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# Brillouin Light Scattering from Crystals in the Hydrodynamic Region*

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With the availability of modern lasers, light scattering can now be used as a probe of the energy, damping, and relative weight of the various hydrodynamic collective modes in anharmonic insulating crystals. We first give a general review of the distinction between hydrodynamic and high-frequency (or dynamic) vibrational modes. We then express the intensity and spectral distribution of scattered light in terms of the Fourier transform of the displacement–displacement correlation function $\chi''(\mathbf{K}\Omega)$, which is the spectral weight of the phonon propagator. This follows some work of Loudon, who has discussed first-order Raman (or Brillouin) scattering using standard quantum-mechanical perturbation theory. Next we summarize what can be said about the spectral weight $\chi''(\mathbf{K}\Omega)$ in the region of low frequencies (or small energy transfer). We use the model calculations of Kwok and Martin, as well as the standard theory of an elastic medium with a nonlocal form of Fourier's law of heat diffusion. In the case of pure isotropic anharmonic crystals, $\chi''(\mathbf{K},\Omega)$ has resonances corresponding to first-sound (pressure) and second-sound (temperature) waves, in addition to that from transverse or shear elastic waves. Unless fairly restrictive conditions are met, the second-sound wave does not propagate and reduces to the ordinary thermal diffusion mode of Landau and Placzek. The special nature of second sound in He II is discussed in an Appendix.

## I. INTRODUCTION

In most many-body systems, there is a fairly sharp distinction between the elementary excitations (or quasi-particles) and the collective modes involving a coherent mixture of quasi-particles. One well-known example is the particle-like excitation and plasma oscillation of an interacting electron gas. It is now generally agreed that the most natural way of studying the dispersion relation, damping, and relative weight of the quasi-particles is from the poles and their residues in the spectral representation of the single-particle thermodynamic Green's function $G_1$ (Fourier-transformed in space and time). Similarly, collective modes can be associated with the analytic singularities in the two-particle Green's function $G_2$. This generally involves the use of infinite-order perturbation theory to deal with the interactions. However, the Green's functions can be expressed in terms of self-energies and vertex functions, and these may be evaluated by lowest-order perturbation theory in the interactions.[1] From the point of view of studying the quasi-particles, only the simplest self-energy Feynman diagrams need be included, often with a simple vertex and bare propagators. The approximations used for $G_2$ are usually those corresponding to a simple self-consistent field. The basic idea is that the quasi-particles are well-defined entities with a lifetime $\tau(\omega)$ satisfying[2] $\omega \gg 1/\tau(\omega)$. Moreover, if $\bar{\tau}$ is the mean lifetime of the majority of quasi-particles in the system, then a collective mode of energy $\Omega$ can only be treated by some sort of self-consistent field method if $\Omega \gg 1/\bar{\tau}$.

This brings us to the possibility of a "hydrodynamic" collective mode—namely, one of such low energy that $\Omega \ll 1/\bar{\tau}$. Since the very existence of hydrodynamic modes seems to depend on frequent "collisions" between the quasi-particles, the self-consistent field method used for "dynamic" collective modes is no longer applicable. The latter are referred to as being in the "collisionless" region. In terms of Boltzmann transport equations, hydrodynamic modes are related to the possibility that the right-hand side, or "collision integral," will vanish. This possibility is closely tied up with "collisional invariants" or the conservation laws for energy, momentum, etc.

The standard way of treating hydrodynamic modes is still that of Chapmann and Enskog, although this method can be formulated in terms of single-particle Green's functions[3] instead of distribution functions. The "collisions" do not alter a Green's function appropriate to local thermal equilibrium, which is identical to that for thermal equilibrium except that the thermodynamic parameters (temperature $T$, pressure $p$, etc.) now depend on space and time. Substitution of this local equilibrium Green's function into the various conservation equations results in self-consistent equations for $T(\mathbf{r}, t)$, $p(\mathbf{r}, t)$, etc., the solutions of which

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[1] For many examples, see A. A. Abrikosov, L. P. Gor'kov, and L. Dzyaloshinskii, *Quantum Field Theory Methods in Statistical Physics* (Prentice-Hall, Inc., Englewood Cliffs, N.J., 1963).

