Vibrational Spectrum of Topologically Disordered Systems

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The topological nature of the disorder of glasses and supercooled liquids strongly affects their high-frequency dynamics. In order to understand its main features, we analytically studied a simple topologically disordered model, where the particles oscillate around randomly distributed centers, interacting through a generic pair potential. We present results of a resummation of the perturbative expansion in the inverse particle density for the dynamic structure factor and density of states. This gives accurate results for the range of densities found in real systems.

The high-frequency dynamics of glasses and supercooled liquids has recently received a large amount of experimental [1–3], numerical [4–6], and theoretical [7–12] attention. High-resolution inelastic x-ray scattering techniques have made accessible to experiment the region where the exchanged external momentum p is comparable to p_0, the maximum of the static structure factor. A number of facts have emerged from these experiments: (i) The dynamic structure factor (DSF) $S(p, \omega)$ has a Brillouin-like peak for momenta up to $p/p_0 \sim 0.1$–0.5, usually interpreted in terms of propagating acousticlike excitations, whose velocity extrapolates to the macroscopic sound velocity when $p \to 0$. (ii) The peak has a width Γ, due to disorder, which in a large variety of materials seems to scale as $\Gamma = Ap^\alpha$, with $\alpha \sim 2$ and A depending very slightly on the temperature. (iii) The density of states (DOS) exhibits an excess respect to the Debye behavior [$g(\omega) \propto \omega^2$], known as the *Boson peak,* which is most remarkable for strong glasses.

From the theoretical viewpoint, the challenge is to explain the above features of the scattering spectra. For a dense system such as glass, the short time dynamics is naturally interpreted as a consequence of vibrations around a quenched disordered structure. Indeed, molecular dynamic simulations have shown that *harmonic vibrations* are enough to describe the DSF [5] and specific heat [6]. Nevertheless, the analytical problem is very hard even in this first approximation, because it involves a matrix (the Hessian) with random elements. So the study of vibrations in glasses is related to the general problem of analyzing the statistical properties of large random matrices [13]. This is a venerable problem, with applications that include the theory of nuclear spectra, conductivity in alloys, and many others [13]. We should distinguish between matrices obtained as a result of random perturbations of a reference lattice and those for which no reference lattice can be defined [14]. Lattice-based random matrices arise typically in problems of the solid state (Anderson localization, transport in mesoscopic systems, etc.). A num-

ber of well-known approximations were developed to deal with these types of matrices: these approximations can be derived by considering the disordered part of the random matrix as a perturbation of the solvable crystalline problem [14] and partially resumming the perturbative expansion. On the other hand, *off-lattice* random matrices arise in many problems, such as amorphous semiconductors, instantaneous normal modes in liquids, and the vibrational excitations of glasses. These matrices lack a natural separation between a solvable ordered part and a disordered perturbation. As a consequence, the theoretical tools for their study started to be developed much more recently [15] and are best suited for low densities, with emphasis on the DOS rather than the DSF. Furthermore, the Debye behavior of the DOS is not reproduced by the above methods, even in the glassy phase (see Cavagna et al. in [15]).

The purpose of this Letter is to address the problem of harmonic vibrations in glasses and to find a self-consistent integral equation. This equation is somewhat analogous to the lattice-based approximations mentioned above, but is appropriate for the off-lattice matrices that arise in this case [8]. Our approach is based on an expansion in $1/\rho$ (ρ is the number of particles per unit volume) [8,9].

Somehow complementary to our approach is a recent modification of mode coupling theory [7] to describe excitations around a quenched structure, which was applied to a hard-sphere fluid. Also, lattice-based models were proposed [10,11], but it turns out [12] that they definitely miss the p^2 behavior of the peak width. Other differences between the lattice and off-lattice cases regarding the DOS will be discussed.

