Theory of vibrational anomalies in glasses

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ARTICLE INFO

ABSTRACT

The theory of elasticity with spatially fluctuating elastic constants (heterogeneous-elasticity theory) is reviewed. It is shown that the vibrational anomalies associated with the boson peak can be qualitatively and quantitatively explained in terms of this theory. Two versions of a mean-field theory for solving the stochastic equation of motion are presented: the coherent-potential approximation (CPA) and the self-consistent Born approximation (SCBA). It is shown that the latter is included in the former in the Gaussian and weak-disorder limit. We are able to discuss and explain cases in which the change of the vibrational spectrum by varying an external parameter can be accounted for by changing the Debye frequency (elastic transformation) and cases in which this is not possible. In the latter case a change in the distribution of the elastic moduli has occurred.

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1. Introduction

The vibrational properties of glasses in the THz frequency range have remained an intensively studied and controversially discussed field of research for more than 50 years [1–5]. The vibrational spectra of glasses — as revealed by inelastic neutron and X-ray scattering [6,7], Raman scattering [8], calorimetric experiments [9] and computer simulations [10] deviate strongly from the predictions of Debye's elasticity theory [11–13] in a frequency range, where it had been supposed to be still valid. Roughly one order of magnitude below the Debye frequency the vibrational density of states (DOS) $g(\omega)$ of almost all glasses (the exception seems to be amorphous Si [14,15]) exhibits an enhancement with respect to the Debye $g(\omega) \propto \omega^2$ law, which shows up as a maximum in the "reduced DOS" $g(\omega)/\omega^2$. This maximum has been called "boson peak" (BP) for historical reasons, because the only temperature dependence of the vibrational anomalies in the scattering experiments comes from the Bose factor $n(\omega) + 1 = [1 - exp\{-\hbar\omega/k_BT\}]^{-1}$ if the spectral function $\chi''(\omega)$ is temperature independent (harmonic excitations). The relation between the results of Raman, neutron and X-ray scattering to the DOS will be clarified below.

In inelastic X-ray experiments and simulations it was found recently that the BP is related to two anomalous features in the Brillouin spectrum of glasses: Near the boson-peak frequency the group velocity $\partial\Omega/\partial k$ (where $\Omega(k) =$ is the Brillouin resonance frequency) shows a pronounced dip and the Brillouin line width [16–19] $\Gamma(k)$ shows a strong increase $\propto k^4$, which has been interpreted as disorder-induced Rayleigh scattering.

The BP in the DOS is related to a similar feature in the temperature dependence of the specific heat in the $T \approx 10$ K regime [9]. The peak

of the function $C(T)/T^3$ has also been called BP and can be shown [20] to be related to a pronounced shoulder in the temperature dependence of the thermal conductivity $\kappa(T)$ [21,20]. These boson-peak-related thermal anomalies have to be distinguished from low-temperature anomalies of $C(T)$ and $\kappa(T)$ around and below 1 K. In this temperature regime in almost all glasses $C(T) \propto T^x$ and $\kappa(T) \propto T^y$ with $x \approx T$ and $y \approx 2$. This low-temperature behavior can be explained in terms of bi-stable tunneling defects (two-level systems, TLS [22,23]).

Many suggestions have been published for explaining the boson-peak-related vibrational anomalies. In the time in which it was realized that many features of complex solids involved self-similar (fractal) structures, the anomalies were attributed to a "phonon–fracton crossover" [24]. But neither were fractal features of glasses found in scattering experiment nor a BP in a simulated percolation system with phonon–fracton crossover [25]. So this model had to be discarded as candidate for an explanation of the BP.

In many materials (glassy or crystalline) there exist internal low-frequency vibrational modes, which couple to the center-of-mass acoustical vibration. This hybridization leads to a peak in the DOS and also in the reduced DOS. So many authors favor models in which glasses are assumed to have quasi-local disorder-induced oscillators similar to the molecular systems [26–28]. These oscillators are assumed to be created by glass-specific soft bistable potentials, similar to those in the TLS model. The present authors are of the opinion that the soft-potential model, if coarse-grained over a mesoscopic volume, should lead to spatially fluctuating elastic constants, which is the starting point of the present theory.

Quite recently it was claimed that the BP is just due to a (smeared) van-Hove singularity of a crystal-like transverse sound dispersion [29–32]. So according to the present status of discussion it is still a matter of controversy, whether the BP is a disorder-induced phenomenon or not.

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We believe that now from experimental and simulational work and in the light of the present theory there is ample evidence that the boson-peak-related anomalies are indeed produced by the glass-specific structural quenched disorder. In particular, we shall show below that the mentioned anomalies can all be qualitatively and in many cases quantitatively explained in terms of spatially fluctuating elastic constants.

Models involving spatially fluctuating elastic constants and/or force constants have been put forward already for a while using phenomenological effective-medium theories [33–36]. The concept of fluctuating elasticity has also been used in the qualitative explanation of experimental data [37,38]. A fluctuating-force-constant scalar-vibration model on a cubic lattice was solved both numerically and in coherent-potential approximation (CPA) by Schirmacher et al. [39]. In this model calculation a Gaussian distribution of nearest-neighbor force constants K was taken, with a lower cutoff, which was allowed to extend into the negative K regime. It was both shown that the disorder in this model leads to a BP in the regime of 1/10 of the Debye frequency and that the CPA and the numerics give almost identical results. It was furthermore shown by an energy-level-statistics analysis that the states near the BP are delocalized. Localized states were only found near the Debye frequency. The localized states in the high-frequency regime of the vibrational spectrum, which lead to an exponential tail in the DOS [40], have been addressed recently by instanton methods [41]. At small disorder (fine-tuned by the low-K cutoff) a maximum in the reduced DOS due to the van-Hove singularity corresponding to the simple-cubic dispersion appears at $\approx$ half the Debye frequency. Shifting the cutoff down, i.e. increasing the disorder, leads to a downshift of the maximum. These results (and other findings, to be discussed below) were later interpreted [42,29,43,30] in such a way, that the BP would be just a smeared quasi-crystalline van-Hove singularity due to a flattening of the transverse dispersion. However, it was shown subsequently that a disorder-induced BP exists in a model, in which the host system does not have a crystalline dispersion [44]; the calculated DOS agreed to the simulation results of Rahman et al. [10] for the vibrational spectrum of a structural Lennard–Jones glass.