[2] We generally set $\hbar = 1$.

[3] L. P. Kadanoff and G. Baym, *Quantum Statistical Physics* (W. A. Benjamin, Inc., New York, 1961).

are referred to as hydrodynamic collective modes. While these modes also correspond to analytic singularities in the spectral representations of $G_1(\mathbf{q}, \omega)$, physically speaking they are quite different from the quasiparticles and dynamic collective modes previously mentioned.

Generally, a system of strongly interacting quasiparticles (with nonzero mass) exhibits two low-frequency, long-wavelength hydrodynamic modes. One is a longitudinally propagating density oscillation or sound wave [$\omega \simeq cq$, where $c$ is the velocity related to the usual thermodynamic derivative $(dp/d\rho)_s$]; the other is a damped temperature wave ($\omega \simeq -iDq^2$, where $D$ is the ratio of the ordinary thermal conductivity to the specific heat).

In the usual discussions of insulating solids, the distinction between the hydrodynamic and dynamic collective vibrational modes is either not mentioned or, if it is, the relation between them is not discussed at all. This is not merely a matter of academic interest, since, with the availability of intense, highly monochromatic light beams from lasers, it should soon be possible to use light scattering in order to study the excitation spectrum at low and intermediate energies in crystals (and possibly in He II) in a very detailed way. We refer to the so-called first-order Raman effect,[4,5] sometimes also called Brillouin–Mandel'stham scattering or the fine structure of Rayleigh scattering. This method perfectly complements the low-energy studies using artificially introduced sound waves ($\omega \lesssim 10^9$ sec$^{-1}$) and the high-energy studies using thermal neutron spectroscopy (energy transfers of the order $10^{11}$ sec$^{-1}$ and higher).

With the expectation that the present small trickle of Brillouin scattering experiments on solids (and quantum liquids such as He$^3$ and He II) will soon grow into a major river, we think it useful to review what the spectral distribution and intensity of scattered light tells us about the collective modes in condensed systems, with emphasis on simple crystals and liquids.[6] In the next section, we show that the first-order Raman effect is a direct probe of the time-ordered displacement–displacement correlation function $D(\mathbf{K}, \Omega)$. Here $\mathbf{K}$ and $\Omega$ are the momentum and energy difference between the scattered and incident photons. We give a quantum-mechanical derivation which is based on an effective "photon–phonon" Hamiltonian, and is related to recent work of Loudon[7] and Fetter.[8] The usual formulation[4,5] is based on the scattering of a light wave by fluctuations in the dielectric tensor of the medium, and this is briefly sketched for comparison with the quantum-mechanical discussion. Neutron scattering determines Van Hove's density–density correlation function $S(\mathbf{K}, \Omega)$, which is a less direct and less complete probe of the excitation spectrum.

In Sec. III, we discuss what recent microscopic calculations[9,10] of $D(\mathbf{K}, \Omega)$ predict about the velocity and damping of the collective modes. Attention is called to the occurrence of "second sound" in crystals and the conditions under which it is weakly damped. The optimal conditions for its detection are reviewed in Sec. IV. Additional modes due to atomic diffusion, crystal surfaces, and phase transitions are also mentioned in this last section.

### A. High- and Low-Energy Phonons

We shall now discuss the difference between high-energy and low-energy phonons in crystals, and how this depends on the temperature and anharmonic interactions. Similarities and differences are pointed out between these phonons in crystals and "phonons" in classical liquids, He II and Fermi liquids such as He$^3$. The distinction between high- and low-frequency collective modes has been extensively discussed for quantum liquids.[11] We emphasize that this is an important distinction in crystals as well, but one which is not sufficiently stressed in the literature.[11a]

The energy spectrum of dielectric crystals considered as an elastic continuum is a very old and well-known subject.[12] The proof that one can treat a crystal as an elastic medium involves the same sort of problems (in principle, at least) that arise in justifying the classical hydrodynamical equations for a fluid. The modern quantum theory of a crystal was developed[4,13] between 1910 and 1930 by Einstein, Debye, Born, Von Karman, Peierls and others. Here the atoms (of mass $M$, there being $N$ of them) are considered to be vibrating around certain equilibrium positions (the crystal lattice) as a result of two-body forces. If the force on an atom is proportional to its displacement from its equilibrium position, the Hamiltonian can be diagonalized in terms of elastic waves. When the displacements from the equilibrium positions are

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[4] The classic reference is M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford, England, Clarendon Press, 1954).