We consider a model of particles oscillating harmonically around (disordered) equilibrium positions. For simplicity we assume that they can move only along a direction $\boldsymbol{u}$: $\boldsymbol{x}_j(t) = \boldsymbol{x}_j^{\text{eq}} + \boldsymbol{u}\varphi_j(t)$, $j = 1, \ldots, N$. The vibrational potential energy is then $V(\{\varphi_i\}) = \frac{1}{2}\sum_{i,j} f(\boldsymbol{x}_i^{\text{eq}} - \boldsymbol{x}_j^{\text{eq}})(\varphi_i - \varphi_j)^2$, where f is the second derivative of the pair potential. Of interest is the spectrum of the dynamical matrix (Hessian) [9,16]

$$M_{ij} = \delta_{ij} \sum_{k=1}^{N} f(\boldsymbol{x}_i^{\text{eq}} - \boldsymbol{x}_k^{\text{eq}}) - f(\boldsymbol{x}_i^{\text{eq}} - \boldsymbol{x}_j^{\text{eq}}). \quad (1)$$

By neglecting quantum effects, in the harmonic approximation the DSF can be obtained as (see, e.g., [9])

$$S(p, \omega) = \frac{k_B T p^2}{m \omega^2} \overline{\sum_n \left| \sum_i e_{n,i} e^{i \boldsymbol{p} \cdot \boldsymbol{x}_i^{\text{eq}}} \right|^2 \delta(\omega - \omega_n)}, \quad (2)$$

where $e_{n,i}$ is the i-th component of the n-th eigenvector of the Hessian (1), the eigenfrequencies ω_n are the square root of the corresponding eigenvalues, T is the temperature, and the overline stands for the average over $\{\boldsymbol{x}_j^{\text{eq}}\}$ (hereafter we set the mass $m = 1$).

The model is defined by the probability distribution of the $\{\boldsymbol{x}_j^{\text{eq}}\}$ and by the function $f(r)$. Obviously, in a real system the $\{\boldsymbol{x}_j^{\text{eq}}\}$ are highly correlated. However, as discussed in detail in [9,16], it is a good approximation to take $\{\boldsymbol{x}_j^{\text{eq}}\}$ uncorrelated while at the same time using an effective interaction which weights the physical f with the radial distribution function $g(r)$. For a given f, the only free parameter is ρ.

As usual, we consider the resolvent $G(p,z) \equiv \sum_{jk} \exp[i \boldsymbol{p} \cdot (\boldsymbol{x}_j^{\text{eq}} - \boldsymbol{x}_k^{\text{eq}})][z - M]_{jk}^{-1}/N$, since the DSF can be obtained as $S(p,\omega) = -2k_B T p^2 \, \text{Im} G(p, \omega^2 + i0^+)/(\omega \pi)$. Our aim is to compute G by using the appropriate self-consistent equations. Although here there is no separation between an ordered reference state and a random perturbation, it has been observed [8] that in the limit of infinite density the spectrum coincides with that of an elastic homogeneous medium, since the resolvent is simply $G(p,z) = [z - \lambda(p)]^{-1}$ [where $\lambda(p) = \rho[\hat{f}(0) - \hat{f}(p)]$ and $\hat{f}(p)$ is the Fourier transform of $f(r)$]. A systematic perturbative expansion in $1/\rho$ has been constructed in Ref. [9]. Technically, an expansion is found for the resolvent, which is written as

$$G(p,z) = \frac{1}{z - \lambda(p) - \Sigma(p,z)}. \quad (3)$$

The self-energy $\Sigma(p,z) = \Sigma'(p,z) + i\Sigma''(p,z)$ is then expanded in powers of $1/\rho$ [8,9] in the relevant region where $\rho = O(z)$. At infinite density, $\Sigma = 0$ and the dispersion relation is $\omega(p) = \sqrt{\lambda(p)}$, which is linear at small p. The real self-energy $\Sigma'(p,z)$ renormalizes the dispersion relation, while the imaginary part gives the peak width: $\Gamma = \Sigma''(p, \omega_p^2)/\omega_p$, where ω_p is the position of the maximum of the DSF.

