Neutron Scattering Evidence for Localized Soft Modes in Amorphous Polymers

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The localization of low-frequency vibrational modes in amorphous solids can be determined from incoherent neutron scattering. Time-of-flight data from polystyrene and polybutadiene show a localization of the boson peak modes to about ten monomers. [S0031-9007(96)00693-X]

At present, there is still no satisfactory understanding of the low-frequency excitations in glasses and undercooled liquids. Recently, numerical work discovered a localization of some low-frequency vibrational modes [1–6]. The evidence is not fully conclusive, because the modes tend to delocalize with increasing cell size and the influence of long wavelength modes is missing.

In real glasses, there is no direct evidence so far. One does find low-frequency vibrations coexisting with the sound waves and giving rise to the boson peak in Raman and neutron scattering [7]. If there is a continuous crossover from the low-barrier tunneling states [8] to these additional vibrational modes, one would expect them to be localized. Such a crossover has been postulated in the soft potential model [9]. An evaluation of low-temperature specific heat data in terms of that model [10] estimates a number of 20 to 100 atoms partaking in a single vibrational mode, in good agreement with the numerical work [1–6]. One begins to understand vibrational localization in porous solids [11], but the physical reason for the vibrational localization in disordered bulk matter is not yet clear.

In this Letter, we show that incoherent inelastic neutron scattering allows one to measure the localization of low-frequency vibrational modes in glasses. The method is applied to two amorphous polymers, polystyrene and polybutadiene.

Consider a localized low-frequency mode at a frequency ω_s. For simplicity, let us assume N_s atoms with the total mass M_s and vibrating with the same amplitude u_s (though not necessarily in the same direction) in that mode. For $k_B T \gg \hbar \omega_s$,

$$\langle u_s^2 \rangle = \frac{k_B T}{M_s \omega_s^2}. \tag{1}$$

As an example, the low-frequency vibrations in amorphous selenium seem to be localized to 20 atoms [10]. At the boson peak frequency (1.4 meV), one calculates a mean square displacement $\langle u_s^2 \rangle$ of 0.012 Å^2 for such a localized mode at 100 K. The average mean square displacement measured at that temperature [12] is 0.009 Å^2 for a single direction. Thus the mean square displacement contribution from the localized mode at a participating

atom exceeds the average contribution from all the other modes, at least in the direction of vibration of the localized mode. Since it is precisely that direction which is sampled in the inelastic neutron scattering from the localized mode, one expects to see an increase of the effective Debye-Waller factor exponent in the one-phonon scattering at the mode frequency.

The contribution of atom i participating in the mode to the one-phonon scattering [13] from the localized mode is given by

$$S_{i,\text{loc}}^{(1)}(\mathbf{Q}, \omega) = \frac{1}{2} e^{-2W_i(\mathbf{Q})} Q^2 \langle u_s \rangle^2 \cos^2 \theta \, \delta(\omega \pm \omega_s). \tag{2}$$

Here θ is the angle between the direction of vibration of atom i in the mode and the direction of the momentum transfer vector $\mathbf{Q}$. The Debye-Waller factor $W_i(\mathbf{Q})$ is given by

$$2W_i(\mathbf{Q}) = (\overline{\alpha} + \langle u_s^2 \rangle \cos^2 \theta) Q^2, \tag{3}$$

where $\overline{\alpha} Q^2$ describes the contribution from all other modes.

Averaging over θ and the participating atoms, one finds that the one-phonon scattering from the localized mode is seen with a Debye-Waller factor $2W = (\overline{\alpha} + \Delta\alpha) Q^2$, where

$$\Delta\alpha = \frac{3}{5} \langle u_s^2 \rangle. \tag{4}$$

Measuring $\Delta\alpha$ through the Q dependence of the inelastic scattering, one can determine the localization of the mode.

The inelastic scattering does not only contain the one-phonon term, but also multiphonon terms [13], which give a negative contribution to the effective Debye-Waller exponent in the inelastic scattering. They result from all possible combinations of different vibrations, so their calculation is rather cumbersome. However, there is an easy way to take them into account, at least to a reasonable approximation. One fits the Q dependence of the full inelastic intensity at a given energy $\hbar\omega$ by the one-phonon form

$$S_{\text{inc}}^{(1)}(Q, \omega) = f(\omega) Q^2 e^{-\alpha(\omega) Q^2} \tag{5}$$

over the whole relevant frequency range of the spectrum. Thus one gets at each frequency two parameters, namely, the initial slope $f(\omega)$ against Q^2 at small Q and the effective Debye-Waller exponent $\alpha(\omega)$. The latter contains the $\Delta\alpha$ of the one-phonon scattering which one is looking for.