[5] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Addison–Wesley Publ., Co., Inc., Reading, Mass., 1960), p. 393 ff.

[6] Among the many references on the subject of probing crystals by scattering techniques, we might mention the brief review of A. Sjoländer, *Phonons and Phonon Interactions*, T. A. Bak, Ed. (W. A. Benjamin, Inc., New York, 1964), p. 84.

[7] R. Loudon, Proc. Roy. Soc. (London) **A275**, 218 (1963); a more general review is given in R. Loudon, Advan. Phys. **13**, 423 (1964).

[8] A. L. Fetter, Phys. Rev. **139**, A1616 (1965).

[9] P. C. Kwok and P. C. Martin, Phys. Rev. **142**, 495 (1966).

[10] P. C. Kwok, thesis, Harvard University, 1965 (unpublished); the results are briefly summarized in P. C. Kwok, P. C. Martin, and P. B. Miller, Solid State Commun. **3**, 181 (1965), which includes further references to the literature.

[11] See, for example, D. Pines and P. Nozieres, *Theory of Quantum Liquids* (W. A. Benjamin, Inc., New York, 1966).

[11a] See, however, R. A. Cowley, Proc. Phys. Soc. (London) 90, 1127 (1967).

[12] A good reference is L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Addison-Wesley Publ. Co., Inc., Reading, Mass., 1960).

[13] A nice summary (which includes transport theory as well) is available in R. Peierls' *Quantum Theory of Solids* (Clarendon Press, Oxford, England 1955).

quantized,

$$\hat{\mathbf{u}}(\mathbf{r}_n)=\sum_{\mathbf{k}j}\frac{\mathbf{e}(\mathbf{k},j)}{[2NM\omega_j(k)]^{1/2}}(a_{\mathbf{k}j}+a_{-\mathbf{k}j}^*)\exp(i\mathbf{k}\cdot\mathbf{r}_n), \tag{1.1}$$

one can think of the crystal as a gas of noninteracting phonons, described by the harmonic Hamiltonian

$$H_0=\sum_{\mathbf{k}j}\hbar\omega_j(\mathbf{k})[a_{kj}^*a_{kj}+\tfrac{1}{2}]. \tag{1.2}$$

Here $\omega_j(k)$ is the energy of phonon with wave vector $\mathbf{k}$ and polarization $\mathbf{e}(\mathbf{k},j)$, there being three mutually orthogonal polarization vectors for a given $\mathbf{k}$. We consider only crystals with one atom per unit cell, so that there are no optical modes.

A caret on a vector $\mathbf{A}$ denotes a unit vector in the same direction. Sometimes, however, it is used to denote a quantum-mechanical operator, as in Eq. (1.1).

One next includes anharmonic terms which are cubic and higher in the displacements of the atoms, as well as scattering effects from impurity atoms (mass impurities, paramagnetic impurities, etc.). If these perturbations are "small," one can still use (1.2) as a good starting point. At $T=0°\mathrm{K}$, where a simple perturbation theory is valid, the additional terms give rise to interactions between the bare phonons. The result is that their energy $\tilde{\omega}_j(k)$ is slightly renormalized, but is generally still proportional to the wave vector

$$\tilde{\omega}_j(\mathbf{k})=\tilde{v}_j(\hat{\mathbf{k}})k, \tag{1.3}$$

where $\tilde{v}_j(\mathbf{k})$ is the renormalized velocity which depends on the polarization and direction of propagation. This linear dispersion relation is generally true for all frequencies $\lesssim 10^{12}\ \mathrm{sec}^{-1}$, which is the region of interest. In addition, the phonons now have a lifetime $\tau_j(k)$, although $\tilde{\omega}_j(k)\gg 1/\tau_j(k)$ [for cubic anharmonicity, $1/\tau_j(k)\propto\omega_j^5(k)$]. These zero-temperature phonons might be considered to be the elementary excitations of the crystal.

