PHONON ENERGIES AND LIFETIMES IN SOLID Ne AND He IN THE FIRST-ORDER SELF-CONSISTENT APPROXIMATION*

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We discuss the response of a crystal in the presence of a neutron distortion in the first-order self-consistent approximation and we stress the importance of the self-consistency condition. The resultant integral equation for the phonon energies is solved by direct matrix inversion instead of truncating a series expansion. Numerical results are presented for solid Ne and fcc He^4 at 10.0 and 11.5 cm^3/mole.

In his book Choquard[1] has shown how to obtain thermodynamic derivatives of the self-consistent free energy. In spite of the pseudoharmonic nature of the theory, there are additional terms which occur because of the self-consistency condition imposed upon the frequencies. Similarly Götze and Michel[2] in their treatment of elastic constants have shown that in the first-order self-consistent approximation the expression for the self-energy Σ can be represented diagrammatically by the equation shown in Fig. 1. The first term represents the usual thermodynamic self-consistent frequencies. The remaining terms, which yield a shift and a width, represent an iterative solution to an integral equation, and, just as for the compressibility discussed by Choquard, they occur because of the self-consistency condition imposed upon the frequencies. Applications of the self-consistent approximation to elastic constants[3] and neutron-scattering phonon spectra[4-7] in noble-gas solids (mostly helium) have made use of up to the second term only in Fig. 1. But recent calculations of compressibilities and elastic constants in those solids[8-10] have shown that such inconsistency can be serious (except for low T and high mass) and grows worse with increasing temperature and decreasing mass.

In this Letter we express the self-consistent self-energy of Fig. 1 in a fashion that can be implemented numerically and we obtain results for phonon spectra in fcc neon and helium at high pressures.

In studying the response of a lattice to neutron scattering we shall be concerned only with the one-phonon Green's function $G_{JJ'}(\vec{Q}, \Omega)$. In particular we are interested in the peaks of its imaginary part

$$\mathrm{Im}G_{JJ'}(\vec{Q},\Omega)=\frac{2\omega_J(\vec{Q})\Gamma_{JJ'}(\vec{Q},\Omega)}{[\Omega^2-\omega_J^2(\vec{Q})-2\omega_J(\vec{Q})\Delta_{JJ'}(\vec{Q},\Omega)]^2+4\omega_J^2(\vec{Q})\Gamma_{JJ'}^2(\vec{Q},\Omega)}, \tag{1}$$

where $\vec{Q}$ and Ω are the momentum and energy transferred, respectively. Generalizing the method of Götze and Michel[2] in the first-order self-consistent phonon approximation, Δ and Γ are given by the following equations:

$$2\omega_J(\vec{Q})\{\Delta_{JJ'}(\vec{Q},\Omega)+i\Gamma_{JJ'}(\vec{Q},\Omega)\}\equiv\delta\Sigma_{JJ'}(\vec{Q},\Omega)$$
$$=-\frac{2}{m}\sum_{\rho_1\rho_2\rho_3}\sum_{\substack{\alpha\beta\gamma\sigma\\ \alpha'\beta'\gamma'\tau}}\sin\frac{\vec{Q}\cdot\vec{R}_{\rho_1}}{2}e_\alpha(\vec{Q},J)\Phi_{\alpha\beta\gamma}{}^{\rho_1}W_{\beta\gamma\beta'\gamma'}{}^{\rho_1\rho_2}\{[I+C]^{-1}\}_{\beta'\gamma'\sigma\tau}{}^{\rho_2\rho_3}\Phi_{\sigma\tau\alpha'}{}^{\rho_3}$$
$$\times e_{\alpha'}(\vec{Q},J')\sin(\tfrac{1}{2}\vec{Q}\cdot\vec{R}_{\rho_3}), \tag{2}$$

where

$$I_{\alpha\beta\alpha'\beta'}{}^{\rho_1\rho_2}=\delta_{\rho_1\rho_2}\delta_{\alpha\alpha'}\delta_{\beta\beta'}, \tag{3}$$