Schirmacher et al. [39] showed further that shifting the lower cutoff of the truncated Gaussian distribution of force constants below a critical (negative) value led to an instability in both the numerical and CPA results, which resulted from the presence of too many negative force constants. From this Schirmacher et al. [39] concluded that the BP is a precursor of an elastic instability, a conclusion, which is shared by later theoretical investigations [45–48].

A field-theoretical derivation of a mean-field theory of heterogeneous elasticity was published 2006 by Schirmacher [20]. In heterogeneous elasticity theory the shear modulus is assumed to fluctuate in space due to a given probability distribution. Evaluating the average over the Green's function by the replica trick and performing a saddle-point approximation for the resulting effective field theory result in an effective-medium-like approximation for the frequency-dependent shear modulus. As in the old effective-medium theories [33,35], the spatial disorder leads to a frequency-dependent elastic modulus, which, by the dictate of causality must have a real and imaginary part. The imaginary part of the shear modulus leads to disorder-induced sound attenuation, which renders a Debye-like description impossible, once the imaginary part becomes comparable to the real part of the modulus. Transformed to a wave language, this statement is equivalent to the very old findings of Ioffe and Regel [49], which was quoted by Mott [50] and many other authors [51], that waves in disordered systems can only exist if the mean-free path is larger than its wavelength. So we can say that the BP signifies the upper frequency limit of a wave description and the lower one of a description in terms of "random-matrix states". This classification is adequate, because the discretized equation of motion of heterogeneous elasticity is equivalent to a (sparse) random-matrix eigenvalue problem. It was established in several publications that fluctuating elasticity models belong to the Gaussian-Orthogonal Ensemble of random-matrix models [39,52].

Recent inelastic scattering experiments [53,54,16,55,56,18] and molecular-dynamics simulations [57–62,17,63,19,64] gave valuable insights into the nature of the high-frequency and small-scale vibrational properties of glasses. It emerged that the transverse degrees of freedom of local elasticity play a key role for producing the anomalies. It became clear that the dip in the differential sound velocity and the strong increase of the sound attenuation near the boson-peak position are related to each other (by the Kramers–Kronig relation) and are further manifestations of the boson-peak anomalies. In particular, from the recent simulations of model glasses it became clear beyond doubt that the anomalies are caused by the elastic heterogeneities [19,64].

The present short review is organized as follows: In Section 2 the description of experimental data in terms of frequency-dependent moduli will be given. In Section 3 heterogeneous elasticity and its solution in coherent-potential approximation (CPA) [65] are presented. It is shown that it reduces to the earlier solution in self-consistent Born approximation (SCBA) [20,66] in the weak-disorder limit. The CPA procedure is based on the concept of coarse-graining the elasticity fluctuations over spatial regions of the size of a correlation length. As these regions are larger than an interatomic spacing, the high-wavenumber cutoff, which is inversely proportional to this length, is different to that used to calculate the density of states. It is shown that by recognizing this the boson peaks predicted by heterogeneous-elasticity theory are not restricted to a factor of 2, as stated previously [66], based on the assumption that the two cutoffs are the same. Section 3 comprises the discussion of model calculation using the CPA with a Gaussian distribution of shear moduli, truncated at the lower end. Changing the parameters of this distribution leads to a change in the spectrum, which cannot be described by an elastic transformation, i.e. by just changing the Debye frequency. In Section 4 some conclusions are drawn.

2. Basic definitions

2.1. Correlation functions and frequency-dependent elastic moduli

The correlation function, which is proportional to the scattering cross-section of inelastic X-ray and neutron scattering is the one-phonon dynamical structure factor $S(k, \omega)$. It is related to the longitudinal dynamical susceptibility by the fluctuation–dissipation theorem [67]:

$$S(k, \omega) = \frac{\hbar}{\pi m}[n(\omega) + 1]\chi_L''(k, \omega) \quad \omega \neq 0. \tag{1}$$

Here m is the ratio of the mass density ρ_m and the number density N/V of the material. In the classical $\hbar\omega/k_B T \to 0$ limit we have

$$S(k, \omega) = \frac{k_B T}{\pi m \omega} \chi_L''(k, \omega) \quad \omega \neq 0. \tag{2}$$

