

Phonons in Glasses: Numerical Simulations and Phenomenological Theory

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The phonon spectrum $\omega(k)$ of a model glass is investigated by classical molecular dynamics. While the longitudinal branch looks like one of a crystal, the transverse branch saturates at an almost k -independent characteristic frequency ω_c , which tends to zero at the glass transition temperature. These results confirm an earlier picture in which a glass is a solid containing liquid “pockets” of finite sizes. For $\omega > \omega_c$, the transverse phonons are absorbed by the resonant modes of the finite clusters, the latter being responsible for the “boson peak.” [S0031-9007(96)00752-1]

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In the last two decades, most of the studies devoted to glasses were focusing on the anomalies of the low frequency modes, namely, the “quasielastic light scattering excess” (QLSE) at very low frequencies (≈ 100 GHz), and the strong broad line located around 1 THz called the “boson peak” (BP). While the QLSE turns out to be quite well explained by the two-level tunneling theories [1] and their recent “soft modes” generalizations [2], the BP is still the subject of a theoretical controversy. As it appears in both light and neutron scattering experiments [3], it is now believed that it is due to a mode excess in the density of vibrational states $g(\omega)$, but different theoretical explanations have been proposed: frequency resonance of finite clusters [4] or localization of phonons by disorder [5].

In order to explain these features we present, for the first time, a classical molecular dynamics calculation of the phonon spectrum for a model argon glass, which, despite disorder, exhibits well-defined $\omega(k)$ branches. While the longitudinal branch behaves like in a solid up to a maximum wave vector, which is the half of the location q_m of the so-called first sharp diffraction peak (FSDP) [6], the transverse branch saturates at a characteristic frequency ω_c , which tends to zero at the glass transition. We interpret these results in terms of the Thorpe model [7], which describes a glass like a solid containing finite liquid clusters. We suggest that the transverse phonons are absorbed for frequencies larger than the smallest eigenfrequency of the largest cluster. Therefore for the first time a satisfying picture of the classical low frequency modes of glasses is given. We confirm the earlier ideas that the BP is due to resonant modes of finite clusters [4], but we make this argument much more precise by invoking the resonant scattering of transverse phonons only. Furthermore, on the basis of this approach, we can make some conjectures on the shape of the BP and its behavior at the glass transition.

We performed computer simulations on a system of N soft spheres interacting via an inverse sixth power potential [8]:

$$U(r) = \epsilon \left(\frac{\sigma}{r} \right)^6 + Ar^4 + B. \quad (1)$$

To simplify the calculations the potential was cut off at $r/\sigma = 3$, and A and B were chosen so that both the potential and the force are zero at the cutoff. In order to give some physical meaning to the simulations, we choose for ϵ and σ the Lennard-Jones (LJ) values of argon: $\epsilon = 0.0103$ eV, $\sigma = 3.405$ Å. The mass of the particles was determined using the standard LJ unit of time $\tau = (m\sigma^2/\epsilon)^{1/2}$ and is equal to 40 amu [9], whereas the time step is $\Delta t = 0.004\tau$. The simulations are considering $N = 1000$ atoms in a cube of edge L , with periodic boundary conditions (PBC) at a density $(N/L^3)\sigma^3 = 1$, but we have checked on a few larger systems that the results are almost insensitive to the size. The glass configurations were obtained by quenching a well-equilibrated initial liquid sample obtained by melting a simple cubic crystal using constant energy-molecular dynamics at a temperature of about 50 K well above the melting temperature which is known to be about 25 K [8]. After full equilibration of the liquid (during 1000 iterations) the system was cooled down to $T = 0$ K at a quench rate of 10^{12} K/s (lasting 15 000 iterations). Configurations during the quenching process were saved every 1000 iterations and used as input for preparing samples of various temperatures. The temperature was determined after a relaxation time of 5000 time steps, after which it was observed to be reasonably constant.

