THEORY OF THE PHASE TRANSITION FROM A DISORDERED CUBIC CRYSTAL TO A GLASS

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Abstract

We calculate thermodynamic properties of a disordered model insulator, starting from the ideal simple-cubic lattice \(g = 0\) and increasing the disorder parameter \(g\) to \(\geq 1/2\). As in the earlier Einstein- and Debye- approximations, the ground state energy is discontinuous at \(g_c = 1/2\). For \(g < g_c\) the low-T heat-capacity \(C \sim T^3\) whereas for \(g > g_c\), \(C \sim T\). The van Hove singularities disappear at any finite magnitude \(g\) of the disorder. For \(g > 1/2\) we discover novel fixed points in the self-energy and spectral density of this model glass.

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The anomalous thermal properties observed in dielectric glasses[1, 2], has prompted numerous theoretical and experimental studies on the subject[3]. Arguably, the best well-known model consists of the phenomenological two-level states (TLS) proposed by Anderson[4] some time ago. Although the physical nature of the TLS remains elusive the theory does predict linear specific heat at low-\(T\) and enhanced ultrasonic attenuation, both universal properties of glassy materials[3]. An alternative microscopic theory entirely based on phonons was subsequently advanced by one of the authors and his collaborators[6]. It relies for its results on the interplay between disorder, parametrized by a dimensionless \(g\), and anharmonicity, parametrized by a dimensionless \(\xi\) (the Grüneisen parameter) that is ultimately taken to 0. The solutions of two “toy” models, the one based on the unperturbed Einstein model of the phonon spectrum in the “crystalline” phase and the other, on the Debye model[6, 7], both exhibited the following features: at a critical threshold \(g_c\) the system undergoes a transition from a “disordered crystal” phase with partial long-range order (LRO) to a “glassy” phase characterized by a linear specific heat and a divergent Debye-Waller exponent-i.e. by a total loss of LRO[7].

Here, for the first time, we have extended this type of model disorder \(cum\) anharmonicity into the study of a bone-fide crystal and have obtained closed-form solutions in the simple-cubic lattice. This approach is the most realistic so far, given that initially the phonon density-of-states of the ideal crystal exhibits the van Hove singularities (vHS) thought to be characteristic of a crystal with LRO. The results are also much richer than in the toy models. In Fig. 1 we see that at low \(T\) our calculated specific heat is in better agreement with experiment than is the specific heat from molecular dynamics.

Principally our findings are as follows: In the disordered crystalline phase, where the vHS might be thought to weaken with increasing \(g\) and ultimately disappear, instead they soften and disappear \textit{immediately} at any finite \(g > 0\), despite the persistence of LRO and of a finite Debye-Waller exponent up until \(g \geq g_c\). There is an exothermic first-order phase transition as \(g\) is increased above \(g_c = 0.5\). Nevertheless the elastic properties in the glassy phase are intimately related to those of the crystal, as we shall show. Additionally, in the glassy phase \(g > g_c\), we discovered that the spectral density function \(\rho\) exhibits \textit{fixed points}: frequencies at which the spectral density is independent.
of $g$. This feature bring us close to the ultimate goal of being able to express a microscopic law of corresponding states for glassy materials. The specific heat exhibits a Debye $T^3$ law throughout the crystalline phase, up to $g_c$. The exact coefficient $B(g)$ is given in closed form below. Beyond $g_c$ the low-T specific heat is linear in $T$, with coefficient $A(T)$ also given in closed form below.

**THE HAMILTONIAN.** In an effort to make this paper self-contained we review here the main features of the model. The starting point is the Hamiltonian of the reference crystal

$$H_0 = \sum_k \omega_k \left( a_k^\dagger a_k + \frac{1}{2} \right) \quad (\hbar = 1),$$

where $k$ contains the wavevector and polarization of the phonons. The operator $a_k^\dagger (a_k)$ are the familiar creation (destruction) phonon operators. Disorder is introduced in the model via the rather general phonon scattering term

$$H_1 = \frac{1}{4} \sum_{k,k'} M(k,k') \sqrt{\omega_k \omega_{k'}} Q_k Q_{k'},$$

