DISPERSIVE ANHARMONIC EFFECTS IN THE LATTICE DYNAMICS OF QUANTUM CRYSTALS WITH HARD-CORE POTENTIALS*

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A simple approach to lattice dynamics provides a treatment of noninstantaneous (dispersive) anharmonicities in highly anharmonic crystals with singular (hard-core) interparticle potentials. The theory may be used to study the balance between single-particle and collective motions (phonons) in solid helium.

A partial summation of a series of anharmonicities is necessary in the lattice dynamics of highly anharmonic crystals. This has been achieved in the self-consistent phonon theory,[1] which can more readily be adapted to numerical computation than a second approach which emphasizes the single-particle aspect of the crystal.[2,3] However, the theory remains inapplicable to quantum crystals, such as solid helium, due to the restriction to nonsingular interparticle potentials and the omission of noninstantaneous (dispersive) anharmonicities. It has been suggested[3] that an adequate generalization would be to sum proper ladder diagrams and simultaneously to include phonon lifetime effects due to dispersive anharmonicities. However, the method of accomplishing such refinements from the self-consistent phonon theory has been considered "to be not at all obvious." Therefore, present generalizations[4] are largely approximate. Some neglect dispersive anharmonicities completely, and are also restricted to zero temperature. All of them treat instantaneous anharmonicities approximately and replace the singular interparticle potential by a nonsingular effective one, essentially in the spirit of a cluster-variational approach.[5]

In contrast, we present in this Letter a simple approach to the lattice dynamics of quantum crystals, which treats instantaneous anharmonicities rigorously, is valid for singluar interparticle potentials at all temperatures, and includes dispersive anharmonicities. Exact formulas for sound velocities and phonon spectra are given. Because of their structure they can be used to determine dispersive anharmonic contributions unambiguously. The corresponding spectral width function can be studied by employing a moment approximation. This is of interest for examining the balance between single-particle and collective motions in solid helium, especially since present single-particle and phonon-excitation approaches to the lattice dynamics are in apparent contradiction.[3]

We begin with the usual simple but rigorous way of studying the excitation energies of a lattice by considering the response of the crystal to a suitable external probe. The poles of the appropriate response function—or the zeros of its inverse—then determine the relation between frequency ω and wave vector $\vec{q}$ of the associated modes. We have been able to obtain the following exact spectral representation for the inverse of the displacement response function:

$$\chi_{kk'}^{-1}(\vec{q}, z=\omega+i\delta) = Mz^2\delta_{kk'} - \Phi_{kk'}(\vec{q}) - \int_{-\infty}^{+\infty} \frac{d\omega'}{2\pi} \frac{\Gamma_{kk'}(\vec{q},\omega')}{z-\omega'}, \tag{1}$$

where M denotes the mass of a single lattice particle, and $k(=1,2,3,)$ the Cartesian indices. The spectral width function $\Gamma_{kk'}(\vec{q},\omega)$ has the same symmetry properties as the spectral function $\tau_{kk'}(\vec{q},\omega)$, which is the Fourier transform of the commutator of the displacement operators.[6,7] We have used sum-rule techniques to calculate the frequency-independent "dynamical matrix" $\Phi_{kk'}(\vec{q})$ exactly. For a two-particle interatomic potential $v(r)$ we obtain

$$\Phi_{kk'}(\vec{q}) = N^{-1} \sum_{\alpha\neq\alpha'} [1-\exp(-i\vec{q}\cdot\vec{R}_{\alpha\alpha'})] \int d^3r \nabla_k \nabla_{k'} v(r) \langle \delta(\vec{r}-\vec{x}^{\alpha}+\vec{x}^{\alpha'})\rangle \quad (\vec{R}_{\alpha\alpha'} \equiv \vec{R}^{\alpha}-\vec{R}^{\alpha'}), \tag{2}$$

where the lattice vector of the αth particle $\vec{R}^{\alpha}$ is given by its mean equilibrium position $\langle x^{\alpha}\rangle$. The singular behavior of a Lennard-Jones potential is compensated, since

$$g(\vec{r}) = (MN)^{-1} \sum_{\alpha\neq\alpha'} \langle \delta(\vec{r}-\vec{x}^{\alpha}+\vec{x}^{\alpha'})\rangle$$

represents the pair distribution function of the crystal. Zeros of the real part of eigenvalues of the three-by-three matrix $\chi_{kk'}^{-1}(\vec{q}, \omega)$ define physical phonons having frequencies $\omega_s(\vec{q})$ which satisfy

$$M\omega_s^2(\vec{q}) - \Phi_s(\vec{q}) - P\int_{-\infty}^{+\infty} \frac{d\omega'}{2\pi} \frac{\Gamma_s(\vec{q}, \omega')}{\omega_s(\vec{q}) - \omega'} \equiv 0. \tag{3}$$

The quantities of (3) are related to those of (1) by introducing left and right polarization vectors $\tilde{e}_k^s(\vec{q}, z)$ and $e_{k'}^s(\vec{q}, z)$, which formally diagonalize $\chi_{kk'}^{-1}(\vec{q}, z)$. An exact expression for the long-wavelength isothermal sound velocity v_s follows from (1) for $z = 0$, due to the compressibility sum rule[7]:

$$v_s^2\left(\frac{\vec{q}}{|\vec{q}|}\right) = \lim_{q \to 0} (Mq^2)^{-1} \left\{ \Phi_s(\vec{q}) - \int_{-\infty}^{+\infty} d\omega \frac{\Gamma_s(\vec{q}, \omega)}{2\pi\omega} \right\}. \tag{4}$$

Becasue of its symmetry properties, $\Gamma_s(\vec{q}, \omega)/\omega \geq 0$.