After that relaxation period, relevant physical quantities were calculated. The results for the two-point correlation curve and its Fourier transform $S(q)$, as well as for the diffusion constant, will be reported elsewhere. We found that $S(q)$ presents a sharp maximum at $q_m\sigma \approx 7.5$ roughly independent on T . The behavior of the diffusion constant permits us to locate the glass transition temperature between 10 and 15 K. Here we report on the phonon spectrum that we have determined by calculating the following quantities:

$$V_\alpha(\mathbf{k}, t) = \sum_i \mathbf{u}_\alpha \cdot \mathbf{v}_i \cos(\mathbf{k} \cdot \mathbf{r}_i), \quad (2)$$

where \mathbf{r}_i and \mathbf{v}_i are the time dependent positions and velocities, respectively, for the i th atom. The polarization

vectors are defined such as $\mathbf{u}_1 = \mathbf{k}/k$ in the longitudinal case, while \mathbf{u}_2 and \mathbf{u}_3 form a direct orthogonalized basis with \mathbf{u}_1 in the transverse case. Note that (2) is not a true spatial Fourier transform, as the plane waves $\exp i\mathbf{k}\cdot\mathbf{r}_i$ are not orthogonal. However, they satisfy the pseudo-orthogonalization relation:

$$\sum_i \exp(-i\mathbf{k}\cdot\mathbf{r}_i) \exp(i\mathbf{k}'\cdot\mathbf{r}_i) \propto S(|\mathbf{k} - \mathbf{k}'|). \quad (3)$$

As the $S(q)$ peak is quite sharp, the glass can be considered as pseudoperiodic on quite large distances [6]. This is why we can speak of phonons in glasses.

During 2000 time steps we have calculated the time-Fourier transforms $V_\alpha(k, \omega)$ of the $V_\alpha(\mathbf{k}, t)$'s that we have averaged over the direction of \mathbf{k} for a given $k = |\mathbf{k}|$, assuming isotropy. They generally exhibit a broad maximum at an ω value that defines $\omega(k)$ with some half-width $\Delta\omega(k)$. The determination of both $\omega(k)$ and $\Delta\omega(k)$ has been done for several values of k up to $q_m/2$, and some typical results are shown in Figs. 1(a) and 1(b) for $T = 0.30$ and 30 K, below and above the glass temperature, respectively. Even if the results are quite scattered, some general features can be observed in these figures. Despite the width due to disorder (larger in the

liquid case) the longitudinal branch looks like the one of a crystal, saturating at $q_m/2$, confirming that the system is pseudoperiodic, even at $T = 30$ K. The transverse branch, which disappears in the liquid phase, appears to be highly anomalous in the glass case. In an ordinary solid, it should roughly go like the longitudinal branch divided by $\sqrt{3}$. Here $\omega(k)$ saturates at a characteristic value ω_c , which vanishes at the glass transition. Correlatively, the width $\Delta\omega(k)$ does not stay almost constant (as in the longitudinal case) but increases with k . We have performed other calculations at various temperatures. The variation with T of some characteristic features of the spectrum, namely, the slopes of the branches estimated at $k = 0, V_L$ and V_T , as well as ω_c , are shown in Fig. 2. One sees that, while V_L is roughly independent on T , both V_T and ω_c , which are very small in the liquid phase, vary in a very limited region of temperature around T_g and saturate in the glass phase. The typical length $2\pi V_T/\omega_c$ built with these saturation values is about 10 \AA consistent with the previous estimations for the resonant clusters size [4].