In a glass the longitudinal dynamical susceptibility $\chi_L(k, z) = \chi_L'(k, \omega) + i\chi_L''(k, \omega)$ ($z = \omega + i\epsilon$, $\epsilon \to +0$) can be represented as [66,19]

$$\chi_L(k, z) = \frac{k^2}{-z^2 + k^2 v_L^2(z)} = k^2 G_L(k, z) \tag{3}$$

where the longitudinal frequency-dependent sound velocity $v_L(z)$ is related to the frequency-dependent longitudinal modulus $M(z)$ by

$$M(z) = \rho_m v_L(z)^2 = M'(\omega) - iM''(\omega). \tag{4}$$

$G_L(k, z)$ is the longitudinal (disorder-averaged) Green's function [68] corresponding to the longitudinal wave equation (see next section). The sound attenuation coefficient can be defined as [19]

$$\Gamma_L(\omega) = \omega M''(\omega)/M'(\omega). \tag{5}$$

Taking Eqs. (2), (3) and (5) together and defining the resonance frequency $\Omega_L(\omega) = v_L(\omega)k$ we obtain

$$S(k,\omega) = \frac{k_B T}{m\omega} k^2 \frac{1}{\pi} \frac{\Omega_L^2 \Gamma_L(\omega)/\omega}{(\Omega_L^2 - \omega^2)^2 + (\Omega_L^2 \Gamma_L(\omega)/\omega)^2}. \tag{6}$$

Near resonance $\omega = \Omega_L$ we obtain the "damped-harmonic-oscillator" (DHO) function, with which many Brillouin-scattering spectra have been fitted:

$$S(k,\omega) = \frac{k_B T}{m\omega} k^2 \frac{1}{\pi} \frac{\omega \Gamma_L(\omega)}{(\Omega_L^2 - \omega^2)^2 + \omega^2 \Gamma_L(\omega)^2}$$
$$\stackrel{\Gamma_L \to 0}{=} \frac{k_B T}{m\Omega_L^2} k^2 \frac{1}{2} [\delta(\omega - \Omega_L) + \delta(\omega + \Omega_L)]. \tag{7}$$

In this context it is important to remark that the inverse line width Γ in a disordered system is *not* equivalent to a "life time" of an excitation. In fact, in a disordered *harmonic* system there is no damping. This means that all oscillatory degrees of freedom, if excited, live forever. They can only die out by an anharmonic mechanism. A finite Γ is just due to the disorder and describes static scattering. Similar to electrons in impure metals [69] $\tau = \Gamma^{-1}$ is proportional to the elastic mean-free path, divided by the wave velocity, which involves no dissipation.

On the other hand, at frequencies much below the BP there is evidence for an anharmonic origin of sound attenuation [70–73]. In this case the corresponding inverse sound attenuation frequency is a true decay time.

The scattering law $S(k,\omega)$ is connected via the equation of continuity to the longitudinal current-correlation function

$$C_L(k,\omega) = \frac{\omega^2}{k^2} S(k,\omega) = \frac{k_B T \omega}{\pi m} G_L''(k,\omega). \tag{8}$$

In a similar way, one can define transverse correlation functions as [61]

$$C_T(k,\omega) = \frac{\omega^2}{k^2} S_T(k,\omega) = \frac{k_B T \omega}{\pi m} G_T''(k,\omega) \tag{9}$$

with the transverse Green's function

$$G_T(k,z) = \frac{1}{k^2} \chi_T(k,z) = \frac{1}{-z^2 + k^2 v_T(z)^2}. \tag{10}$$

The frequency-dependent transverse sound velocity is related to the frequency-dependent shear modulus by

$$\rho_m v_T(z)^2 = G(z) = G'(\omega) + i G''(\omega). \tag{11}$$

$G(z)$ is related to $M(z)$ by

$$M(z) = K(z) + \frac{4}{3} G(z) \tag{12}$$

where $K(z)$ is the macroscopic (frequency-dependent) bulk modulus. One can define a transverse acoustic attenuation coefficient as

$$\Gamma_T(\omega) = \omega G''(\omega)/G'(\omega). \tag{13}$$

One can relate the longitudinal and the transverse sound attenuation functions with an elastic, disorder-induced mean free path:

$$\frac{1}{\ell_{L,T}(\omega)} = \frac{\Gamma_{L,T}(\omega)}{2 v_{L,T}(0)}. \tag{14}$$

The Ioffe–Regel (IR) limit is reached when this length becomes equal to the wavelength $\lambda_{L,T} = \omega/2\pi v_{L,T}(0)$, i.e. for $\omega_{L,T}^{IR} = \pi \Gamma_{L,T}(\omega)$.

In molecular-like model glasses the *transverse* IR limit is reached near the BP [61,17,19], whereas in network glasses, where these frequencies are nearer to each other, both limits appear to be reached near the BP [74].

2.2. Wavenumber-independent spectra

Within a generalized Debye model, which is described by the Green's functions $G_{L,T}$ defined in Eqs. (3) and (10) the vibrational density of states (DOS) is given by

$$g(\omega) = \frac{2\omega}{3\pi} \frac{1}{N} \sum_{|\mathbf{k}| < k_D} \left(G_L''(k,\omega) + 2 G_T''(k,\omega) \right)$$
$$= \frac{2\omega}{3\pi} \frac{3}{k_D^3} \int_0^{k_D} dk\, k^2 \left(G_L''(k,\omega) + 2 G_T''(k,\omega) \right) \tag{15}$$

where $k_D = \sqrt[3]{6\pi^2 N/V}$ is the Debye cutoff wavenumber, V being the total volume of the sample and N the total number of atoms or molecular units.

