Molecular-dynamics simulations of the scattering of neutrons from solid argon

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(Received 19 August 1991)

Phonon line shapes corresponding to zone-boundary modes in crystalline argon at a temperature close to the melting point have been calculated with a realistic pair potential, using molecular-dynamics simulations. The longitudinal peak is considerably broadened and distorted, in agreement with both experiment and earlier calculations, but now the transverse peak is also substantially broadened, removing an earlier disagreement.

The inelastic scattering of neutrons from crystalline argon has been studied by Eckert and Youngblood at a temperature close to the melting point.[1] In an earlier work[2] we showed that the frequencies corresponding to the centers of the scattering peaks were in excellent agreement with calculations using the Horner ansatz[3] to account for short-range correlation effects. However, at that time we also pointed out that the widths of the peaks were not in such good agreement. In particular, the experiments show that both the longitudinal and transverse peaks at the [100] zone boundary are broadened. In the lattice-dynamical calculation, the longitudinal mode was broad but the transverse mode was quite sharp. The present work adresses this discrepancy. Using the Aziz-Chen[4] pair potential for argon, we carry out molecular-dynamics simulations to calculate the scattering function for the modes of interest. We find that both phonon peaks are indeed broadened. Thus the earlier discrepancy must be a failure of the lattice-dynamical treatment.

The two experimental peaks are shown in (a) and (b) of Fig. 1. The transverse mode in Fig. 1(a) was measured at a scattering vector $\mathbf{Q}$ of $(2\pi/a_0)(2,-1,0)$, and the longitudinal mode in Fig. 1(b) was measured at $(2\pi/a_0)(3,0,0)$. The vertical scales begin at what we estimate to be the background scattering, in order to make the curves in the other parts of Fig. 1 more nearly comparable. Parts (c) and (d) of Fig. 1 show the results of the earlier calculation, for the transverse and longitudinal modes, respectively. The calculated peak for the longitudinal mode shows considerable width, but the discrepancy in the case of the transverse mode is obvious. Of course, a part of the disagreement arises from the finite resolution of the neutron spectrometer. We can estimate this contribution to the width from the experimental results at lower temperatures as about 0.5 meV. We shall also assume, for simplicity, that the two contributions to the width add orthogonally. Then experimentally the transverse peak has a full width at half maximum (FWHM) of 1.4 meV, and the natural width is 1.3 meV. The calculated FWHM is only 0.2 meV. The longitudinal mode has a calculated natural width of 2.0 meV, which is a little small. There have been other calculations which gave qualitatively similar results. Klein, Barker, and Koehler[5] used quasiharmonic perturbation theory, and Glyde and Smoes[6] used self-consistent phonon theory supplemented with the cubic contribution to the widths. At the highest temperature both of those calculations predicted a FWHM for the transverse mode of about 0.6 meV, less than half of what is observed. Note that the figures in the paper by Glyde and Smoes already have the instrumental resolution folded in. Of the three calculations the Horner method in fact gives the worst result, for reasons we shall discuss below, but all predict too sharp a transverse peak.

To throw more light on this, we have performed a series of molecular-dynamics simulations on argon at a temper-

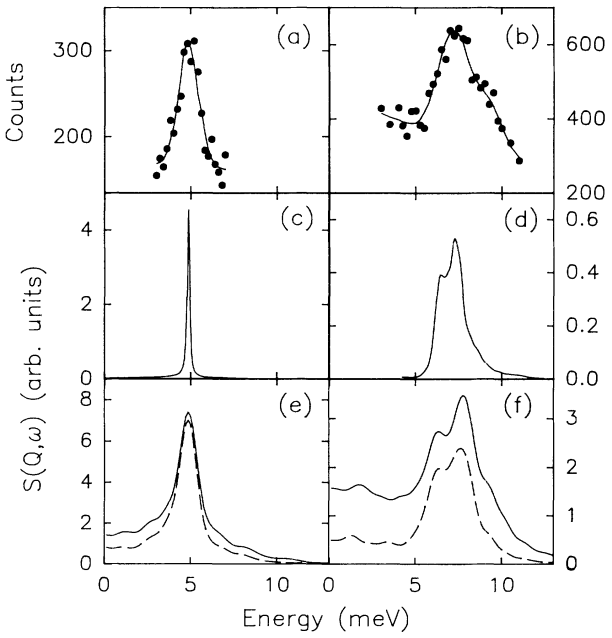

FIG. 1. Measured and calculated scattering peaks in argon at 81 K. (a) and (b) are the experimental results for the transverse and longitudinal modes from Ref. 1, (c) and (d) are lattice-dynamical calculations from Ref. 2, and (e) and (f) are MD results. Solid lines are full calculations and dashed lines are one-phonon approximations.

