Quantum Mode-Coupling Theory for Vibrational Excitations of Glasses

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We exploit the fact that the mean-field theory for the vibrational anomalies of disordered solids, derived recently by the authors, is equivalent to a quantum mode-coupling theory. For small anharmonicities this theory predicts a continuous transition to a different glassy state if the degree of disorder is increased ("glass-to-glass transition"). It is argued that the vibrational glassy anomalies (boson peak, anomalous temperature dependence of the specific heat) are precursor phenomena of this transition.

1 Introduction The anomalous low-frequency vibrational properties of glasses and other disordered solids and their associated low-temperature thermal properties keep being a matter of controverse debate both among experimentalists and theorists. Such anomalies are the deviation of the vibrational density of states (DOS) from Debye's law at low frequencies ("boson peak") and the almost-linear temperature variation of the specific heat at very low temperatures, followed by a boson-peak-like anomaly at higher temperatures. Progress in understanding the nature of the boson peak has been achieved by noting that models with spatially fluctuating elastic constants [1–4] exhibit the boson-peak anomaly as observed in the experimental data. These model ideas are corroborated by recent nuclear-inelastic scattering investigations of glassy materials which shows that the boson-peak excitations are of collective character. This rules out models [5–7] in which the boson peak is due to localized excitations.

The present authors have developed recently a field-theoretical treatment of a disordered solid which allows for the inclusion of anharmonic interactions into the considerations [8]. The mean-field theory derived within this formalism boils down to the self-consisten Born approximation(SCBA) in the absence of the anharmonicity. The SCBA is equivalent to the coherent-potential approximation (CPA) [1, 3] for small degree of disorder. Within the SCBA experimentally measured boson peak data (i. e. the reduced DOS $g(\omega)/\omega^2$) with a characteristic maximum in the meV regime) can be explained quantitatively with only two adjustable parameters, namely, the mean sound velocity c_0 and its mean-square fluctuations ("degree of disorder") $\gamma \propto \langle(\Delta c)^2\rangle$. It was mentioned in Ref. [8] that in the presence of the anharmonic coupling the mean-field equations derived from the field-theoretical treatment are mathematically equivalent to the quantum-mechanical analogon of Götze's [9, 10] mode-coupling equations for the dynamic susceptibility of glass-forming viscous liquids. Here we exploit this idea further and show that (i) there is a continuous transition to another non-ergodic state if γ exceeds a critical value γ_c, and that (ii) the boson peak and the anomalous temperature variation of the specific heat can be considered as precursor phenomona of this transition.

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2 Mean-Field equations As in Ref. [8] we deal with a model solid with longitudinal excitations only. We consider elastic disorder, characterized by the fluctuation parameter γ and an anharmonic coupling, featuring the Grüneisen parameter g. The mean-field equations derived from an effective field theory by means of a saddle-point approximation are expressed in terms of the local dynamic susceptibility $Q(z) = i\int_0^\infty \mathrm{d}t \exp\{izt\}Q(t)$ with

$$Q(t) = \lim_{\mathbf{r}\to\mathbf{r}'} \frac{\tilde{m}_0}{6}\overline{\langle[\nabla\cdot\mathbf{u}(\mathbf{r},t+t_0),\nabla\cdot\mathbf{u}(\mathbf{r}',t_0)]\rangle}. \tag{1}$$

Here m_0 is the mass density [11], $\mathbf{u}(\mathbf{r},t)$ are the displacement fields, and $z=\omega+i0$. The self-consistent mean-field equations are

$$Q(z) = \frac{1}{2}\sum_{|\mathbf{k}|<1}\frac{k^2}{-z^2+k^2[1-\Sigma(z)]} = \frac{1/2}{(1-\Sigma(z))}[(1+z^2G(z)], \tag{2}$$

with the self energy

$$\Sigma(z) = \gamma Q(z) + \tilde{g}Q_2(z). \tag{3}$$

The mode-coupling parameter is given by $\tilde{g} = 4\gamma g^2/m_0$, where g is the Grüneisen coupling constant. $Q_2(z)$ is the convoluted dynamical susceptibility. Its imaginary part $Q_2"(\omega)$ can be related to the Fourier transform $S(\omega)$ of the van-Hove correlation function $S(t) = \lim_{\mathbf{r}\to\mathbf{r}'}\overline{\frac{\tilde{m}_0}{6}<\nabla\cdot\mathbf{u}(\mathbf{r},t+t_0)\nabla\cdot\mathbf{u}(\mathbf{r}',t_0)>}$ by $Q"(\omega) = \frac{1}{2}(1-\exp\{-\beta\omega\})S(\omega)$ with $\beta = [k_BT]^{-1}$. A similar relation holds for Q_2 and S_2, and we have