In order to extract $\Delta\alpha$, one can compare the fitted values of the effective Debye-Waller exponents $\alpha(\omega)$ with those calculated in the Gaussian approximation. The Gaussian approximation assumes for each atom a Gaussian probability distribution around its position at time zero. The time-dependent width $\gamma(t)$ of that probability distribution is assumed to be the same for each atom and each spatial direction. $S(Q,\omega)$ is then obtained as the Fourier transform in time of the intermediate scattering function

$$S(Q,t) = e^{-\gamma(t)Q^2}. \qquad (6)$$

The Gaussian approximation has been found to be reasonably accurate in high resolution experiments on polymers at elevated temperatures [14,15], but seems to fail at lower temperatures in other substances [16,17], indicating an influence of localized low-frequency modes at low temperatures.

Equating the Q^2 coefficients in the expansions of $S(Q,t)$ and of the Fourier transform of $S(Q,\omega)$, one finds

$$\gamma(t) = \int_{-\infty}^{\infty} f(\omega)\,(1 - \cos\omega t)d\omega\,. \qquad (7)$$

Thus one can calculate the full Gaussian scattering from $f(\omega)$ alone and fit the scattering law with the one-phonon form, Eq. (5), to see what the effective Debye-Waller exponent in the measurement range should be without any localized modes. The difference can then be attributed to the localization.

We evaluated time-of-flight data on amorphous protonated *cis-trans* polybutadiene [18] and amorphous polystyrene [19]. To check the validity of the procedure, we also did a measurement of a 98% crystalline *trans* polybutadiene sample. All data were taken on the spectrometer IN6 at the HFR at Grenoble with a wavelength of the incoming neutrons of 4.1 Å. At that particular wavelength, one has the largest Q range available at the instrument and an exceptionally high intensity.

The comparison of experiment and theory requires substantial corrections for self-absorption, resolution tails, multiple scattering, and coherent scattering contributions. This is illustrated in Fig. 1, which shows raw and corrected data. The dashed line shows the result of a global fit of the whole data set in terms of Gaussian scattering. The deviations from that fit are larger than the statistical error of the measurement, but they are smaller than the corrections, which therefore require due care.

The self-absorption correction is a standard procedure which requires good knowledge of the scattering, absorption, and shape of the sample. The correction for tails of the elastic line are pleasantly small at the chosen wave-
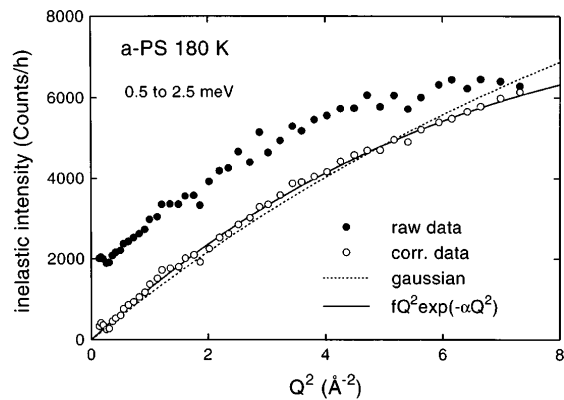

FIG. 1. Q dependence of the inelastic scattering from polystyrene between 0.5 and 2.5 meV at 180 K, showing a comparison of raw and corrected data and the difference between Gaussian and non-Gaussian fits.

length because of the sharp cutoff of the beryllium filter. We only used the energy gain part of the spectrum and calculated the other part via detailed balance. After subtracting these tails, the inelastic scattering from single-scattering processes must extrapolate to zero for zero Q. This can be used to judge the quality of the multiple-scattering correction. We used different procedures to do that correction, including numerical calculations and a new analytical procedure, with similar results. After subtracting multiple scattering, the curves did indeed extrapolate to zero at zero Q for all frequencies. Once this is guaranteed, it is possible to extrapolate $S(Q,\omega)$ for higher frequencies to small Q. This allows a final normalization correction using $\int S_{\text{inc}}(Q,\omega)d\omega = 1$ to remove the remnants of coherent scattering. A more detailed account of these corrections will be given in a forthcoming paper [20].