We have reformulated the $1/\rho$ expansion [17] in a way that reduces the number of diagrams and allows us to identify those with the simple topology of Fig. 1. Topologically, these diagrams are exactly those considered in the usual lattice coherent potential approximation (CPA) and in other self-consistent approximations. The sum of this infinite subset is given by the solution of the integral equation:

$$\Sigma(p,z) = \frac{1}{\rho} \int \frac{d^3q}{(2\pi)^3} [\rho(\hat{f}(\boldsymbol{q}) - \hat{f}(\boldsymbol{p} - \boldsymbol{q}))]^2 G(p,z), \quad (4)$$

where the resolvent is given by Eq. (3). The solution gives us the resolvent and, hence, the DSF and DOS [Eq. (5) below].

We are interested in the solution of Eq. (4) for different values of z and ρ. To be definite, we consider an explicit case where the function $f(r)$ has a simple form, namely, $f(r) = \exp[-r^2/(2\sigma^2)]$. This is a reasonable first approximation for the effective interaction [16]. We shall take σ as the unit of length and set $p_0 = 1/\sigma$, which is a reasonable choice for p_0 for this Gaussian $f(r)$, as discussed in [16]. In this particular case we will solve numerically the self-consistence equation. We will also evaluate by simulation (using the method of moments [18]) the exact DSF and DOS by computing the resolvent for concrete realizations of the dynamical matrix, and by considering a sufficiently high number of particles so that finite volume effects can be neglected. These numerical results will be supplemented by analytic results that are f independent and can be obtained in the limits $p \to \infty$ and $p \to 0$.

The infinite momentum limit is particularly interesting because of the remarkable result [9] that the DOS $g(\omega)$ can be written as

$$g(\omega) = \lim_{p \to \infty} \frac{\omega^2 S(p, \omega)}{k_B T p^2}. \quad (5)$$

We easily find that in this limit Eq. (4) can be written as $[\mathcal{G}(z) = \lim_{p \to \infty} G(p,z)$ and $\mathcal{A} = (2\pi)^{-3} \int \hat{f}^2(\boldsymbol{q}) d^3q]$:

$$\frac{1}{\rho \mathcal{G}(z)} = \frac{z}{\rho} - \hat{f}(0) - \mathcal{A} \mathcal{G}(z)$$
$$- \int \frac{d^3q}{(2\pi)^3} \hat{f}^2(\boldsymbol{q}) G(\boldsymbol{q}, z). \quad (6)$$

A simple approximation consists of neglecting the last term in the right-hand side of (6), which is reasonable at large z. This approximation implies a DOS which is semicircular as a function of ω^2, with the width proportional to $\sqrt{\rho}$ and centered at $\omega^2 = \rho \hat{f}(0)$. Translational invariance also requires low-frequency modes. These are given by
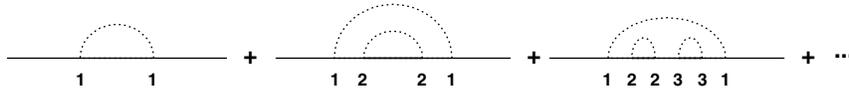

FIG. 1. The diagrams of the $1/\rho$ expansion which are taken into account in our approach. The numbers correspond to the particle-label repetitions.

the neglected term, and in fact it is easy to show that at high density it produces a Debye spectrum which extends between zero frequency and the semicircular part.

In the limit $p \to 0$, the leading contribution to Σ'' comes from $q \gg p$ in Eq. (4), where $G(q,z) \approx \mathcal{G}(z)$, so we can write for the peak width $\Gamma(p) \approx \Gamma_0(p)$, where

$$\Gamma_0(p) \equiv \pi\rho \, \frac{g(\omega_p)}{2\omega_p^2} \int \frac{d^3q}{(2\pi)^3} \, [\hat{f}(\mathbf{q}) - \hat{f}(\mathbf{p} - \mathbf{q})]^2.$$

(7)

The integral is of order p^2, so that, if the spectrum is Debye-like for small frequencies, we get $\Gamma(p) \sim p^2$.