The results obtained for $T > T_g$ correspond to what is usually known for a liquid, namely, that the longitudinal modes can propagate (with attenuation), while the transverse modes cannot. This is due to the existence of

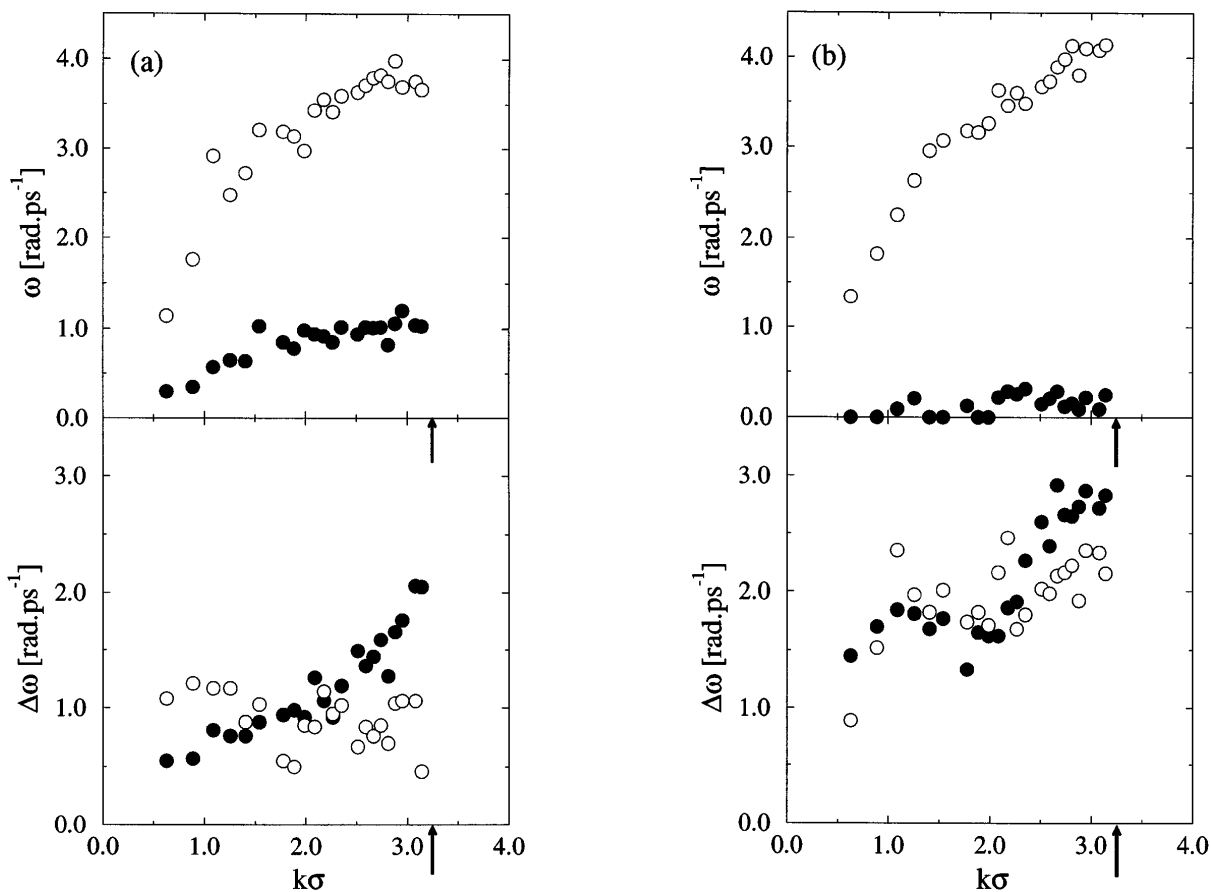


FIG. 1. Numerical results for $\omega(k)$ (top) and $\Delta\omega(k)$ (bottom) for $T = 0.30$ K (a) and $T = 30$ K (b). Closed and open circles correspond to transverse and longitudinal modes, respectively. The arrow indicates $k = q_m/2$.