After correcting, one can fit the Q dependence of an inelastic channel with the one-phonon term, Eq. (5). The one-phonon form with an effective adapted Debye-Waller factor turned out to describe the data within experimental error for all three samples at all frequencies and temperatures. Figure 1 shows an example for the quality of the fit. Repeating the same fit up to frequencies of $3k_BT$, one gets a set of $f(\omega)$ from which one can determine the Gaussian values for the effective Debye-Waller exponents $\alpha(\omega)$.

Figure 2 compares the Debye-Waller exponents $\alpha(\omega)$ fitted to the measured data with those determined from the Gaussian approximation for three different examples. The first in Fig. 2(a) shows amorphous *cis-trans* polybutadiene at 60 K (glass transition temperature 183 K). One observes deviations from the Gaussian values at low frequencies, consistent with a mass M_s of 580 atomic units (eleven monomers) participating in a single localized mode. The second example in Fig. 2(b) is amorphous polystyrene at 180 K, well below its glass transition temperature of 373 K. One finds good agreement between experiment

and Gaussian calculation above 5 meV (note that at 15 meV the Debye-Waller exponent becomes negative, because the density of states is low and the multiphonon scattering prevails), but at low frequencies one finds deviations. These deviations again seem to follow the $1/\omega^2$ behavior predicted by Eq. (1) down to about
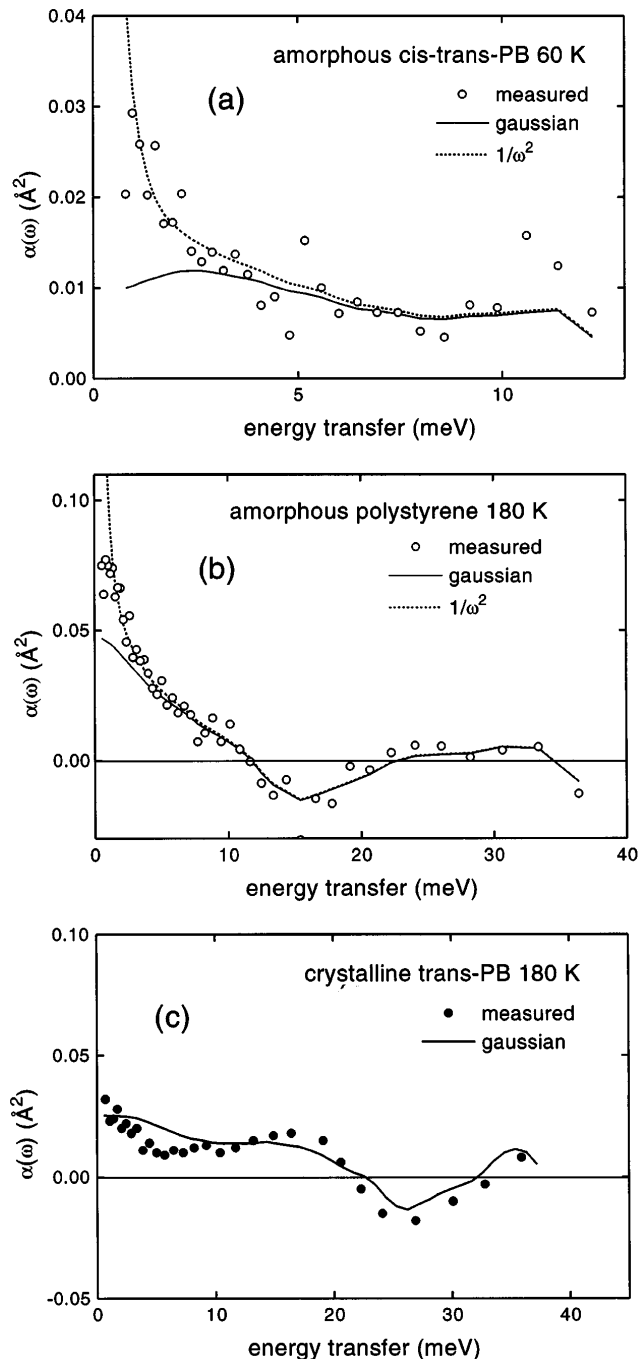

FIG. 2. Comparison of measured and calculated $\alpha(\omega)$. The dashed line adds a $1/\omega^2$ term to the Gaussian calculation. (a) Amorphous *cis-trans* polybutadiene at 60 K, (b) amorphous polystyrene at 180 K, and (c) crystalline *trans* polybutadiene at 180 K.