All of the foregoing results are exact. We now indicate how they can be used to examine current approximations and remove existing deficiencies in lattice dynamics. (I) The exact instantaneous displacement response of the crystal is obtained by neglecting the dispersive term $\int d\omega' \Gamma_{kk'}(\vec{q}, \omega')/2\pi(z - \omega')$ in (1). The phonon frequencies $\omega_s(\vec{q})$ then obey the eigenvalue equation

$$\omega_s^2(\vec{q}) e_k^s(\vec{q}) = M^{-1} \sum_{k'=1}^{3} \varphi_{kk'}(\vec{q}) e_{k'}^s(\vec{q}). \tag{5}$$

Equation (5), together with the definition of $\varphi_{kk'}(\vec{q})$ in (2), shows that the phonon frequencies $\omega_s(\vec{q})$ in the instantaneous approach are determined for a given two-particle interaction $v(r)$ by the static two-particle correlation function or the pair distribution function $g(\vec{r}) \propto \langle \delta(\vec{r} - \vec{x}^\alpha + \vec{x}^{\alpha'}) \rangle$. The fluctuation-dissipation theorem in connection with the third frequency moment of the density-density spectral function could be used to obtain a complicated nonlinear integral equation for $g(\vec{r})$. Therefore, excitations of the displacement response are related to excitations of the density response, and this integral equation, coupled to Eq. (5), replaces the self-consistent condition of earlier approximate schemes.[4] The self-consistent harmonic as well as the well-known harmonic approach are approximations to (5). They may readily be obtained from the corresponding approximations to the static two-particle correlation function or to $\langle \delta(\vec{r} - \vec{x}^\alpha + \vec{x}^{\alpha'}) \rangle$, respectively.[8] However, the Monte Carlo method represents another and numerically easier way to compute not only $\langle \delta(\vec{r} - \vec{x}^\alpha + \vec{x}^{\alpha'}) \rangle$ but also higher static particle correlation functions rigorously. Futhermore, it avoids the usual cluster variational expansion, the limitation of which has been demonstrated.[9] Such calculations for solid helium at zero temperatures are now in progress. (II) Rigorous calculations of (5) can be used for two basic purposes: (a) In the long-wavelength limit we get the instantaneous contributions to the exact formula (4) for sound velocities. A comparison with measured sound velocities therefore provides an unambiguous determination of dispersive contributions,[10] since they enter additively into (4). (b) Frequencies $\omega_s(\vec{q})$ of (5) determine the contribution of the instantaneous displacement response to the one-phonon term of the neutron scattering function[11]:

$$S^{(1)}(\vec{q}, \omega) = (1 - e^{-\beta\omega})^{-1} [d(\vec{q})]^2 \sum_{k,k'} q_k \tilde{\tau}_{kk'}(\vec{q}, \omega) q_{k'},$$

where $[d(\vec{q})]^2$ is the Debye-Waller factor and

$$\tilde{\tau}_{kk'}(\vec{q}, \omega) \simeq 2\pi \sum_s e_k^s(-\vec{q}) e_{k'}^s(\vec{q}) [2M\omega_s(\vec{q})]^{-1} \{\delta[\omega - \omega_s(\vec{q})] - \delta[\omega + \omega_s(\vec{q})]\} \tag{6}$$

is the spectral function in the instantaneous approach. Therefore, a comparison of $S^{(1)}(\vec{q}, \omega)$ with inelastic neutron-scattering experiments in single-crystal helium[12] gives subtractively an estimate of dispersive anharmonic contributions to phonon frequencies. (III) Frequency moments of $\tau(\vec{q}, \omega)$ and $\Gamma(\vec{q}, \omega)$ can be connected to a high-z expansion of (1). Sum-rule techniques can again be used to obtain higher frequency moments of $\tau(\vec{q}, \omega)$ in terms of higher static particle-correlation functions, com-

puted by the Monte Carlo method. The coupling of the particle motion to the phonon modes then is reflected in the related moments of the spectral width function $\Gamma(\vec{q}, \omega)$, which determine, e.g., shift and lifetime of phonon frequencies from (5) due to dispersive anharmonicities. Rapidly varying parts may, of course, appear in $\Gamma(\vec{q}, \omega)$.[13] In particular, at finite temperatures they are responsible for the difference between isothermal and adiabatic sound propagation and for the possible appearance of second sound in solid helium. As in each of the previous theories of solid helium,[4,5] we shall not, in this Letter, consider such resonant terms in $\Gamma(\vec{q}, \omega)$ on the grounds of simplicity. Details of the theoretical analysis of dispersive anharmonicities, including a discussion of the nonregular parts in $\Gamma(\vec{q}, \omega)$, will be published subsequently, together with extensive results of the Monte Carlo calculations.

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