FROM DISORDERED CRYSTAL TO GLASS: EXACT THEORY

J. M. Yáñez†, M. I. Molina† and D. C. Mattis∗

†Facultad de Ciencias, Departamento de Física, Universidad de Chile
Casilla 653, Santiago, Chile.
*Department of Physics, JFB Bldg. #201, 115 S. 1400 E
Salt Lake City, UT 84112-0830, U.S.A.

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 $\gg 1/2$. As in earlier Einstein- and Debye- approximations, there is a phase transition 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 $g$. For $g > 1/2$ we discover novel fixed points in the self-energy and spectral density of this model glass.

†email: jyanez@macul.ciencias.uchile.cl, mmolina@abello.dic.uchile.cl
*email: mattis@physics.utah.edu

PACS number(s): 63.50.+x, 63.20.Dj, 63.20.Mt, 65.40.+g
The anomalous thermal properties observed in dielectric glasses\cite{1, 2}, has prompted numerous theoretical and experimental studies on the subject\cite{3}. Arguably, the best well-known model consists of the phenomenological two-level states (TLS) proposed by Anderson\cite{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\cite{5}. An alternative microscopic theory entirely based on phonons was subsequently advanced by one of the authors and his collaborators\cite{6}. It relies for its results on the interplay between disorder, parametrized by a dimensionless $g$, and anharmonicity, parametrized by a dimensionless $\xi$ (the Gruneisen 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\cite{6, 7}, both exhibited the following features: at a critical threshold $g_c$ the system transitions 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\cite{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 and can, in principle, be contrasted or compared with molecular dynamics performed on the identical simple-cubic lattice.

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 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 fixed points: frequencies at which the spectral density is independent of $g$. This feature brings 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

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

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

$$H_1 = \frac{1}{4} \sum_{k,k'} M(k,k') \sqrt{\omega_k \omega_{k'}} Q_k Q_{k'}, \quad (2)$$

where $Q_k = a_{-k}^\dagger + a_k$ and the $M(k,k')$ are random scattering amplitudes which depend on the location and type of disorder. Anharmonic effects are introduced next in order to stabilize the spectrum, since $H_0 + H_1$ possess an unstability threshold where the phonons become overcoupled[6, 7]. A simple quartic term suffices for this purpose,

$$\xi \frac{1}{N\omega_0} \sum_{k,k'} \omega_k \omega_{k'} Q_k Q_{-k} Q_{k'} Q_{-k'}, \quad (3)$$

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. We model $M(k,k')$ by a set of random phases ($g/\sqrt{N}) \exp[\theta(k,k')]$, where the $\{\theta(k,k')\}$ 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). Then, after a symmetry-breaking transformation is performed and the limit $\xi \to 0$
is taken, we find the ground state energy is a discontinuous function of $g$ at $g_c = 1/2$. The dynamical Hamiltonian[6, 7] governing lattice vibrations is, however continuous, and independent of $\xi$ in the limit. It is:

$$H = \sum_k \omega_k \left( a^+_k a_k + \frac{1}{2} \right) + \frac{g}{4} \sum_{k,k'} \sqrt{\omega_k \omega_{k'}} M(k, k') Q_k Q_{k'},$$

$$+ \frac{1}{2} \left( g - \frac{1}{2} \right) \vartheta \left( g - \frac{1}{2} \right) \sum_k \omega_k Q_k Q_{-k},$$

(4)

where $\vartheta$ is the Heaviside step function. The model is characterized by the existence of a ‘critical’ disorder concentration $g_c = 1/2$. In the disordered crystal phase ($g < 1/2$), the anharmonic corrections can be neglected, while in the “glassy” phase ($g > 1/2$) they give rise to an additional quadratic contribution responsible for an anomalous shift in the density-of-states to low frequencies. This, in turn, results in $C \sim T$ rather than $T^3$ at low $T$. This remarkable mechanism is quite general, transcending the particular dispersion $\omega(k)$ of the reference crystal.

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 spectral densities $\rho_1(\omega)$ 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)

$$\rho_2(\omega) = \frac{\vartheta(g - 1/2)}{\pi g^2} \int_{(2g)^{-1}}^1 d\lambda \frac{\partial}{\partial \omega} \left[ -I(\omega, \lambda) \right],$$

(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[8]

$$Z(\omega, \lambda) = (\lambda g)^2 \sum_k \frac{\omega_k^2}{N} \frac{\omega^2}{\omega^2 - \omega_k^2(1 + \phi + Z(\omega, \lambda))}$$

(9)

with $\phi = (2\lambda g - 1) \vartheta(\lambda g - 1/2)$. 

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RESULTS FOR THE SIMPLE-CUBIC LATTICE. The integral (9) 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.(9) and taking the continuum limit, the equation for the self energy $Z(\omega, \lambda)$ can be written implicitly as,

$$W[3, \tau(\omega)] = \left(1 - 3 \frac{\omega_0^2}{\omega^2} (1 + \phi + Z(\omega))\right) \left(1 + \frac{Z(\omega)}{g^2} (1 + \phi + Z(\omega))\right),$$  \hspace{1cm} (10)$$

where the argument $\tau(\omega)$ is given by,

$$\tau(\omega) = \frac{3(1 + \phi + Z(\omega))}{3(1 + \phi + Z(\omega)) - (\omega/\omega_0)^2}$$  \hspace{1cm} (11)$$

and $W[3, z]$ is the generalized Watson integral evaluated by Joyce, who expressed it compactly in terms of complete elliptic integrals of the first kind:

$$W[3, z] = \left(\frac{2}{\pi}\right)^2 \sqrt{1 - \frac{3x_1}{4}} K(k_+)K(k_-),$$  \hspace{1cm} (12)$$

where $x_1 = (1/2) + (z^2/6) - (1/2)\sqrt{1 - z^2} \sqrt{1 - (z^2/9)}$, $x_2 = x_1/(x_1 - 1)$, $k_\pm^2 = (1/2) \pm (1/4)x_2 \sqrt{4 - x_2} - (1/4)(2 - x_2) \sqrt{1 - x_2}$. 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.(9), for $\lambda > 1$ and $g > 1/2$ we deduce a sort of duality relation,

$$Z(\omega, \lambda g) = \lambda Z(\omega/\sqrt{\lambda}, g)$$  \hspace{1cm} (13)$$

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 only at $g = 0$, and that $\rho$ losses its van Hove cusps and becomes analytic in $\omega$ for 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 $T$,

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

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 $\int_0^\infty d\omega \rho_0(\omega) = 3$. 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 $0 < T/T_0 < 0.6$.

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.M.
ACKNOWLEDGMENTS
This work was supported in part by FONDECYT grant 3980038.

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Captions List

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

Figure 2: Imaginary part 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
FIG. 3
Specific Heat / $k_B$

$\rho_0$

$\rho_1$

$\rho_2$

$T/T_0$

FIG. 4