$$S_2(t) = S(t)^2. \tag{4}$$

In Eq. (2) $G(z)$ is the Green's function

$$G(z) = \sum_{|\mathbf{k}|<1}\frac{1}{-z^2+k^2[1-\Sigma(z)]}, \tag{5}$$

from which the DOS $g(\omega)$ can be obtained as

$$g(\omega) = \frac{2\omega}{\pi}\Im m\{G(z)\}. \tag{6}$$

We can rewrite the mean-field equations in terms of Kubo's relaxation function $\Phi(t) = \int_0^\beta \mathrm{d}\lambda S(t-i\lambda)$, which is related to the susceptibility by $Q(t) = i\frac{\mathrm{d}}{\mathrm{d}t}\Phi(t)$, which implies $Q(z) = Q_0 + z\Phi(z)$ with $Q_0 = Q(z=0) = \Phi(t=0)$. In the same fashion we define $Q_2(z) = Q_2(z=0) + z\Phi_2(z)$ and $\Sigma(z) = \Sigma(z=0)+zM(z)$, where $M(z)$ is called memory-function. Introducing normalized quantities $\phi(z) = \Phi(z)/Q_0$, $\phi_2(z) = \Phi_2(z)/Q_0^2$, and $m(z) = 2Q_0M(z)$we obtain a self-consistency equation for $\phi(z)$

$$m(z) = \lambda_1\phi(z) + \frac{1}{T}\lambda_2\phi_2(z) = \frac{\phi(z)-zG(z)}{1+z\phi(z)} \tag{7}$$

where we have introduced the two parameters $\lambda_1 = 2\gamma Q_0^2$ and $\lambda_2 = T\tilde{g}Q_0^3 = T\gamma g^2 4Q_0^3/m_0$. In the classical limit $\omega \ll T$ we have $\Phi(t) = S(t)/T$, from which follows $\Phi_2(t) = T[\Phi(t)]^2$ In this limit (7) agrees mathematically with the Mode-coupling equation for the so-called λ_1-λ_2 model [9] (or F_{12} model [10]) of W. Götze This equation is a schematic representation of the mode-coupling theory for the liquid-glass transition of viscous liquids [10], because it shows the same critical phenomena as the full theory.

3 Non-Ergodicity transition It has been noted in the literature dealing with disordered harmonic models [1,3] that if the disorder-induced fluctuations of the elastic constants are too strong, an instability occurs, which manifests itself by the appearance of negative values of ω^2 in the spectrum, implying that $G(z)$ is no more a positive analytic function. The unstable situation arises because in the harmonic theory with too strong force constant fluctuations some atoms are sitting on potential hills instead in potential wells. Such an instability occurs also in the harmonic version of the present theory, namely in the SCBA (Eqs. (2) and (3) with $\tilde{g} = 0$) for $\gamma > \gamma_c = 0.5$. This unphysical situation is, of course, an artifact due to the absence of anharmonic interactions. Within our anharmonic mean-field theory (quantum mode-coupling theory) there appears also an instability for $\gamma > \gamma_c$. But now the spectrum remains positive. Instead of the non-physical unstable eigenvalues a phase transition to a non-ergodic state occurs. The order parameter for such a transition (non-ergodicity parameter) is