We now define the local velocity correlation function as

$$Z(\omega) = \frac{1}{<v^2>} \frac{1}{N} \sum_{|\mathbf{k}| < k_D} \left(C_L''(k,\omega) + 2 C_T''(k,\omega) \right) \tag{16}$$

with $<v^2> = \frac{3}{2} k_B T/m$. Inserting Eqs. (9) and (8) into Eq. (16) we find by comparing with Eq. (15) [10]

$$g(\omega) = Z(\omega). \tag{17}$$

For the following it will be useful to define longitudinal and transverse susceptibility integrated up to a certain wavenumber cutoff k_ξ

$$\chi_{L,T}^\xi(z) = \frac{3}{k_\xi^3} \int_0^{k_\xi} dk\, k^2 \chi_{L,T}(k,z) \tag{18}$$

k_ξ can be related to the correlation length ξ of the spatially fluctuating density ρ, the elastic constants K, G or the Pockels (light-elastic) coupling constants α by $k_\xi = \nu/\xi$, where ν is a constant of order unity. For Raman scattering [75,76] these functions (with ξ referring to the Pockels constant fluctuations) enter as follows into the observed intensities

$$I_{VV}(\omega) = A f_1 [n(\omega) + 1] \left[\chi_L^{\xi_\alpha}(\omega) \right]'' + \frac{4}{3} I_{VH}(\omega) \tag{19}$$

$$I_{VH}(\omega) = A[n(\omega) + 1] f_2 \frac{1}{30} \left(2 \left[\chi_L^{\xi_\alpha}(\omega) \right]'' + 3 \left[\chi_T^{\xi_\alpha}(\omega) \right]'' \right) \tag{20}$$

where A is a proportionality constant and $f_{1,2}$ are the longitudinal and transverse mean-square Pockels constant fluctuations. As pointed out by Martin and Brenig [75] and Schmid and Schirmacher [76] the correlation length ξ in these expressions refers to the correlation functions of the spatially fluctuating light-vibration (Pockels) constants.

For *incoherent neutron scattering* the observed intensity is proportional to the density of states:

$$S(k,\omega)_{\text{incoh}} \propto [n(\omega) + 1] \frac{g(\omega)}{\omega}. \tag{21}$$

In materials, which scatter predominantly incoherently this is a way to obtain the DOS directly [77]. Similarly is the *inelastic nuclear scattering* (INS) a direct way to obtain the DOS of glasses [40].

In many materials, which have been investigated by inelastic neutron scattering, the scattering is *coherent*, which precludes the usage of Eq. (21). However, it is known [78,46,79] that in the limit $k \to \infty$ all coherence is lost, i.e. $S(k,\omega) \to S_{\text{incoh}}(k,\omega)$. This limit is expected to hold for k values at which the static structure factor $S(k)$ becomes

equal to its coherent counterpart $S(k)_{incoh} = 1$. Typical values for inelastic coherent neutron scattering, however, range around and somewhat beyond the central peak of $S(k)$. In the *incoherent approximation* [78, 80–82], the coherent dynamical structure factor is replaced by expression (21). In order to make the data more incoherent (and to gain statistics) it can be useful [78,80–82], to average the data over the k range accessible by the kinetic window of the neutrons and write

$$\langle S(k, \omega) \rangle = \frac{1}{k_{max} - k_{min}} \int_{k_{min}}^{k_{max}} dk S(k, \omega) \propto [n(\omega) + 1] \frac{g_{neutron}(\omega)}{\omega}. \quad (22)$$

The error made by this approximation has been discussed in detail by Taraskin and Elliot [81] and by Fabiani et al. [82].

For many years an incoherent approximation like Eq. (21) was assumed to hold approximately also for the Raman intensity [8,83]. After some time, however, it became clear, that the DOS $g_{Raman}(\omega)$ extracted using Eq. (21) in this way had little in common with $g_{neutron}(\omega)$, extracted via Eq. (22). So one invented [84,76] a "Raman coupling function" $C(\omega)$ and wrote

$$I_{VH}(\omega) \propto [n(\omega) + 1] C(\omega) \frac{g(\omega)}{\omega}. \quad (23)$$

Comparing Eq. (23) with Eq. (20) we get

$$C(\omega) = \frac{\omega}{g(\omega)} \left(2 \left[\chi_L^{\xi_\alpha}(\omega) \right]'' + 3 \left[\chi_T^{\xi_\alpha}(\omega) \right]'' \right). \quad (24)$$

An expression like this has already been given by Viliani et al. [85], which shows that $g(\omega)$ drops out of the formula [86]. The idea of the workers [84] using $C(\omega)$ was, however, the assumption that this function might be the same for all glasses, for which we cannot find any justification. For the future we advertise to use the susceptibilities $\xi_{L,T}^{\xi_\alpha}$ instead, which can be directly related to inelastic scattering data.

2.3. Thermal properties

The specific heat can be calculated from the DOS by the usual formula

$$C(T) \propto \int_0^\infty d\omega g(\omega) (\omega/T)^2 \frac{e^{\hbar \omega/k_B T}}{\left[e^{\hbar \omega/k_B T} - 1 \right]^2}. \quad (25)$$

In terms of the *transport* mean-free path $\ell_{tr}(\omega)$ the thermal conductivity is given by

$$\kappa(T) \propto \int_0^\infty d\omega \ell_{tr}(\omega) g(\omega) (\omega/T)^2 \frac{e^{\hbar \omega/k_B T}}{\left[e^{\hbar \omega/k_B T} - 1 \right]^2}. \quad (26)$$

As shown by Schirmacher [20] by an analysis of the Gaussian contributions beyond the SCBA saddle-point (which are important for transport properties [87,88]) the transport mean-free path $\ell_{tr}(\omega)$ to be inserted into Eq. (26) is not the one-particle mean-free path $\ell(\omega)$ calculated from the sound attenuation, but has to be multiplied with the inverse reduced DOS:

$$\ell_{tr}(\omega) \propto \frac{\omega^2}{g(\omega)} \ell(\omega) \quad (27)$$

where $\ell(\omega) \propto \ell_T(\omega)$ if the disorder scattering is due to the transverse shear fluctuations.

