will now sketch a scenario (developed in collaboration with Clare Yu) which may hold out some promise of explaining this striking feature, and also some other puzzles such as the temperature-dependence of the thermal conductivity, in a natural way. I emphasize that at present it is *only* a scenario, not a theory: indeed, the technical difficulties of doing concrete calculations on the basis of these ideas have so far largely frustrated us (though cf. below). For a more detailed discussion, see ref. [15].

What do all amorphous materials have in common (other than being amorphous) which distinguishes them from crystals on the one hand and liquids on the other? Directly from the fact that the observed ultrasound attenuation, while small, is much too large to be explicable in terms

of static disorder or phonon–phonon interactions, we infer that they all have *low-lying non-phononic degrees of freedom which couple to the strain*. The conjecture is that it is the interaction of large subvolumes, carrying non-phonon entropy, via the strain field which is responsible for the observed universality of glassy properties.

The considerations which follow are largely independent of the nature of the excitations at the atomic-scale level, but, purely for the sake of a familiar *language*, let us suppose for definiteness that they are something like the two-level systems of the standard model. The crucial difference between this model and the present scenario is that we suppose that the interactions between the TLSs mediated by the strain field are not a small perturbation but are in fact much *greater* than any intrinsic level splitting. A concrete model of this general type has been studied by Klein [16], who shows that in the dilute limit one can obtain from it in a natural way what are in effect new two- (or few-) level systems with just the properties needed to explain most of the typical “glassy” behavior. We, however, shall be less specific and in particular will not assume the TLSs are dilute. Thus the model is inherently collective in nature and the Hamiltonian can be conceived as something like that of a spin glass with an interaction which is proportional at large distances to r^{-3} . It is crucial to our argument that the coefficient of r^{-3} is $\gamma^2/\rho c^2$, where γ is essentially the γ_1 of eq. (1) and c a typical speed of sound. (For the purposes of the present qualitative discussion we need not distinguish between longitudinal and transverse phonons.)

Now, almost any reasonable argument, be it dimensional, mean-field or something more sophisticated, gives the result that for an Ising spin glass (which is the model most discussed in the spin-glass literature) with an interaction proportional to A/r^3 , the “density of states” (in the sense of one-particle-like excitations) at low energies ε is proportional either to A^{-1} or to $A^{-1}(\ln \varepsilon_0/\varepsilon)^{-1}$ where ε_0 is some characteristic cutoff. Not only does this give the experimentally observed form of the specific heat ($\sim T$ or $T/\ln(T_0/T)$), but by eq. (1) it immediately indicates that the quantity α is universal, as ob-

^{#2} SiO₂ and PMMA. Note that in these cases the directly measured value of $(dn/d\varepsilon)$ does *not* agree with the inferred one.

served! (In practice, of course, we should expect it to depend weakly on dimensionless ratios such as γ_l/γ_t and c_l/c_t , and also possibly to contain a factor $\sim[\ln(T_0/T)]^{-1}$; but this is quite consistent with the data.) So at first sight we have an obvious explanation of the “striking coincidence” noted above.

Also, there is a major snag in this picture: although the value of α (hence l/λ) calculated in this Ising-like spin glass picture is indeed universal, concrete calculations always give a value of l/λ of order 1, not of order 150 as observed! Quite apart from this, this picture, while attractive below 1 K, apparently does nothing to explain (e.g.) the behavior of the thermal conductivity at higher temperatures.

But now a sudden thought strikes us: suppose we have all along been staring at the wrong end of the diagram? After all, there *is* a temperature regime where the value of l/λ is, at least arguably, of order 1 – namely, the range of temperature *above* the plateau in κ ! What if our “naive” scenario is actually right in *that* region? But then, why should there be a plateau, and why should the behavior below it be even more strikingly universal? Above all, why, given those two at least arguably “universal” regions, why should the behavior of κ at the plateau itself be so obviously *non-universal*?

I believe there is a way, albeit highly speculative at present, of making possible sense of all this. Consider the interactions of subvolumes of dimension R large compared to the atomic scale. At any value of R the typical phonon-generated interaction is g/R^3 , where $g = \gamma^2/\rho c^2$, and we may therefore assume that the spacing of relevant levels, ΔE , is of the same order. On the other hand, the energy E_ϕ of a typical phonon which must be exchanged in order to generate interactions between two such volumes is of order $\hbar c/R$. Now, when $\Delta E \gg E_\phi$ as is the case for small R , the interaction energy (or more precisely that part of it which is simply given by g/R^3) relates entirely to “diagonal” (“non-flop”) processes, that is, processes in which the “spin” is not flipped by emission or absorption of the virtual phonon; the resulting Hamiltonian is precisely of the *Ising* spin-glass form considered

above, and we should expect the results discussed above to apply. On the other hand, at large R where we have $\Delta E \ll E_\phi$, all processes including “flip-flop” (and also “flip-non-flop”) can contribute to the effective interaction, and the resulting Hamiltonian is of *Heisenberg* spin-glass type. While little work seems to have been done on the thermodynamics of the latter model, it does not seem obviously out of the question that it could generate a density of states which is still (as in the Ising case) approximately independent of energy but thinned down by the factor ~ 100 – 150 required to fit the experiments.