These considerations are verified by the numerical solution of the Gaussian case, which is shown in Fig. 2 for $\rho = 1.0\sigma^{-3}$, together with the results for the simulations [9]. Note the good agreement, to be expected for high densities, and how, for large p, $S^{(1)}(p,\omega)$ (Fig. 2, top) tends to the DOS. The DOS from the self-consistent equation (Fig. 2, bottom) also agrees very well with the results from simulations, and is a big improvement over the first term of the expansion in powers of ρ^{-1}. The two contributions (Debye and semicircle) mentioned above can be clearly identified. Our approximation fails in reproducing the exponential decay of the DOS at high frequencies, which is nonperturbative in $1/\rho$ [19] and corresponds to localized states.

Next, in Fig. 3 we plot the linewidth as a function of p as obtained from Eq. (4). Notice that we recover the behavior predicted from the first two nontrivial terms in the expansion in powers of ρ^{-1} [9]: the linewidth is proportional to p^2 at small p (also predicted by the argument above), then there is a faster growth, and finally it approaches to a constant as $S^{(1)}(q,\omega)$ starts to collapse onto the DOS. The inset shows that the contribution Eq. (7) is

indeed dominant at small p. However, rigorous p^2 scaling is found only for very small momenta ($p/p_0 < 0.1$), while experiments are done at $0.1 < p/p_0 < 1$. In this crossover region, our model predicts deviations from p^2, which are probably hard to measure experimentally. In any case, the effective exponent is certainly less than 4, in contrast to lattice models and consistent with experimental findings. Similar conclusions can be drawn from mode coupling theory (Fig. 8 of [7]).

Finally, let us discuss the low-density case. As mentioned, Eq. (6) shows that the position of the center of the semicircular peak in the DOS goes to 0 as $\omega^2 \sim \rho$, but with a width that decreases only as $\sqrt{\rho}$. So at low enough densities the DOS develops a tail that extends into negative values of ω^2. In our Gaussian case, this starts happening at $\rho_c = 0.31\sigma^{-3}$. Since our original Hessian is positive definite, one could regard such an instability as just a failure of the $1/\rho$ expansion. However, the structure that Eqs. (4) and (6) (wrongly) predict from the hybridization between the Debye and semicircle spectra for $\rho \gtrsim \rho_c$ is extremely suggestive of a Boson Peak. In fact, it can be shown [17] that for $\rho \gtrsim \rho_c$ and very small values of ω a crossover occurs from the Debye ω^2 behavior at low ω to an $\omega^{3/2}$. This structure (Fig. 4, bottom) can be compared with the Boson peak predicted by the lattice integral equations [10,11], close to their instabilities (see Fig. 4, top). The Boson peak predicted by the off-lattice equations is a subtle feature of the spectrum that can only be seen when dividing the DOS by the Debye behavior. It is also striking that this off-lattice Boson peak shifts towards $\omega = 0$ when the instability is approached, as does the experimental peak upon heating. On the other hand, it is fair to say that the Boson peak of the lattice integral equations is just the first maximum of the DOS (which experimentally is not very temperature dependent) shifted to low ω by the division by ω^2.

In conclusion, we have presented a random-matrix approach to study an off-lattice model for the vibrational
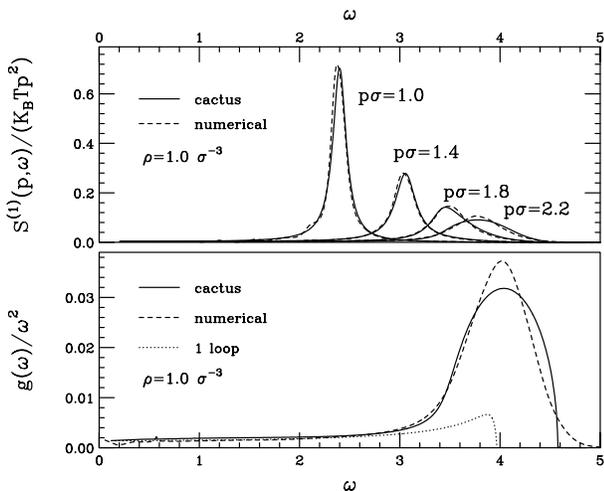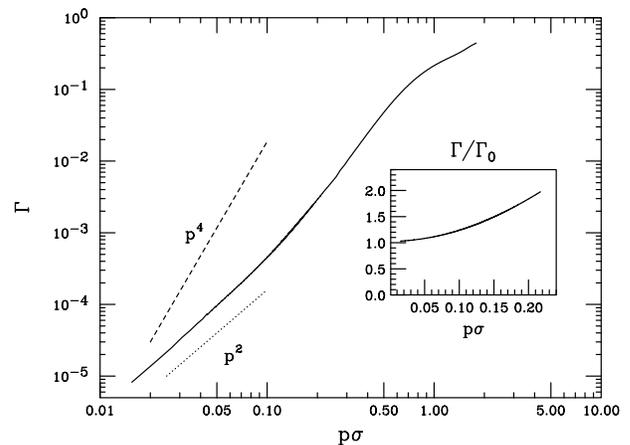