3. Heterogeneous-elasticity theory

3.1. Model

Heterogeneous-elasticity theory is formulated in terms of standard elasticity theory [89]. The equations of motion for the Cartesian components i, j of the displacement vector $\mathbf{u}(\mathbf{r}, t)$ are given by

$$\rho_m \frac{\partial^2}{\partial t^2} u_i(\mathbf{r}, t) = \sum_j \partial_j \sigma_{ij}(\mathbf{r}, t) \quad (28)$$

where ρ is the mass density and σ_{ij} is the stress tensor, which, for a homogeneous and isotropic medium is given by

$$\sigma_{ij} = \lambda \delta_{ij} \text{Tr} \{\epsilon\} + 2G\epsilon_{ij} = K\delta_{ij} \text{Tr} \{\epsilon\} + 2G(\mathbf{r})\hat{\epsilon}_{ij}. \quad (29)$$

Here $\lambda = K + \frac{2}{3}G$ is the longitudinal Lamé modulus, K is the bulk modulus, and G is the shear modulus. ϵ_{ij} is the strain tensor

$$\epsilon_{ij} = \frac{1}{2} \left(\frac{\partial}{\partial x_i} u_j + \frac{\partial}{\partial x_j} u_i \right). \quad (30)$$

In the second line of Eq. (29) the terms have been rearranged in such a way that the second summand involves only shear stresses, the first only dilatational stresses. This is not the case for the first line.

The traceless strain tensor, which appears in the second line is defined by

$$\hat{\epsilon}_{ij} = \epsilon_{ij} - \frac{1}{3} \delta_{ij} \text{Tr} \{\epsilon\}. \quad (31)$$

We now are generalizing the theory for allowing the elastic constants to fluctuate in space. Of course, there is no reason, why isotropy should still hold on a mesoscopic length scale. In fact, computer simulations [62,63,19,64] show that this is not so. However, to keep the theory tractable we make the two assumptions: (i) that the breakdown of the homogeneity is more important than that of the isotropy and (ii) that the (relative) fluctuations of the shear modulus G are stronger than those of the bulk modulus. Indirect evidence for correctness of the second assumption comes from the fact that the macroscopic bulk modulus K, extracted from numerical simulations on model glasses, is not frequency dependent [17,19]. Marruzzo et al. [19] and Mizuno et al. [64] have shown by directly calculating local elastic moduli from their simulations, that indeed in these model glasses the relative fluctuations of K are much smaller than those of G.

We now assume that the shear modulus in the representation of the second part of Eq. (29) randomly fluctuates in space: $G = G(\mathbf{r})$. For the case of the Gaussian disorder we, as before, distinguish between an average G_0 and fluctuations.

3.2. Coherent-potential approximation (CPA)

The coherent-potential approximation (CPA) is a well-established theory for wave spectra and transport in quenched-disordered systems [90–97]. It has been generalized recently to apply to diffusion in a heterogeneous medium and to heterogeneous-elasticity theory with the help of replica field-theoretic methods [65]. It was shown that this theory reduces to the earlier version of heterogeneous elasticity theory based on Gaussian statistics [20,66] in the weak-disorder limit, i.e. in the limit $\Delta G/G_0 < 1$, where ΔG is the root-mean-square deviation of the fluctuations of $G(\mathbf{r})$. As in the earlier theory the spatial fluctuations of G are transformed in the macroscopic limit to a disorder-induced frequency dependence of G. In our CPA theory we assume that the microscopic fluctuations of G are averaged over a coarse-graining volume of diameter ξ_G, where ξ_G is the correlation length of the G fluctuations. This means, that the resulting values of G_i corresponding to the volume

with center $\mathbf{r}_i$ can be assumed to be statistically uncorrelated. The self-consistent equations for $G(\omega)$ are

$$0 = \left\langle \frac{G_i - G(z)}{1 + \frac{\tilde{\nu}}{3}(G_i - G(z))\Lambda(z)} \right\rangle_i \tag{32a}$$

$$G(z) = \left\langle \frac{G_i}{1 + \frac{\tilde{\nu}}{3}(G_i - G(z))\Lambda(z)} \right\rangle_i \tag{32b}$$

$$\Lambda(z) = \frac{4}{3}\chi_L^{\xi_G}(z) + 2\chi_T^{\xi_G}(z) \tag{32c}$$

where $\tilde{\nu}$ is related to the correlation-length parameter ν by $\tilde{\nu} = \nu^3/2\pi^2$. Eqs. (32a) and (32b) are equivalent.

From the frequency-dependent shear modulus $G(z)$ the DOS is calculated by means of Eq. (15) with

$$G_L(k,z) = \frac{1}{-z^2 + k^2[K + \frac{4}{3}G(z)]} \tag{33a}$$

and

$$G_T(k,z) = \frac{1}{-z^2 + k^2 G(z)}. \tag{33b}$$

In the following we re-derive the previous SCBA theory [20,66] for the case of weak disorder, i.e. $\Delta G < \langle G \rangle$. We define fluctuations $\delta G_i = G_i - \langle G \rangle$ and a self energy $\delta G(z) = G(z) - \langle G \rangle \equiv -\Sigma(z)$. Then we have from Eq. (32a)

$$0 = \left\langle \frac{\delta G_i - \delta G(z)}{1 + \frac{\tilde{\nu}}{3}(\delta G_i - \delta G(z))\Lambda(z)} \right\rangle_i \tag{34}$$

which is equivalent to

$$\delta G(z) = \left\langle \frac{\delta G_i}{1 + \frac{\tilde{\nu}}{3}(\delta G_i - \delta G(z))\Lambda(z)} \right\rangle_i. \tag{35}$$