Evidently, the cross-over between these two regimes occurs at a value of R given by $R \sim (g/\hbar c)^{1/2} \equiv (\gamma^2/\rho \hbar c^3)^{1/2} \equiv R_0$. While ρ and c are directly measurable, γ is not (it would be inconsistent to infer it from an interpretation of the low-temperature data in TLS terms!). However, on general a priori grounds a value of a few eV seems reasonable. With such a value, R_0 is of order 50 \AA , and if we relate distances to temperatures by $T \sim \hbar c/k_B R$ then the associated “cross-over” temperature T_0 is of order 10 K and is moreover appreciably material-dependent. Now of course we have no a priori reason to believe that the crossover between the two regimes will lead to a plateau in κ ; however, if we take this feature from experiment, we see that the height of the plateau, even in the *dimensionless* form plotted in fig. 2 of ref. [8], should also be material-dependent. Thus, the scenario might explain not only the observed universality above and below the plateau, but also the non-universality in the plateau region itself.

It is clear that these ideas are at a very preliminary and qualitative stage. Yu [17] has attempted to implement them quantitatively in a simple model, with intriguing results: if one carries out a scaling-type calculation starting at $R \ll R_0$, then (and only then) it is possible to obtain a value of l/λ in the low-temperature region which is of order 150 as observed, but the value is extremely sensitive to the initial input parameters, in prima facie contradiction to the spirit of the scenario (which, ideally, would require that everything should iterate to a fixed point which is *independent* of the input parameters). Further analysis

using different specific models is clearly desirable. Fu [18] has considered possible ways of testing the scenario, in particular by using systems of restricted dimensionality

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References

- [1] *Amorphous Solids-Low Temperature Properties*, W.A. Phillips, ed. (Springer, Berlin, 1980).
- [2] J.J. De Yoreo, W. Knaak, M. Meissner and R.O. Pohl, *Phys. Rev. B* 34 (1986) 8828.
- [3] K.J. Dahlhauser, A.C. Anderson and G. Mozurkewich, *Phys. Rev. B* 34 (1986) 4432.
- [4] Da-ming Zhu, A.C. Anderson, E.D. Bukowski and D.M. Ginsberg, *Phys. Rev. B* 40 (1989) 841.
- [5] R.N. Kleiman, G. Agnolet and D.J. Bishop, *Phys. Rev. Letters* 59 (1987) 2079.
- [6] D.A. Ackerman, A.C. Anderson, E.J. Cotts, J.N. Dobbs, W.M. Macdonald and F.J. Walker, *Phys. Rev. B* 29 (1984) 966.
- [7] J.C. Lasjaunias, A. Ravex, M. Vandorpe and S. Hunklinger, *Solid State Commun.* 17 (1975) 1045.
- [8] J.J. Freeman and A.C. Anderson, *Phys. Rev. B* 34 (1986) 5684.
- [9] J.J. Freeman, private communication.
- [10] M.P. Zaitlin and A.C. Anderson, *Phys. Rev. B* 12 (1975) 4475.
- [11] P.W. Anderson, B.I. Halperin and C.M. Varma, *Philos. Mag.* 25 (1972) 1; W.A. Philips, *J. Low Temp. Phys.* 7 (1972) 351.
- [12] S. Hunklinger and A.K. Raychaudhuri, in: *Progress in Low Temperature Physics*, D.F. Brewer, ed. 9 (1986) 265.
- [13] J.F. Berret and M. Meissner, *Z. Phys. B* 70 (1988) 65.
- [14] J.F. Berret, Thèse d'Etat, Université de Montpellier (1987) unpublished; U. Reichert, thesis, Universität Heidelberg (1986) unpublished.
- [15] C.C. Yu and A.J. Leggett, *Comments on Condensed Matter Physics*, 14 (1988) 231.
- [16] M.W. Klein, *Phys. Rev. B* 40 (1989) 1918.
- [17] C.C. Yu, *Phys. Rev. Letters* 63 (1989) 1160.
- [18] Y.T. Fu, *Phys. Rev. B* 40 (1989) 10056.