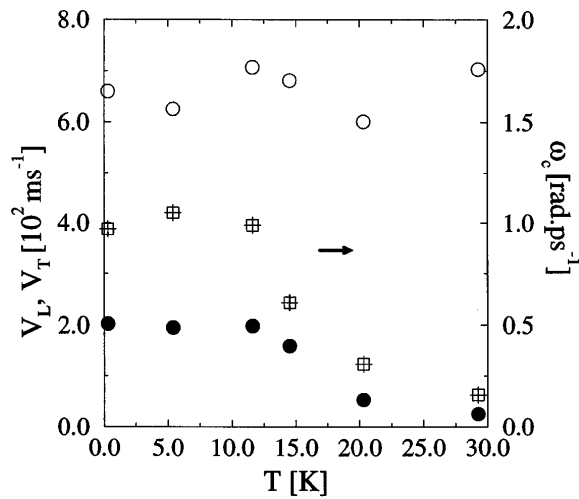


FIG. 2. Plot of the slopes at the origin of the transverse (closed circles) and longitudinal (open circles) phonon branches and ω_c (squares) as a function of T .

a nonzero viscosity η in the liquid phase. A transverse phonon of frequency ω and wave vector \mathbf{k} would create a shear force per unit volume $\mathbf{f} = -\eta k^2 \mathbf{v}$, where the rate of displacement of matter \mathbf{v} is perpendicular here to \mathbf{k} . Therefore, from the first principle of dynamics, $\mathbf{f} = i\omega\mu\mathbf{v}$ (where μ is the volumic mass), one gets the well-known dispersion relation $i\omega = -(\eta/\mu)k^2$, leading to a pure imaginary frequency (relaxation mode) $\Delta\omega = (\eta/\mu)k^2$. If one forgets a k -independent width that we can attribute to disorder this relation turns out to be quite well verified by our numerical results and leads to $\eta \approx 5 \times 10^{-4}$ P, a reasonable value for a model liquid argon [10]. Note that apparently $\Delta\omega$ increases also with k in the longitudinal case. This might be explained by some coupling between longitudinal and transverse modes due to disorder, which can hardly be neglected in the liquid case.

The results in the glass phase ($T < T_g$) can be simply explained using the Thorpe model [7], which considers a glass like a solid containing liquid pockets of limited sizes. We can reasonably assume that the vibrational eigenmodes of these pockets form a quasicontinuum starting from the lowest frequency of the largest cluster that we call ω_c . If a transverse phonon has a frequency larger than ω_c , it is able to excite the resonances of some pockets, via the shear force mentioned above. Therefore such a phonon should be strongly absorbed, and this explains why $\omega(k)$ after a short linear regime saturates at ω_c , while $\Delta\omega$ roughly exhibits the same k^2 behavior as in the liquid case. Such an effect is analogous, in the case of phonons, to the resonant scattering mechanism introduced almost 40 years ago by Friedel and Anderson (FA) [11] in order to explain the electronic properties of d impurities in s metals. Any analytical calculation would need some modelization of the pocket structure, and this is not our purpose here. However, some general

qualitative features can be found from textbooks and/or by transposing the FA results by replacing electron energies by squared frequencies. Imagine there would be only one single resonant state at frequency Ω and a band of itinerant transverse phonons with density of states $g(\omega)$. The coupling (due to the viscosity) would produce a resonance broadening traduced by a Lorentzian shape (in ω^2) for the density of states of the localized state (which becomes a “virtual bound state” [11]) with a width proportional to η^2 and to $g(\Omega)$. Correlatively, the density of states of the itinerant transverse phonons should be depressed at $\omega \approx \Omega$ due to the absorption. As, in our case, there are more and more localized states available as ω increases above ω_c , the density of states of the phonons vanishes and the bound states becomes less broadened. A rough picture of the resulting density of states is given in Fig. 3. Globally, when comparing with a regular solid, modes from the top of the transverse phonon band are transferred to lower frequencies and get localized. This mechanism provides a simple explanation of the mode excess observed in most glasses, evidenced by the BP when plotting $g(\omega)/\omega^2$ vs ω . From the above reasoning, one can explain why the BP is strongly asymmetric. Its abruptness at ω_c should be related to the viscosity of the corresponding liquid, while on its large- ω side its shape is related with the mass size distribution of the pockets and the characteristics of their resonance spectrum which extends up to ω_M , top of the transverse phonon band.