where $Q_k = a^\dagger_{-k} + a_k$ and the $M(k,k')$ are random scattering amplitudes which depend on the location and type of disorder. We model $M(k,k')$ by a set of random phases $(g/\sqrt{N}) \exp[i \theta(k,k')]$, where the $\theta(k,k') = -\theta(k',k)$ are random and distributed uniformly in $[0,2\pi]$ and $g$ measures the strength of the disorder ($g^2$ is proportional to the concentration of defects in the crystal). This choice is what allows the calculation of the exact spectrum of eigenvalues of the random matrix\[8\]. Anharmonic effects are introduced next in order to stabilize the spectrum, since $H_0 + H_1$ possess an unstaibility threshold where the phonons become overcoupled\[6, 7\]. A simple quartic term suffices for this purpose,

$$\xi \frac{1}{N\omega_0} \sum_{k,k'} \omega_k \omega_{k'} Q_k Q_{-k} Q_{k'} Q_{-k'},$$

where $\xi$ is the Gruneisen parameter, typically a small quantity, expressed here in dimensionless form. $N$ is the number of normal modes and $\omega_0$ is a characteristic frequency of the reference crystal. Then a symmetry-breaking transformation $Q_k \rightarrow Q_k^\dagger + (f_k/\xi^{1/2})$ is performed in order to maintain all the $\omega^2$’s positive. This shift, required for $g > 1/2$ to restore stability in the dynamics, produces new terms linear in $Q$’s that have coefficients $O(1/\xi^{1/2})$. 
but that arise from two distinct sources: from the quadratic terms (linear in the $f$'s) and from the quartic (Grüneisen) terms (third-order in the $f$'s). These must be canceled if the individual atoms are all to be in positions of stable equilibrium. The relevant equations admit only a trivial solution $f_k \equiv 0$ for $g < 1/2$, but for $g > 1/2$ the cancellation is effected by choosing $f_k$ to be an eigenfunction of the random scattering matrix. (To minimize the free energy one picks the eigenvalue belonging to the largest eigenvalue.) The ground state energy is then a discontinuous function of $g$ at $g_c = 1/2$. At this value of the disorder the original locations of the atoms are no longer positions of stable equilibrium. Each atom moves to new, random, position that is essentially uncorrelated with the motion of the other atoms. This picture is confirmed by a calculation of the Debye-Waller factor; we find it to be finite below $g_c$ but divergent ($\propto 1/\xi$) once $g$ exceeds $g_c$, thereby confirming that all long-range correlations are lost. The dynamical Hamiltonian\cite{6,7} governing lattice vibrations is, however continuous, and independent of $\xi$ in the limit. It is:

$$H = \sum_k \epsilon_k \left( a_k^\dagger a_k + \frac{1}{2} \right) + g \frac{4}{\pi} \sum_{k,k'} \sqrt{\epsilon_k \epsilon_{k'}} M(k,k') Q_k Q_{k'}$$

$$+ \frac{1}{2} \left( g - \frac{1}{2} \right) \theta \left( g - \frac{1}{2} \right) \sum_k \epsilon_k Q_k Q_{-k} + O(\xi) +$$

$$+ \theta \left( g - \frac{1}{2} \right) \left\{ O(\xi^{1/2}) - O \left( \left( g - \frac{1}{2} \right)^2 / \xi \right) \right\} \tag{4}$$

where $\theta$ is the Heaviside step function. The origin of the individual powers in $\xi$ in $H$ is as follows.

The $\xi$-independent correction to the elastic forces is the result of all contributions second-order in the $f$'s in the quartic (Grüneisen) term. The singular, discontinuous, shift ($\propto 1/\xi$) in the ground state energy comes from the quartic term, when all four factors are $f$’s and from quadratic terms in which both factors are $f$’s. But, however large it may be, this shift in ground state energy does not affect the dynamics.

Two remaining contributions to the transformation vanish in the limit $\xi \to 0$: terms with a single factor $f$’s in the quartic term yield contributions are $O(\xi^{1/2})$ and those that are quartic in $Q$’s (with no $f$’s) yield the original quartic term $\propto \xi$.

The free energy of the model can be expressed as an integral over the
coupling constant,
\[ F = k_B T \int_0^\infty d\omega \left[ \rho_0(\omega) + \rho_1(\omega) + \rho_2(\omega) \right] \log(2 \sinh(\beta \omega/2)), \quad \beta \equiv 1/k_B T \]
(5)