FIG. 2. Top: dynamic structure factor as obtained from Eq. (4) (solid line) and from simulations [9] (dashed line). Bottom: DOS divided by ω^2 (Debye behavior) as obtained from Eq. (6) (solid line), simulations (dashed line), and first order in the $1/\rho$ expansion (dotted line).

FIG. 3. Peak width vs p, for $\rho = 0.6\sigma^{-3}$. The inset shows that $\Gamma_0(p)$ is the dominant contribution at small p.
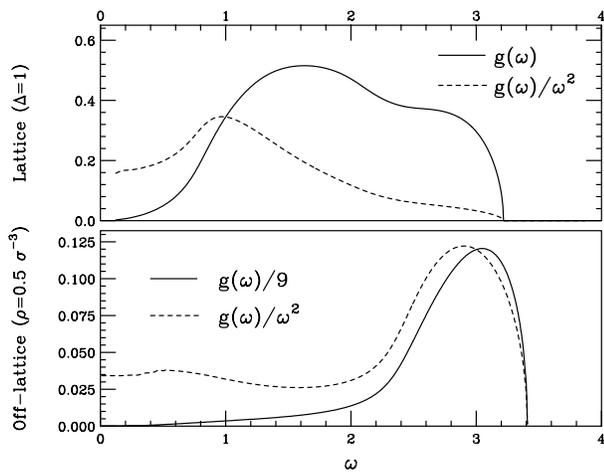
FIG. 4. Top: $g(\omega)$ (solid line) and $g(\omega)/\omega^2$ (dashed line) of the model of Ref. [10], as predicted by the single-link CPA, at $\Delta = 1$. Bottom: $g(\omega)/9$ (solid line) and $g(\omega)/\omega^2$ (dashed line) for our model at $\rho = 0.5\sigma^{-3}$. Note that, for the values of the parameters shown here, the lattice model is nearer to its critical point [$(\Delta_c - \Delta)/\Delta_c \approx 0.22$ while $(\rho - \rho_c)/\rho_c \approx 0.61$].

dynamics of glasses, in which particles oscillate harmonically along a given direction around quenched equilibrium positions. At variance with disordered systems defined as a perturbation of a reference crystal, our system lacks a natural separation between a *solvable* and a *random-perturbation* term. Nevertheless, an expansion in $1/\rho$ can be obtained [9]. Here we have reformulated this expansion in a way that allows us to resum an infinite subset of terms, obtaining an integral self-consistent equation (4) for the dynamic structure factor and the DOS. This equation predicts a p^2 scaling of the linewidth for a generic potential, as well as the appearance of a Boson-peak–like structure at low densities, linked to a mechanical instability. Since the dynamic structure factor tends to the DOS at large momentum, we argue that Boson-peak–like features found experimentally in the former at large p [2,3] are just another manifestation of the Boson peak. We compared the results of Eq. (4) with numerical calculations for a Gaussian potential and found satisfactory agreement at densities comparable to those of real glasses. At low densities, the resummation finds a spectrum at negative squared frequencies, which is nonphysical for this potential. However, for $\rho \gtrsim \rho_c$ a structure appears which is definitely different from those found in lattice models [10,11], and extremely remindful of the experimental Boson peak.

These results can be extended in several ways (potentials with instabilities at low densities, noncollinear vibrations, and detailed study of the correlated case); work in these directions is in progress.

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