Let us push further the Thorpe model by assuming that the glass transition corresponds to the percolation threshold for the pockets as, when T increases, one needs the formation of a macroscopic liquid pocket to permit the whole system to flow. In that case one can calculate the shape of the boson peak at T_g assuming, like in percolation theory [12], that the pockets are fractals with spectral dimension d_s and are distributed in mass according to a power law $m^{-\tau}$ [12,13]. The density of states can

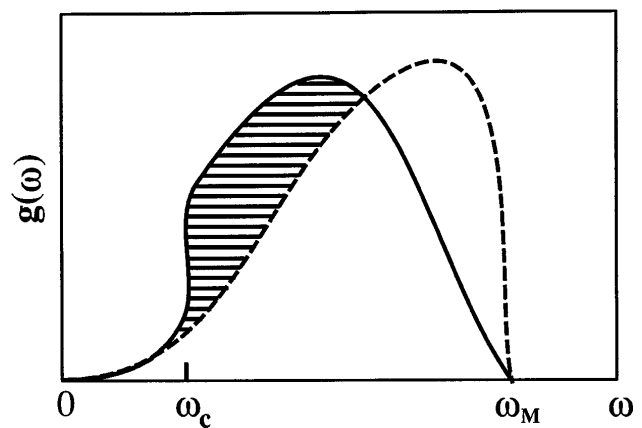


FIG. 3. Sketch of the density of states for the transverse phonons (solid line) compared with their density of states in a regular solid (dashed curve). The mode excess (responsible for the boson peak) is shown by the dashed region.

be obtained by multiplying the density of states for one pocket ($\propto \omega^{d_s-1}$) by the number of pockets of mass larger than a mass proportional to ω^{-d_s} . This reasoning gives $g(\omega)/\omega^2 \propto \omega^{-\alpha}$ with $\alpha = 3 - d_s\tau$. Considering the percolation values $\tau = 2.2$ and $d_s = 1.3$, this gives $\alpha = 0.14$, a much lower value than the α exponent of order 1 experimentally observed on the right side of the BP [14]. But, since these experiments have been done in the glass phase, i.e., below the percolation threshold of the liquid pockets, the power law should be valid only in a limited range of frequencies ($\omega_c \ll \omega \ll \omega_M$), and it is more reasonable to consider $\tau = 2$ and $d_s \approx 1.1$, as it is known from the statistics of clusters ("animals" [12,13]) below the percolation threshold leading a value $\alpha \approx 0.8$ closer to 1. In this framework one could again speak of "fractons" in glasses as it was first proposed by Alexander and Orbach [15] but only for transverse phonons.

In conclusion, we have not only shown, prior to experiments, the acoustic phonon spectrum of glasses and its behavior through the glass transition, but we have given also a satisfactory interpretation of the boson peak. We have explained our results in the framework of the Thorpe model which states that a glass is like a solid containing finite liquid regions. An interesting feature of our theoretical interpretation is that it conciliates the previous contradictory approaches, based either on cluster resonance [4] or on phonon localization [5], by adding some new key ingredients which are the liquid character of the clusters and the special role played by the transverse phonons. It might also be consistent with the "mode coupling" theories [16] of the glass transition, as, like in these theories, we have slow modes strongly varying with temperature (transverse phonons) coupled, via disorder, to fast T -independent modes (longitudinal phonons). Note also that the liquid pockets can be viewed as unstable regions where the atoms can diffuse locally by hopping over potential barriers. Therefore our picture is not different from the one used in the two-level and soft-mode theories, except that we are not considering the quantum aspects (tunneling) which appear at lower frequencies. We are presently pursuing our numerical calculations to explore further the implications of our model and to estimate the size distribution of the liquid pockets and its variation with quench rate and glass history.

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