Expanding now the expression $1/[1 + \frac{\tilde{\nu}}{3}(\delta G_i - \delta G(z))\Lambda(z)]$ to first order in $\delta G_i - \delta G(z)$ and taking into account $\langle \delta G_i \rangle = 0$ we arrive at

$$\sum(z) = -\delta G(z) = \underbrace{\frac{\tilde{\nu}}{3}\left\langle (\delta G_i)^2 \right\rangle}_{\frac{1}{2}\gamma G_0^2} \Lambda(z) \tag{36}$$

which is the self-consistent Born approximation (SCBA) derived by Schirmacher [20]. The function $\Lambda(z)$ has to be evaluated with $G(z) = G_0 - \sum(z)$. Although the average in Eq. (36) can refer still to any distribution $P(E)$ the fact that only the first cumulant of the elasticity fluctuations has been taken into account is equivalent to assuming a Gaussian distribution (without cutoff).

4. Results and discussion

It is clear that the CPA has several advantages compared to the SCBA:

– one can treat arbitrary distributions $P(G)$;
– one is not restricted to weak disorder;
– one need not (but can) take negative values of G into account.

As the SCBA is based on unrestricted Gaussian statistics it includes negative values of G and therefore has a sharp limit of allowed values of γ. The critical value γ_c only weakly depends on the parameter K/G_0 and has values around $\gamma_c \approx 0.2$. This value is of the same order of

magnitude as obtained by directly determining the fluctuations from the simulation.

Using the SCBA (with $k_{\xi_G} = k_D$) Marruzzo et al. [19] have calculated the real and imaginary part of $G(z)$ (taking $\gamma \approx \gamma_c$) and compared it to the corresponding quantities extracted from $C_{L,T}(k, \omega)$ data obtained by a large-scale molecular-dynamics simulation of a soft-sphere glass with a repulsive-only potential $\phi(r) \propto r^{-12}$. As stated before, the macroscopic bulk modulus K turned out to be frequency independent, so that $G(z)$ evaluated from the longitudinal modulus via $G(z) = \frac{3}{4}[M(z) - K]$ coincides with the complex shear modulus $G(z)$, evaluated from the transverse data. We reproduce these data in Fig. 1. The following points are remarkable:

(i) The SCBA results agree perfectly with the simulation.
(ii) The dip in $G'(\omega)$ is near the strong increase of $G''(\omega)$.
(iii) The frequency of the dip and the strong increase coincide with the BP position and the transverse Ioffe–Regel frequency given by $\pi\Gamma(\omega) = \omega$.

Let us discuss these three points in detail. (i) is due to the fact that the relative fluctuations of G are small (as directly probed), so that the SCBA is valid. (ii) reflects the fact that $G'(\omega)$ and $G''(\omega)$ are related to each other by the Kramers–Kronig relation

$$G(\omega)' = \mathcal{P}\frac{1}{\pi}\int_{-\infty}^{\infty} d\overline{\omega}\frac{G''(\omega)}{\overline{\omega} - \omega} \tag{37}$$

where $\mathcal{P}$ indicates a principle part integration. It is well known [98] that a positive analytical function whose real and imaginary parts obey Eq. (37), has a kink in the real part, where its imaginary part starts to acquire values of the order of the real part. This fact is very important for identifying the role of disorder in the BP-related vibrational anomalies. The dip in the real part of G (and hence in the differential sound velocity) allows for distinguishing disorder-dominated models for the BP from models involving only real sound dispersions (see the van-Hove discussion below). The observation (iii) reinforces the conclusion given in the remarks on (ii): The Ioffe–Regel limit is just the frequency, where (by definition) the imaginary part of $G(z)$ becomes of the same order of magnitude as its real part.
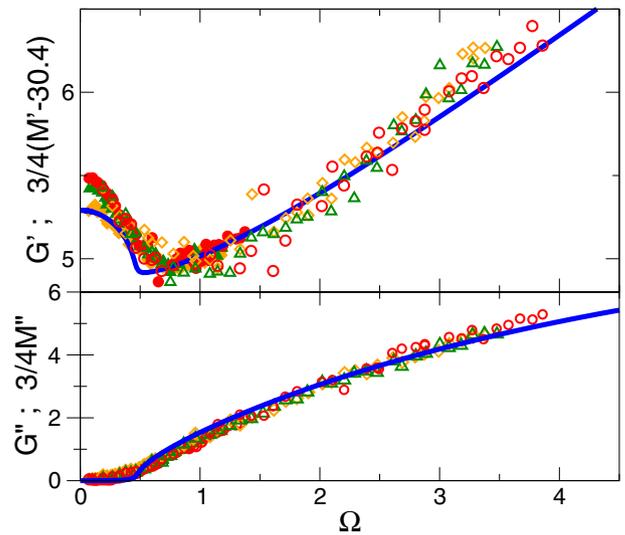
Fig. 1. Comparison of results of a soft-sphere molecular-dynamics simulation (symbols) with the prediction of heterogeneous-elasticity theory in self-consistent Born approximation (SCBA). We show the real parts (upper panel) and imaginary parts (lower panel) of the frequency-dependent shear modulus $G(\Omega_T)$ and the quantity $3/4\left(M(\Omega_L) - \widetilde{K}\right)$ for three temperatures ($5 \cdot 10^{-3}$, $5 \cdot 10^{-4}$, $5 \cdot 10^{-5}$, in Lennard–Jones units) with $K = 30.4$. The SCBA parameters are $\gamma - \gamma_c = 0.08$ and $K/G_0 = 3.166$; from Marruzzo et al. [19].