1 meV within experimental error (below 1 meV, one expects a slower increase of $\langle u_s^2 \rangle$ due to the anharmonicity and to the sound wave contribution to the inelastic scattering [10]). From the prefactor, one calculates [via Eqs. (1) and (4)] a total mass M_s of 650 atomic units (about six polystyrene monomers).

The crystalline sample in Fig. 2(c) shows no deviation at the lowest frequency (the deviations around 5 meV are probably due to the stronger effects of the remnant coherent scattering which is much sharper in Q). The absolute values are about the same as those of the amorphous sample at a 3 times lower temperature. Since the mean square displacement of the crystalline sample increases essentially linearly with temperature, this implies much smaller values in the crystalline polymer.

It is interesting to relate the non-Gaussian behavior of the inelastic data to the corresponding non-Gaussian behavior of the elastic line. The Q dependence of the elastic line of the incoherent scattering for an ensemble of N Gaussian scatterers with different mean square displacements is given to order Q^4 by

$$\frac{1}{N} \sum_{i=1}^{N} e^{-\alpha_i Q^2} \approx e^{[-\overline{\alpha} Q^2 + 1/2(\overline{\alpha^2} - \overline{\alpha}^2)Q^4]}, \quad (8)$$

where $\overline{\alpha}$ and $\overline{\alpha^2}$ are the averages of α_i and α_i^2, respectively. The dimensionless coefficient $(\overline{\alpha^2} - \overline{\alpha}^2)/\overline{\alpha}^2$ is denoted as the *non-Gaussianity* A_0.

For our experiment, the non-Gaussianity parameter A_0 can be calculated from the equations

$$\overline{\alpha} = \int_{-\infty}^{\infty} f(\omega)d\omega \,,$$
$$A_0 = 2 \frac{\int_{-\infty}^{\infty} f(\omega)\alpha(\omega)d\omega}{\overline{\alpha}^2} - 1 \,, \quad (9)$$

where the integrals are taken over the inelastic part of the scattering. For polystyrene at 180 K, one finds a value of 0.52, much higher than the value 0.09 anticipated from the factor of 2 between the average mean square displacements of the five protons on the phenyl ring and the three protons on the chain [21]. However, the value is in good agreement with recent triple axis measurements of the elastic line of polystyrene over a large Q range [22]. For polybutadiene, A_0 is 0.55 at 60 K and decreases to 0.35 at 135 K, in excellent agreement with a recent backscattering measurement on the IN13 at the ILL Grenoble [23].

All three measurements indicate a marked decrease of the non-Gaussianity towards higher temperatures (Fig. 3). A gradual delocalization of the vibrational modes has also been observed in numerical work [5]. Another simulation [3] shows localized modes in low-temperature amorphous ice, but no vibrational localization in room-temperature water. One should note, however, that the criterion for localization of the neutron measurement differs from the eigenmode criterion of the simulations. Two weakly
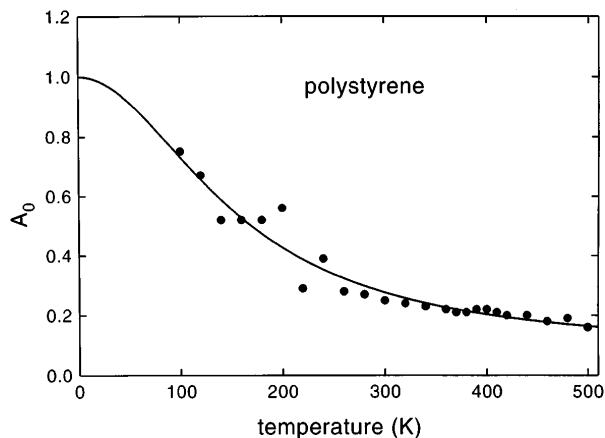
FIG. 3. Temperature dependence of the non-Gaussianity parameter A_0 in polystyrene. The line is a guide to the eye.

coupled localized modes on two neighboring groups of atoms appear as two eigenmodes extended over both groups in the simulation, but as two separate modes in a measurement of the atomic mean square displacements.

Our interpretation of the data in terms of a single type of localized modes oversimplifies the real situation in many ways. In particular, a full treatment will have to take the sound waves and their interaction with the localized modes into account. Such a treatment, however, requires a theoretical understanding which is not yet available.

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