At finite temperatures, the situation becomes considerably more complex. The analysis is somewhat simplified by the fact that the great majority of phonons have energies $\simeq k_BT$ (where $T$ is the absolute temperature), due to the nature of the Bose–Einstein distribution. As a result, it should not be surprising that when computing the self-energy in the Dyson equation for the time-ordered displacement–displacement propagator (or "phonon" Green's function) $D[\mathbf{k},\omega_j(k)]$, we need only consider interactions with the high-energy thermal phonons ($\omega_{\mathrm{th}}\simeq k_BT$) if $\omega_j(k)\ll k_BT$. A further implication is that the phonon's dispersion relation and damping can often be approximated by the results at 0°K. The width of the excitation of interest $\Gamma_j(k)\equiv 2/\tau_j(k)$ can be found by simple perturbation theory, keeping only the simplest decay and absorption processes. Such "Golden Rule" calculations have been discussed in great detail by Kwok[10] and many others.[14]

At low-enough excitation energies at finite temperatures, this procedure breaks down. When the phonon of interest has energy $\omega_j(k)\ll 1/\bar{\tau}$ [where $\bar{\tau}=\tau(\omega\simeq k_BT)$ is the lifetime of a typical (i.e., thermal) phonon], one can no longer treat the damping by the first few orders of perturbation theory. In place of

$$\Gamma_j(k)\simeq AT^4\omega_j(k);\qquad \omega_j(k)\gg 1/\bar{\tau}, \tag{1.4}$$

one finds

$$\Gamma_j(k)\simeq AT^4\omega_j^2(k)\bar{\tau};\qquad \omega_j(k)\ll 1/\bar{\tau}, \tag{1.5}$$

where $A$ is some constant.[10] Thus for low frequencies, the phonon damping is proportional to what is essentially the phonon gas bulk (or second) viscosity. The result given by (1.5) is typical of a hydrodynamic mode, and was first obtained by Akhiezer[15] using a Boltzmann equation approach. At low frequencies, the collective mode is sharpened in energy as the collision rate among the excitations of the crystal (the thermal phonons) increases! Conceptually, this low-frequency mode is similar to a density wave in a gas of interacting atoms. However, the fact that the "particles" are in this case phonons ($\omega\propto k$) to begin with results in the hydrodynamic mode having a velocity essentially identical to the velocity of the bare phonons. In a gas of atoms moving with average velocity $\bar{v}$, hydrodynamic sound waves have a velocity $\bar{v}/\sqrt{3}$.

The preceding results might suggest the use of some terminology introduced by Landau in his theory of Fermi liquids. Thus, low-energy phonons might be called "first-sound" waves, while the high-energy phonons are more analogous to "zero-sound" waves. The "first-sound" description makes sense in that the low-frequency phonon could be approached from the point of view of elasticity theory. In Fermi liquids, zero sound is a collective wave in a system of interacting quasi-particles—the analog is a high-frequency phonon as a wave in the lattice of vibrating atoms. Brillouin light scattering experiments would be especially welcome in the "crossover" region $\omega_j(k)\simeq 1/\bar{\tau}$. This region of strong damping is a difficult (although interesting) area to study theoretically.

The thermodynamic properties of crystals are determined almost entirely by the excitations with energy $\simeq k_BT$. Thus the hydrodynamic modes play no role in their determination. Of course, in a harmonic crystal there are no hydrodynamic modes at all—all the phonons are of zero-sound type.

In Eqs. (1.1) and (1.2), we have been somewhat cavalier about the so-called "zero-momentum" phonons. Strictly speaking, the displacement of the $n$th

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[14] See, for example, A. A. Maradudin and A. Fein, Phys. Rev. **128,** 2589 (1962).