We now shall turn our attention to the role of the correlation length ξ, viz. the distinction between the upper cutoff k_ξ and k_D. In some of our previous publications on heterogeneous-elasticity theory [20,66,19,65] have taken the upper cutoff k_ξ equal to k_D. It turned out – under this assumption – that in SCBA and in CPA for Gaussian and other weak disorder the boson peaks were limited to enhancements of less than a factor two. On the other hand, in the version of the SCBA with correlated disorder Schirmacher et al. [99,100] found unlimited boson peaks with increasing correlation length — as compared to k_D^{-1}. These findings are in excellent agreement with numerical calculations using the method of moments [99,100]. Taking these results into account one can use the self consistent equations of the SCBA and CPA, in which the upper cutoff k_{ξ_G} (we shall drop the subscript G from now on) is different from the Debye wavenumber k_D, which is used to limit the amount of modes for calculating the DOS. If this is done the BP is not limited to a factor of two.

This is demonstrated in Fig. 2, where we plotted the reduced DOS $g(\omega)/g_D(\omega)$ for different values of k_D/k_ξ.

For the calculations presented in Figs. 2 to 4 we used the CPA Eqs. (32a)–(32c), (33a) and (33b) together with Eq. (15) with a truncated Gaussian distribution of shear moduli of the form

$$P(G) = P_0 \, \theta(G - G_{\min}) \, e^{-(G-G_0)^2/2\gamma} \qquad (38)$$

where $\theta(x)$ is the Heaviside step function and $G_{\min}$ is the lower cutoff. In these calculations we used the *renormalized* value of G (i.e. the self-consistently calculated one) for evaluating the Debye frequency ω_D and Debye DOS $g_D(\omega)$ in terms the longitudinal and transverse sound velocities $\rho_m v_L^2 = K + \frac{4}{3}G$, $\rho_m v_T^2 = G$

$$\omega_D = k_D \left[\frac{1}{3}\left(\frac{1}{v_L^3} + \frac{2}{v_T^3} \right) \right]^{-1/3} \qquad (39)$$

$$g_D(\omega) = 3\omega^2/\omega_D^3. \qquad (40)$$

For the bulk modulus of the calculations we used the value $K = 3.3G_0$ and for the cutoff parameter the value $\tilde{\nu} = 1$, which implies that $k_D/k_\xi = \sqrt[3]{3}\xi/a$, where $a = \sqrt[3]{V/N}$ is the mean intermolecular distance. The distribution of shear moduli (Eq. (38)) involves three parameters G_0, γ and $G_{\min}$. Because G_0 is used to fix the elastic-constant scale there remain three adjustable parameters to fix the *state of elastic disorder* of the material, namely $k_D/k_\xi \sim \xi/a$, γ and $|G_{\min}|$. The latter (which we used with negative values or equals zero) specifies the amount of regions with negative shear modulus (soft regions) in the material. As can be seen
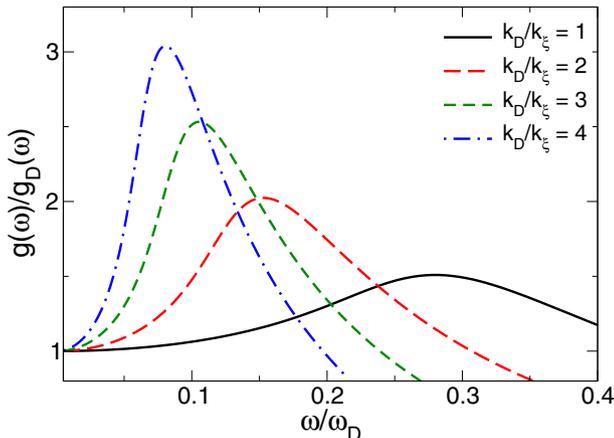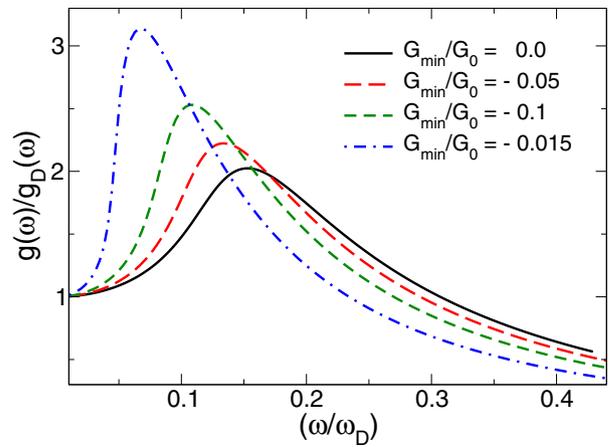

Fig. 3. Reduced density of states $g(\omega)/g_D(\omega)$ vs. the rescaled frequency (ω/ω_D) for different values of the lower cutoff $G_{\min}$ of the Gaussian distribution $P(G)$. The other parameters are $\gamma = /G_0^2 = 1$ and $k_D/k_\xi = 2$.

from Figs. 2 to 4 increasing ξ and $G_{\min}$ enhances the BP *and* shifts its position to lower frequencies, whereas increasing γ just leads to an enhancement, while keeping the BP position constant. It has been pointed out in the literature [101–104] that the position of the boson peak in relation to the Debye frequency correlates with the inverse correlation length of density and elasticity fluctuations.