FIG. 1. Phonon self-energy.

and

$$C_{\alpha\beta\alpha'\beta'}{}^{\rho_1\rho_2}(\vec{Q},\Omega)=\sum{}_{\gamma\delta}\Phi_{\alpha\beta\gamma\delta}{}^{\rho_1}W_{\gamma\delta\alpha'\beta'}{}^{,\rho_1\rho_2}(\vec{Q},\Omega),$$

and

$$W_{\alpha\beta\gamma\delta}{}^{\rho_1\rho_2}(\vec{Q},\Omega)=\frac{\hbar}{M^2N}\sum_{q_1J_1,q_2J_2}\frac{\delta(\vec{Q}+\vec{q}_1+\vec{q}_2)}{\omega_1\omega_2}\sin\frac{(\vec{q}\cdot\vec{R}_{\rho_1})}{2}\sin\frac{(\vec{q}_2\cdot\vec{R}_{\rho_1})}{2}$$
$$\times\sin\frac{(\vec{q}\cdot\vec{R}_{\rho_2})}{2}\sin\frac{(\vec{q}_2\cdot\vec{R}_{\rho_2})}{2}e_\alpha(\vec{q}_1J_1)e_\beta(\vec{q}_2J_2)e_\gamma(\vec{q}_1J_1)e_\delta(\vec{q}_2J_2)$$
$$\times[(n_1+n_2+1)\{P(\Omega+\omega_1+\omega_2)^{-1}-P(\Omega-\omega_1-\omega_2)^{-1}+\pi i\delta(\Omega+\omega_1+\omega_2)-\pi i\delta(\Omega-\omega_1-\omega_2)\}$$
$$+(n_1-n_2)\{P(\Omega-\omega_1+\omega_2)^{-1}-P(\Omega+\omega_1-\omega_2)^{-1}+\pi i\delta(\Omega-\omega_1+\omega_2)-\pi i\delta(\Omega+\omega_1-\omega_2)\}]. \quad (4)$$

Here $n_J=[\exp(\hbar\omega_J/kT)-1]^{-1}$, M is the mass of each ion, $\{\vec{R}_\rho\}$ represent the equilibrium lattice vectors, $\omega_J(\vec{q})$ and $e_\alpha(\vec{q},J)$ represent the frequencies and eigenvectors (polarization J) of the self-consistent equations,[11] and $\Phi_{\alpha\beta\gamma}\cdots$ are the smeared force constants. One should note that $\delta\Sigma$, W, and C are complex quantities. The complex inverse $[1+C]^{-1}$ in Eq. (2) is taken with respect to the tensor multiplication implied in that equation and the unit tensor defined by Eq. (3). One should note that this inverse can be expressed in the series

$$(1+C)^{-1}=1-C+C^2-C^3+\cdots,$$

provided it converges. When substituted into Eq. (2), we obtain the diagrammatic representation in Fig. 1 starting from the second diagram. In the case of helium, the series often diverges and one has to solve for the inverse by exact matrix inversion. The results in this Letter have been obtained by this latter method.

In the [100] direction, the Green's function $G_{JJ'}$ is diagonal. The neutron frequencies are obtained by searching for the peaks of $\mathrm{Im}G_{JJ'}(\vec{Q},\Omega)$ as a function of Ω. The treatment of the principal value and delta function in Eq. (4) has been described elsewhere.[5] The number of points used in the scan of Eq. (4) varied over 256, 2048, and 6912 points depending on the convergence which was set to 1% maximum in the location of the peaks.[12]

Neon.—The results for neon in the [100] direction are depicted in Fig. 2. The calculations were carried out using a (13-6) Mie-Lennard-Jones potential $\varphi(r)$ with nearest-neighbor interactions:

$$\varphi(r)=\epsilon\left(\frac{6m}{m-6}\right)\left\{\frac{1}{m}\left(\frac{R_0}{r}\right)^m-\frac{1}{6}\left(\frac{R_0}{r}\right)^6\right\}. \quad (5)$$