[15] A. Akhiezer, J. Phys. (U.S.S.R.) **1,** 277 (1939).

atom (with equilibrium position $\mathbf{r}_n$) defined by (1.1) is given with respect to the center of mass of the crystal, and the summation should leave out $\mathbf{k}=0$. The total Hamiltonian will contain the kinetic energy of the crystal as a whole ($P^2/2MN$) plus the energy of the phonons (with $\mathbf{k}\neq 0$). Here

$$\mathbf{P}=\sum_n \mathbf{p}_n,$$

where $\mathbf{p}_n$ is the momentum of the $n$th atom, relative to the total crystal momentum

$$\mathbf{p}_n=\mathbf{P}/N-i\sum_{kj}[M\omega_j(k)/2N]^{1/2}\mathbf{e}(\mathbf{k}j)(a_{\mathbf{k}j}-a_{-\mathbf{k}j}{}^*)\times\exp(i\mathbf{k}\cdot\mathbf{r}_n). \quad (1.6)$$

The degree of freedom associated with the center of mass is often referred to as the zero-momentum phonon.

The wave vector associated with a phonon in a regular lattice is defined only up to some multiple of the reciprocal lattice vectors. Thus the summation over wave vectors is restricted to the first Brillouin zone. The fact the phonon quasi-momentum $\hbar\mathbf{k}$ is only defined modulo a reciprocal lattice vector plays a crucial role in the dynamic properties of crystals[13] since it gives rise to the possibility of quasi-momentum-destroying interactions between phonons ("umklapp" processes). Phonons in crystals are quite different from the phonons in He II as well as from the hydrodynamic sound waves in liquids, both of which carry true momentum. The true momentum is associated with the crystal as a whole—in scattering processes the crystal as a whole takes up the momentum transfer. A clear discussion of this point is given in a recent review by Krumhansel.[16]

In a harmonic crystal, the phonons are exact eigenstates at all energies. Presumably in this case a sound wave which would carry momentum would be a superposition of phonon states—such as a Glauber coherent state. In such a situation, the sound wave would be definable at 0°K, and could have any energy up to the Debye cutoff $\omega_D$. In contrast, hydrodynamic modes such as "first sound" are only defined at finite temperatures; they only exist at energies much less than the dominant high-energy thermal phonons. Some further discussion of coherent states is given at the end of Sec. IIIB.

Apart from the greater importance of momentum-destroying processes from umklapp processes, impurities, and walls, there is a close similarity between a crystal viewed as a gas of interacting phonons and Landau's theory of the low-temperature region of the superfluid phase of He$^4$. It was thus natural for Peshkov[17] to suggest that, under certain conditions, crystals should also sustain oscillatory temperature waves just as He II does. This arises because the heat current carried largely by the high-energy phonons cannot be dissipated by the normal (or quasi-momentum-conserving) phonon interactions, as first emphasized by Peierls.[13] In an ordinary gas of particles of finite mass, momentum-conserving interactions give rise to first-sound waves if the collisions are sufficiently rapid. Similarly, in a crystal, one finds the possibility of a density oscillation in the gas of phonons (which Landau aptly christened "second-sound" waves in the case of He II). Physically speaking, second sound can be considered to be a propagating version of the ordinary damped thermal diffusion mode which is predicted (along with first sound) by the usual coupled hydrodynamic equations describing solids and liquids.[12,18] In the last few years, there has been considerable theoretical interest in formulating more precisely the conditions for second sound in crystals.[9,19–22] The most detailed discussion is that of Guyer and Krumhansel,[23] although they based their work on transport equations. Certainly one of the more interesting subjects to study in crystals using Brillouin scattering would be deviations from the well-known Landau–Plazcek central peak.[5] This is discussed in Sec. III.