Let us discuss our findings further in terms of measured vibrational spectra of materials, in which an external parameter (temperature, pressure or the amount of polymerization) is changed. If the Debye frequency (depending on the moduli K and G) is changed, this leads to a modification of the spectrum, which has been called *elastic-medium transformation*. This transformation is taken care of, if the DOS is represented in a normalized way, as is the case in Figs. 2 to 4. A number of boson-peak data, if normalized in this way, lead to a universal curve, i.e. all data points fall onto the same curve if replotted, taking the elastic transformation into account [105,106,56,29,30,107,54]. Other investigations reveal a *deviation* from this scaling [108–116]. In terms of our model calculations this means, if the state of disorder is not changed, but just the value of the mean elastic constants or the density, this corresponds to elastic-transformation scaling. In the other cases obviously the state of disorder is changed by changing the external conditions.

A very interesting case in which the elastic transformation scaling does not hold has been reported recently: the case of prehistoric amber. Pérez-Castaneda et al. [116] measured the temperature dependence of the specific heat of the hyperaged and rejuvenated material.
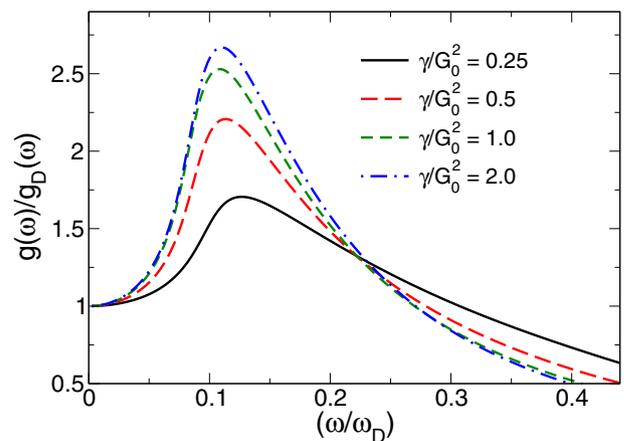

Fig. 2. Reduced density of states $g(\omega)/g_D(\omega)$ vs. the rescaled frequency $(\omega/\omega_D)(k_D/k_x i) = \omega/v_D k_\xi$ for different values of the ratio k_ξ/k_D. The other parameters are $\gamma/G_0^2 = 1$ and $G_{\min} = 0$.

Fig. 4. Reduced density of states $g(\omega)/g_D(\omega)$ vs. the rescaled frequency (ω/ω_D) for different values of the width parameter γ. The other parameters are $G_{\min}/G_0 = -0.1$ and $k_D/k_\xi = 2$.

The height of the boson peak, taken from a $C(T)/T^3$ curve is by 22% lower in the hyperaged material, compared with the rejuvenated one. An elastic transformation using the change in the Debye frequency determined by the authors would only lead to a difference by 7.4%.

This sensitivity of the boson peak to structural changes, which cannot be described by an elastic transformation is at variance with models, in which the BP is described exclusively as an elastic transformation of a crystalline van-Hove singularity [29,30]. The fact that the DOS of some glasses has a BP, which – if re-scaled with the Debye frequency – approximately coincides with the enhancement of the DOS of the corresponding crystals due to the lowest van-Hove singularity does not permit the conclusion that the BP is not a disorder-induced phenomenon. As discussed in detail by Schirmacher [32], the wavenumber scale at which the lowest phonon dispersion in crystals deviates from Debye's linear dispersion is approximately the same as that, where vibrational excitations in a glass start deviating from plane waves: Both scales signify the breakdown of the macroscopic continuous symmetries of the elastic material.

5. Conclusions

We have discussed the theory of heterogeneous elasticity, which is elasticity theory in the presence of spatially fluctuating elastic moduli. The case of spatially fluctuating shear moduli has been considered, but the theory is not restricted to this case. The solutions of the stochastic equations of motions of this theory in coherent-potential approximation (CPA) have been given. It has been shown, that in the small-disorder limit these solutions reduce to the self-consistent Born approximation (SCBA) used earlier by the present authors. Within both theories the disorder fluctuations of the shear modulus are transformed into a frequency dependence of the macroscopic shear modulus $G(z)$, which – by the dictate of causality – acquires an imaginary part, which is proportional to the sound attenuation coefficient and to the inverse mean-free path. If the mean-free path becomes comparable to the wavelength of the vibrational excitations the concept of waves breaks down, and the excitations are random-matrix-type states. The BP and the associated anomalies (strong increase of the attenuation, dip in the real part of $G(z)$) mark the crossover from wave-like to random-matrix-like physics.

The SCBA is valid for Gaussian distributions of elastic moduli in the low-disorder limit and gives very good results for the macroscopic elastic moduli and the BP in comparison with simulations of a soft-sphere glass model. Using the CPA one is not restricted to Gaussian statistics. Within the self-consistent CPA equations the cutoff in **k** space is proportional to the inverse correlation length of the elasticity fluctuations. If this cutoff is taken smaller than the Debye cutoff k_D, rather large boson peaks larger than a factor of 2 can be obtained, contrary to earlier calculations, where k_D was taken as cutoff in the CPA and SCBA equations.

In the light of heterogeneous elasticity theory we have discussed the various experimental methods for obtaining the vibrational spectrum, especially the density of states. The only unambiguous methods for the latter purpose are inelastic neutron scattering in the case of incoherent scattering and inelastic nuclear scattering (INS).

We have demonstrated with the help of model calculations using the CPA that the failure of describing the vibrational change of a material after varying an external parameter by an elastic transformation can be explained by changing the state of disorder of the material, as described by the distribution of elastic constants.

Acknowledgment

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