where \( \rho_0(\omega) \) is the density of states of the reference crystal,
\[ \rho_0(\omega) = \frac{2}{\pi} \omega \text{Im} \left[ \int_{FBZ} \frac{d^3k}{(2\pi)^3} \frac{1}{\omega^2 - \omega_k^2} \right] \]
(6)
and the densities of modes \( \rho_1(\omega) \) and \( \rho_2(\omega) \) are the contributions from disorder and anharmonicity\[7\]:
\[ \rho_1(\omega) = \frac{2}{\pi g^2} \int_0^1 d\lambda \frac{\partial}{\partial \omega} \left[ -I(\omega, \lambda) R(\omega, \lambda) \right] \]
(7)
\[ \rho_2(\omega) = \frac{\theta(g - 1/2)}{\pi g^2} \int_{(2g)^{-1}}^1 \frac{d\lambda}{\lambda^3} (2\lambda g - 1) \frac{\partial}{\partial \omega} \left[ -I(\omega, \lambda) \right], \]
(8)
and \( R(\omega, \lambda), I(\omega, \lambda) \) are the real and imaginary parts of the the self energy \( Z(\omega, \lambda) \) which obeys the transcendental equation\[6\]
\[ Z(\omega, \lambda) = \left( \lambda g \right)^2 \sum_k \frac{\omega_k^2}{\omega^2 - \omega_k^2 (1 + \phi + Z(\omega, \lambda))} \]
(9)
with \( \phi = (2\lambda g - 1) \theta(\lambda g - 1/2) \).

RESULTS FOR THE SIMPLE-CUBIC LATTICE. The integral\[4\] can be performed analytically if the dispersion relation are \( \omega_k^2 = \omega_0^2 (3 - \cos(k_1) - \cos(k_2) - \cos(k_3)) \). After inserting this dispersion into Eq.(5) and taking the continuum limit, the equation for the self energy \( Z(\omega, \lambda) \) can be written implicitly as,
\[ W[3, \tau(\omega)] = \left( 1 - 3\frac{\omega_0^2}{\omega^2} (1 + \phi + Z(\omega)) \right) \left( 1 + \frac{Z(\omega)}{g^2} (1 + \phi + Z(\omega)) \right), \]
(10)
where the argument \( \tau(\omega) \) is given by,
\[ \tau(\omega) = \frac{3(1 + \phi + Z(\omega))}{3(1 + \phi + Z(\omega)) - (\omega/\omega_0)^2} \]
(11)
and \( W[3, z] \) is the generalized Watson integral evaluated by Joyce\[4\], who expressed it compactly in terms of complete elliptic integrals of the first kind\[10\]:
\[ W[3, z] = \left( \frac{2}{\pi} \right)^2 \sqrt{1 - \frac{3}{2} x_1} \frac{1}{1 - x_1} K(k_+) K(k_-), \]
(12)
where \( x_1 = (1/2) + (z^2/6) - (1/2)\sqrt{1 - z^2} \), \( x_2 = x_1/(x_1 - 1) \), 
\( k_{\pm}^2 = (1/2) \pm (1/4) x_2 \sqrt{1 - x_2} - (1/4)(2 - x_2)\sqrt{1 - x_2} \).

Figures 1 and 2 show the real and imaginary parts of \( Z(\omega, g) \). The imaginary part \( I(\omega, g) \) shows the not unexpected systematic broadening of the bandwidth with increasing disorder. \( R(\omega, g) \) exhibits a change in curvature from convex to concave at \( \omega = 0 \) as \( g \) is increased from below to above \( g_c = 0.5 \). Correspondingly, the slope of \( I(\omega, g) \) vanishes at \( \omega = 0 \) for all \( g < 1/2 \) but acquires a finite value for \( g \geq 1/2 \).

\( Z(\omega, g) \) can be expanded at both the low and high frequencies. It is also seen to possess a low-frequency fixed point in the glassy phase. From Eq.(11), for \( \lambda > 1 \) and \( g > 1/2 \) we deduce a sort of duality relation,

\[
Z(\omega, \lambda g) = \lambda Z(\omega/\sqrt{\lambda}, g)
\]

connecting high frequencies, large disorder, to lower frequencies and smaller disorder. \( Z \) is inserted into the global density-of-states \( \rho = \rho_0 + \rho_1 + \rho_2 \) and the indicated integrals performed, with the results shown in Fig.3. For \( g > 1/2 \), \( two \) fixed points in \( \rho \) are discerned: one just below the characteristic frequency \( \omega_0 \) and the other just below \( 3\omega_0 \). A new high-frequency “tail” grows beyond the second fixed point, indicating an accumulation of spectral density at the highest frequency as well as at the lowest.