Recently a thorough discussion of the expected excitation spectrum in He II has been given by Hohenberg and Martin.[24] The problem in He II is to show that the *only* elementary excitations at zero temperature are (longitudinal) phonons up to very high frequencies. This state of affairs is intimately related to the macroscopic occupation by the atoms of a single state. Once one has derived this excitation spectrum, one can interpret it in terms of high- and low-energy phonons in the same way as we have sketched for solids. In general, it seems that the hydrodynamic energy region ends at somewhat higher energies in crystals. Both systems can exhibit second sound, although there is a difference in that phonons in He II carry true momentum. The total momentum $\mathbf{P}_T$ is shared between the phonons and the atoms condensed into some single-particle state (of total momentum $N\mathbf{k}_0$, say). Neglecting mutual friction, both can be treated as independent quantities (although the sum must equal $\mathbf{P}_T$). If a heat current carried by the phonons ($\mathbf{Q}=c^2\mathbf{P}$, where $c$ is the sound velocity) is set up in a certain direction,

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[16] J. A. Krumhansel, in *Perspectives in Modern Physics*, R. E. Marshak Ed. (Interscience Publishers, Inc., New York, 1966), p. 532.

[17] V. Peshkov, J. Phys. (U.S.S.R.) **10**, 389 (1946).

[18] See L. D. Landau and E. M. Lifshitz, *Fluid Dynamics* (Pergamon Press, Inc., New York, 1959), Ch. VIII, p. 298 ff.

[19] J. C. Ward and J. Wilks, Phil. Mag. **43**, 48 (1952).

[20] R. A. Guyer and J. A. Krumhansel, Phys. Rev. **133**, A1411 (1964); also E. Prohofsky and J. A. Krumhansel, *ibid.* **133**, A1403 (1964); and M. Chester, *ibid.* **131**, 2013 (1963).

[21] A. Griffin, Phys. Letters **17**, 208 (1965).

[22] R. N. Gurzhi, Fiz. Tverd. Tela **7**, 3515 (1965) [English transl.: Soviet Physics—Solid State **7**, 2838 (1966)].

[23] R. A. Guyer and J. A. Krumhansel, Phys. Rev. **148**, 766 (1966).

[24] P. Hohenberg and P. C. Martin, Ann. Phys. (N.Y.) **34**, 291 (1965).

the superfluid must have momentum $\mathbf{P}_T-\mathbf{P}$ (this fixes $N\mathbf{k}_0$). This is why second sound is often regarded as an out-of-phase motion of the normal fluid (phonons) and the superfluid. The resulting special nature of second sound in He II is discussed in Appendix B.

The special problem in the case of solid crystals of $He^4$ and $He^3$ arises from the large zero-point energy of these solids which invalidates the standard theory of solids, since this is based on the idea that the displacements around the equilibrium lattice positions are "small." Recently, Fredkin and Werthamer[25] derived the existence and dispersion relation of phonons by a method very similar to Landau's discussion of "zero sound" in Fermi liquids.[26] This method is based on the idea that the interactions between the atoms (or quasiparticles in Landau's case) give rise to a self-consistent field and thus one has the possibility of the atoms moving coherently in a collective oscillation. This approach in no way depends on the harmonic approximation being valid, and thus is potentially useful for $He^3$ and $He^4$ crystals.[27] How the Fredkin–Werthamer phonons are damped is not easily answered; in the "time-dependent" Hartree approximation, the phonon modes are infinitely long-lived. Until the lifetime is known, the energy at which one goes over into the hydrodynamic region is unclear.

This low-frequency region seems potentially interesting in anomalous crystals such as $He^4$—and possibly in ordinary crystals near their melting point, although this problem is somewhat different. If the energy spectrum is not exhausted by acoustic-type collective modes but also contains free-particlelike excitations, (literally speaking, the atoms), then, to the extent that the latter play an important role, one expects that the low-frequency hydrodynamic modes will resemble those of a liquid rather than an elastic continuum. In the extreme case, such as in a Fermi liquid, this means that the low-frequency sound waves have a somewhat lower velocity than the high-energy zero-sound waves. On a strictly empirical level, it is known that even if the atoms are quite "mobile" in crystals, quantities such as the specific heat and heat conduction can be explained nicely in terms of acoustic phonons alone.

Definitive tests of the excitation spectrum of solid helium or solids near the melting point will require direct probes, such as neutrons at high energy and light scattering at low energies. Some direct sound velocity measurements have been done on $He^4$, but the attenuation was not studied. Thus it is not clear whether the frequencies used were in the low-frequency or high-frequency region. In view of our ignorance on this point, the validity of comparisons (such as made in Ref. 27) between theory and experiment is not obvious.