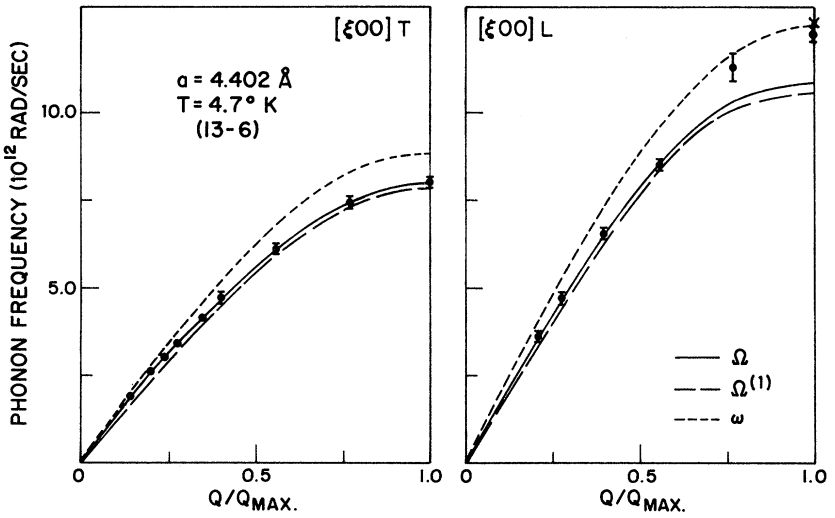

FIG. 2. Phonon energies in the [100] direction in Ne. For longitudinal phonons near the zone boundary we have found a lower second peak in the Green's function which we indicate by a cross (see Ref. 12).

with $m=13$, $R_0=3.029$ Å, and $\epsilon=73.10\times10^{-16}$ ergs. This potential was found to account successfully for a number of thermodynamic properties.[13] The experimental points are those of Leake et al.[14] In this figure the curve labeled ω results from the first diagram of Fig. 1 and it represents simply the thermodynamic frequencies obtained from the self-consistent equations.[11] Curve $\Omega^{(1)}$ represents the peaks of a $G(Q,\Omega^{(1)})$ whose self-energy goes up to the second diagram only in Fig. 1. It is equivalent to the work of Koehler.[4] Curve Ω represents the peaks of the Green's function in the first-order self-consistent theory as determined from Eqs. (2) and (4). We should note that in the long-wavelength limit only the slopes of the Ω curve give the same bulk modulus as the one obtained by numerically differentiating the first-order self-consistent free energy with respect to volume.

Helium.—Calculations were also carried out for[15] fcc He^4. In order to deal with the singularity of the potential at the origin[16] one can look for a region of stability of the self-consistent solutions with respect to a variation of a cutoff of the potential away from the core. Our results for He^4 are for molar volumes of 10 cm^3 at 20°K and 11.5 cm^3 at 16°K where He is in the fcc phase. Thus we find that at 10 cm^3 the free energy is stable to one part in 10^5 when the cutoff is varied from $0.17R_0$ to $0.45R_0$. At 11.5 cm^3 the stability is one part in 8×10^3 for a range of $0.15R_0$ to $0.4R_0$. Our investigation into the cutoff problem shows that for these volumes short-range correlations may safely be neglected as far as the self-consistent approximation is concerned.[17]

The results for He^4 are shown in Figs. 3 and 4 for 10.0 and 11.5 cm^3/mole, respectively, in the [100] direction. A 12-6 Lennard-Jones potential was used with $R_0=3.869$ Å and $\epsilon=14.10\times10^{-16}$ ergs. The $\Omega^{(1)}$ curve is equivalent to the work of Glyde and Cowley[6] and of Horner[7] in the computation of the self-energy. In the case of He, the discrepancy between the two theories is much more decisive both quantitatively and in the shape of the dispersion curves than in Ne, near 4°K. One should note that in the quasistatic limit the slopes of the $\Omega^{(1)}$ curves give abnormally low bulk moduli and velocities.[18] In fact, at 11.5 cm^3/mole the elastic constants obtained by keeping only the second term in Fig. 1 were found to be slightly negative.