It is also clear that the two van Hove cusps at \( \omega/\omega_0 = \sqrt{2} \) and 2 are sharp \emph{only} at \( g = 0 \), and that \( \rho \) loses its van Hove cusps and becomes analytic in \( \omega \) for \emph{any nonzero} value of the disorder, i.e. already in the disordered crystal and not just in the glassy phase! The theory works extraordinarily well for \( g \) from zero into the glassy phase at \( 0.5 + \epsilon \), with almost every noncrystalline material being excellently characterized at low \( T \) by some \( \epsilon < 0.1 \), and it remains trustworthy in every detail until \( g \) exceeds 1, when the mean-field approximation to the quartic terms fails at high frequencies.

**THE SPECIFIC HEAT.** With a knowledge of \( \rho \) the model’s thermodynamic properties, including specific heat, entropy and the other such functions are readily obtained. For \( g < 1/2 \), we find at low \( T \),

\[
c = \frac{C(T)}{Nk_B} = B(g) \left( \frac{T}{T_0} \right)^3
\]

\( B(g) \) is shown in Fig.4.
where \( B(g) = (4\pi^2\sqrt{2}/5) \left( 1 + \gamma( \left[ (1/2) + \sqrt{(1/4) - g^2} \right]^{-3/2} - 1 \right) \) and \( \gamma \approx 1.43 \). For \( g > 1/2 \),

\[
c = \frac{C(T)}{Nk_B} = A(g) \left( \frac{T}{T_0} \right)
\]

where \( A(g) = \pi(2/3)^{5/2} \sqrt{W[3,1]}(1 - (2g)^{-3/2}) \) \( \approx 1.404(1 - (2g)^{-3/2}) \).

The high-\( T \) specific heat is reasonably universal, always tending smoothly to the Dulong-Petit limit because \( \int_0^\infty d\omega \rho(\omega) = 3 \). Figure 4 illustrates the separate contributions \( c_0, c_1 \) and \( c_2 \) from the crystal, disorder and anharmonicity respectively, at \( g = 0.7 \), over the interval \( 0 < T/T_0 < 0.6 \).

**SPEED OF SOUND.** From our calculations using the present model and on the earlier Debye model, we find that, at constant density, the long wavelength speed of sound \( s = (d\omega/dk)_{k \to 0} \), when expressed as a ratio to the speed of sound in the perfect crystal, \( v(g) = s(g)/s(0) \), is a universal function of \( g \) having a cusp minimum at \( g = 1/2 \). Explicitly, we obtain:

\[
v(g) = \begin{cases} 
\left( \frac{1}{2} + \sqrt{\frac{1}{4} - g^2} \right)^{1/2} \text{ for } g < 1/2 \\
\frac{1}{g^{1/2}} \text{ for } g > 1/2
\end{cases}
\]

identical to Fig. 2 in Molina and Mattis [6] for the Debye model. The predicted drop of some 28\% as \( g \) increased from 0 to \( 1/2 + \epsilon \) should be confronted with experiment, after corrections for any changes in density with increasing disorder are taken into account.

We intend to publish the mathematical details of the various calculations elsewhere, but in the meantime the interested reader may request them from the corresponding author, M.I.M.

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Captions List

Figure 1: Detailed comparison of specific heat of a-SiO$_2$ with the present theory and with computer simulation molecular dynamics (S. N. Taraskin and S. R. Elliott, Phys. Rev. B 56, 8605 (1997)). We observe excellent agreement of the present theory with experiment at the low- and high-temperature end, although our result does lack the “bump” at 10 K.

Figure 2: Real and imaginary parts of the self-energy $Z(\omega)$ as a function of frequency for several disorder concentrations, below and above critical ($g = 1/2$).

Figure 3: Total density of states $\rho(\omega) = \rho_0(\omega) + \rho_1(\omega) + \rho_2(\omega)$ as a function of frequency for a wide range of disorder concentrations, proportional to $g^2$. Arranged according to the height of the central maximum, we have $g = 0, 0.1, 0.2, ...$ down to $g = 1$.

Figure 4: The three distinct contributions to the low-temperature specific heat from Eqs. (6), (7) and (8) in the glassy phase ($g = 0.7$).
FIG. 1

The diagram shows the relationship between $C_v / T^3$ and temperature $T$ (in K). The graph displays experimental data (triangles) and calculated results (curves). The calculated curves are further categorized into two types: molecular dynamics and another unspecified category. The y-axis ranges from $10^{-7}$ to $10^{-5}$, and the x-axis ranges from 1 to 100 K.
FIG. 2
Specific Heat / $k_B$

$\frac{T}{T_0}$

from $\rho_0$

from $\rho_1$

from $\rho_2$

FIG. 4