$$f = \lim_{t\to\infty} \phi(t) = \lim_{z\to 0}(-z\phi(z)) \tag{8}$$

from Eq. (7) we obtain the following self-consistency equation for f

$$\frac{f}{1-f} = \lambda_1 f + \lambda_2 f^2 \tag{9}$$

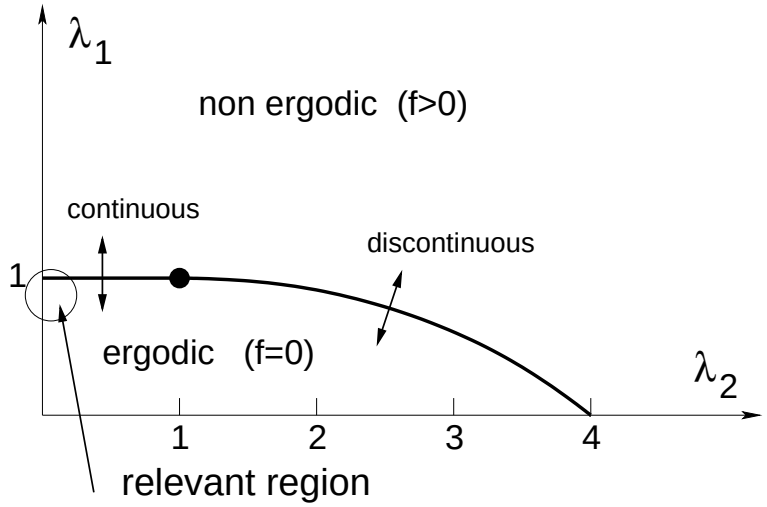

Figure 1
Phase diagram of the quantum mode-coupling theory

Because this is a homogeneous equation for f, there is always the solution $f = 0$. However, it has been shown [10] that the stable solution of the mode-coupling equations is always that with the largest f if a nontrivial solution $f > 0$ exists. The regions in the (λ_1, λ_2) plane where such nonergodic solutions exists are depicted in Fig. 1. For $\lambda_2 < 1$ the transition is continuous, otherwise it is discontinuous. In our case, we are interested in the situation at low temperatures and small anharmonicity which means $\lambda_2 \ll 1$. Therefore we expect a continuous transition for λ_1 exceeding $\lambda_{1,c} = 1$. Because for this value $Q_0 = 1$, this is equivalent to γ exceeding $\gamma_c = 0.5$.

How can we interpret such a transition? The non-ergodicity parameter can be shown [10] to play the role of a Debye-Waller factor, which, in the case of the glassy freezing of a liquid, characterizes the structure of the frozen material. As we have started in our investigation with an already frozen material, f has to be interpreted as a shift of the Debye-Waller factor which occurs, because the disorder has become so large, that a global rearrangement of the structure takes place. We call this transition a glass-to-glass transition.

From the previous investigation of harmonic models [1, 3, 4, 8] it has been shown that the boson peak (maximum in $g(\omega)/\omega^2$) becomes more strongly pronounced (and shifts to smaller frequencies) as γ approaches γ_c. Therefore the boson-peak anomaly can be interpreted as a precursor phenomenon of the glass-to-glass transition.

From the investigation of the dynamics of a liquid near the glass transition by means of the mode-coupling theory it is known [10] that strongly pronounced dynamical critical phenomena in the low-frequency asymptotics of the Kubo function appear. It can be shown [9, 10] that for $\phi"(\omega)$ near $\lambda_1 = 1$ the following asymptotic scaling behaviour holds

$$\phi"(\omega) = A(\lambda_2) \begin{cases} \omega_\epsilon^{a-1} & \omega < \omega_\epsilon \\ \omega^{a-1} & \omega > \omega_\epsilon \end{cases} \tag{10}$$

where $0 < a < 0.5$ and $a \to 0.5$ as $\lambda_2 \to 0$, and $A(\lambda_2)$ is a constant which has to be determined numerically. The cross-over frequency $\omega_\epsilon = [1 - \lambda_2]^{1/a}$ can be estimated to ly near the boson-peak frequency which (in units of the Debye frequency) is roughly given by $\omega_{boson} \approx 1 - 2\gamma$. In the regime $\omega < \omega_\epsilon$ we have a constant Kubo spectral function $\phi"(\omega) = \phi"(0) = A(\lambda_2)/[1 - \lambda_2]^{\frac{1}{a}-1}$ ("white-noise spectrum" [10]) This means that the dynamical response function $Q"(\omega)$ varies linearly with frequency, and therefore the broadening of the Brillouin line (inverse of the mean free path) quadratically with ω, as it is observed frequently in experiments.

Such a white-noise spectrum of $\phi"(\omega)$ implies also a specific heat which varies linearly with temperature in the following way [12]:

From the effective action in saddle-point approximation one can show that the averaged internal energy $\bar{H}$ contains an anomalous contribution $\Delta\bar{H}$, which is essentially the thermal average of the function $Q"(\omega) = \omega\phi"(\omega)$ and therefore its temperature dependence reflects the low-ω asymptotics of $\phi"(\omega)$:

$$\Delta\bar{H} \propto \int_0^\infty \mathrm{d}\omega \frac{1}{\exp\{\beta\omega\} - 1} \omega\phi"(\omega) \propto \begin{cases} T^2\omega_\epsilon^{a-1} & \omega < \omega_\epsilon \\ T^{a+1} & \omega > \omega_\epsilon \end{cases} \tag{11}$$

This implies a T-linear specific heat for $T < \omega_\epsilon$.

In conclusion we have shown that in a model with static disorder and an anharmonic coupling, which is described by a quantum mode-coupling theory, a glass-to-glass transition occurs, which means that with increasing disorder a state with a different ergodic structure is reached. Within this scenario the boson peak anomaly and the T-linear specific heat are precursor phenomena of this transition.

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[11] We use units in which lengths are measured in Debye lengths k_D^{-1}, times in inverse Debye frequencies $\omega_D^{-1} = [c_0 k_D]^{-1}$ and actions in units of $\hbar$. In these units $c_0 = 1$ and $m_0 = \bar{m}_0 c_0 \hbar^{-1} k_D^{-1}$, where $\bar{m}_0$ is the mass density in the usual SI units.
[12] Note that this mechanism of the temperature-linear specific heat is different from that anticipated in Ref. [8].