ature of 81 K. This is sufficiently high that the classical simulation should be reliable. The model used the Aziz-Chen potential[4] truncated after three shells of neighbors. For speed we omitted the three-body Axilrod-Teller interactions which were included in the Horner calculation. Glyde and Smoes[6] have pointed out that this has little effect on the transverse modes particularly. The simulations were carried out for systems of 32, 108, 256, and 500 atoms. A time step of 0.5×10^{-14} s was used, the system was thermalized for 500 time steps, and the pressure and temperature determined over a further 1500 time steps. The pressure was found to be essentially zero at the experimentally observed lattice spacing of 5.465 Å. The simulation was then run for a further 64 000 time steps during which the time correlation functions corresponding to the two phonons were calculated. These were then multiplied by a Gaussian damping function corresponding to a FWHM of 0.46 meV before being Fourier transformed to give $S(\mathbf{Q},\omega)$. The damping function was chosen to take effect strongly in the time range where the time correlation function became unreliable, but it happily corresponds quite closely with the experimental resolution. The results for the 500 atom system are shown as the solid lines in parts (e) and (f) of Fig. 1. Both the transverse and longitudinal peaks have widths in good agreement with the experiments. The longitudinal peak also shows some subsidiary structure. The details of this structure were different for the different sample sizes. However, the result shown, for the 500-atom sample, is quite similar to the lattice-dynamical result, which suggests that the sample is large enough to represent an infinite crystal. For the transverse mode the results were remarkably similar for all the sample sizes.

The main conclusion of this work is therefore that there is no fundamental disagreement between theory and experiment. A good potential used in a technique which includes all anharmonic contributions gives results in agreement with the measurements. Any disagreement with another calculation technique indicates a failure of that technique. The Horner procedure has one peculiarity, in comparison with perturbation theory and self-consistent theory. It attempts to move some of the effects of the cubic anharmonicity into the effective second-order force constants. As a result, the smeared cubic force constants which are used in the width calculation are reduced as compared with those used in the other calculations. In the case of argon at 81 K they are reduced by a factor of 1.3 relative to the unsmeared values and 1.8 relative to the self-consistent values,[7] and these force constants are squared in the matrix elements appearing in the width. This is the reason that the width calculated for the transverse phonon is the lowest of the three methods. The truth probably lies somewhere in the middle. For the longitudinal mode, the widths calculated using perturbation theory and self-consistent theory are actually larger than the experimental width, while the Horner cubic force constants give slightly too small a width.

Finally, it is appropriate to look for the reason for the failure of the lattice-dynamics calculations in the case of the transverse mode. Our calculation[2] and that of Klein, Barker, and Koehler[5] considered only the one-phonon contribution to the scattering. We can easily modify the MD calculation to include only one-phonon scattering and the results are shown as the dashed lines in parts (e) and (f) of Fig. 1. In the case of the longitudinal mode, there is a substantial multiphonon contribution to the scattering, including the strengthening of the shoulder on the high-energy side of the peak. This agrees with the finding of Glyde and Smoes,[6] who did explicitly calculate the two-phonon terms. However, the width of the transverse mode is barely affected by this change in the calculation. We believe that the failure in the lattice-dynamics calculation arises from the neglect of anharmonic processes in which the scattering phonon decays into more than two other phonons. All of the lattice-dynamics calculations considered only the processes in which the phonon either decays into two phonons, or combines with one existing phonon to produce a third phonon. The width function then typically shows two peaks as a function of energy, a high-energy peak corresponding to a sum band and a smaller low-energy peak corresponding to a difference band. Klein, Barker, and Koehler[5] show an example. The zone-boundary transverse mode has an energy which lies between the two bands and hence the calculated width is small. Inclusion of processes in which the phonon decays into three or more intermediate phonons would fill up the gap. The contribution to the width arising from such processes would have a very broad energy dependence, and hence would not have a large effect on the shift function, which apparently was given quite accurately by the Horner calculation. A similar phenomenon has been reported for the zone-center transverse optic mode in some alkali halides.[8]

This work was supported by the National Science Foundation under Grant No. DMR8808756, and by the Pittsburgh Supercomputing Center under Grant No. DMR890022P. We are grateful to Shudun Liu for his assistance in executing the computer programs.

[1] J. Eckert and R.W. Youngblood, Phys. Rev. B **34**, 2770 (1986).
[2] E.R. Cowley and G.K. Horton, Phys. Rev. Lett. **58**, 789 (1987).
[3] H. Horner, in *Dynamical Properties of Solids*, edited by G.K. Horton and A.A. Maradudin (North-Holland, Amsterdam, 1974), Vol. 1.
[4] R.A. Aziz and H.H. Chen, J. Chem. Phys. **67**, 5719 (1977).
[5] M.L. Klein, J.A. Barker, and T.R. Koehler, Phys. Rev. B **4**, 1983 (1971).
[6] H.R. Glyde and M.G. Smoes, Phys. Rev. B **22**, 6391 (1980).
[7] G.K. Horton and E.R. Cowley, in *Physics of Phonons*, edited by T. Paszkiewicz, Lecture Notes in Physics, Vol. 285 (Springer-Verlag, Berlin, 1987).
[8] J.E. Eldridge and K.A. Kembry, Phys. Rev. B **8**, 746 (1973).