Since $\Omega^{(1)}$ contains a pronounced point of inflection, the phonon spectrum based on a truncated self-energy could lead to an anomalous Θ_D curve (with a maximum) at low T. Such behavior is not exhibited by a spectrum based on the complete first-order self-energy. This result may carry over to other volumes and phases.[19,20] In any case, a reliable study of this question would require rather detailed numerical work.[21]

We have applied the one-phonon Green's function to the neutron-scattering phonon spectra in neon and He^4 as predicted from the first-order self-consistent approximation. We stress that we have presented the results of the first-order theory. Higher-order corrections to the free

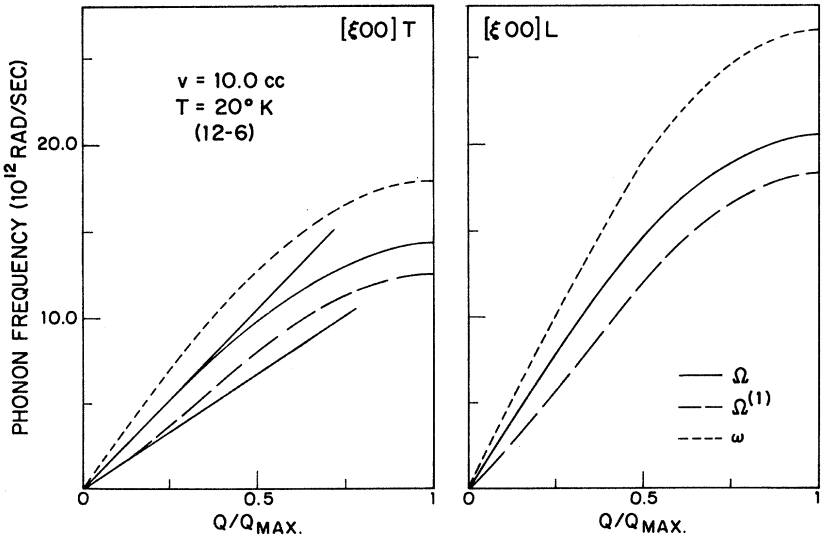

FIG. 3. Phonon energies in the [100] direction in fcc He^4. The slopes of the lines come from isothermal elastic constants obtained independently (see Ref. 10).

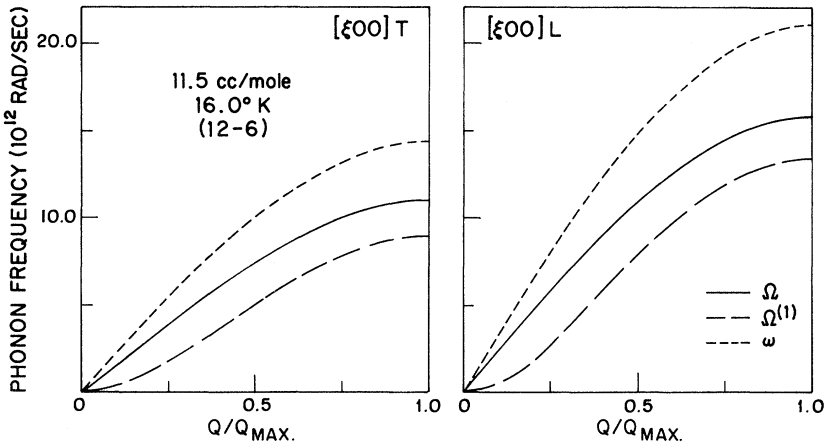

FIG. 4. Phonon energies in the [100] direction in fcc He^4.

energy, such as the improved self-consistent theory[13] or Choquard's full second-order theory, will contribute corresponding corrections to our results.

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[18]See caption of Fig. 3.

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