Many authors[25,28,29] have suggested that the existence and acoustic-type dispersion relation of phonons may be considered as a manifestation of broken symmetry. If one can choose a state of the system which breaks a continuous symmetry of the Hamiltonian, then collective modes of zero energy must exist to restore this symmetry. Since the total momentum $\mathbf{P}$ of a crystal is a constant of the motion, the fixing of the center-of-mass $\mathbf{X}$ breaks translational symmetry. This must be restored by the existence of collective modes corresponding to uniform translations, these translations costing zero energy. Thus one has found a mode of infinite wavelength ($\mathbf{q}=0$) and zero frequency ($\omega=0$). By the uncertainty principle, the last feature implies that it is permissible to take one position and to calculate internal properties of the crystal relative to this center-of-mass—for it takes a very long time before the latter will move to another position.

To go from this zero-momentum phonon to the case of finite $\mathbf{q}$, we require that there be no long-range forces between the particles. This seems to be closely related to the assumption that, at low frequencies, "collisions" dominate over self-consistent field effects, and therefore the system can be described hydrodynamically as a continuous elastic medium. Combining this assumption with the fact that there are infinite fluctuations in the center of mass, one can show that

$$\lim_{q\to 0}[\omega(q)/q^2]\to\infty,$$

and hence $\omega(q)\propto q$ seems to be a good candidate. However, broken symmetry arguments do not tell us that the fluctuations are proportional to $\omega(q)/q^2$.

By separating the center of mass as a distinct degree of freedom with all the momentum, the excitations of finite wavelength $\mathbf{q}$ in a crystal do not carry true momentum. Thus it would seem that the broken symmetry argument has no relevance to liquids or gases. In these systems one does not customarily fix the center of mass, with the result that the excitations of the system carry momentum.[30]

The existence of the discrete crystal lattice structure means that the crystal does not have complete translational symmetry to begin with. In this case, if the lattice is simple cubic with a spacing $a_0$, then broken symmetry arguments show that there is a whole series of zero-energy collective modes, with wave numbers $Q_n=n(2\pi/a_0)$.

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[25] D. R. Fredkin and N. R. Werthamer, Phys. Rev. **138**, A1527 (1965).

[26] L. D. Landau, Zh. Eksperim. i Teor. Fiz. **32**, 59 (1957) [English transl.: Soviet Phys.—JETP **5**, (1957)]. See also J. Goldstone and K. Gottfried, Nuovo Cimento **12**, 849 (1959).

[27] L. Nosanow and N. R. Werthamer, Phys. Rev. Letters **15**, 618 (1965); F. W. de Wette, L. H. Nosanow, and N. R. Werthamer, Phys. Rev. **162**, 824 (1967).

[28] P. W. Anderson, *Concepts in Solids* (W. A. Benjamin, Inc., New York, 1963), p. 175 ff.

[29] R. Brout, *Phase Transitions* (W. A. Benjamin, Inc., New York, 1965), Chap. 4.

[30] See, for example, A. Bardasis, D. S. Falk, and D. A. Simkin, J. Phys. Chem. Solids **26**, 1269 (1965).

The theory of broken symmetry is obviously of some interest, if for no other reason than that it points out a common origin for low-frequency modes in quite different systems.[28,29] However, the usual presentations may lead to confusion in that one seems to be able to derive the existence of collective modes which are ordinarily found by solving the equations of motion in the strong-interaction or hydrodynamic region. In actual fact, broken symmetry arguments often implicitly make use of the well-known hydrodynamic description of the condensed system of interest.

## II. RELATION BETWEEN BRILLOUIN SCATTERING AND THE PHONON PROGAGATOR

The first-order Raman effect or Brillouin scattering of light in condensed systems can be briefly summarized as follows[4,5]: If the incident light wave has frequency $\omega_0$ and wave vector $\mathbf{k}_0$, the scattered light wave at an angle $\theta$ to the incident direction will be shifted in frequency by an amount

$$\begin{aligned}\Omega&=\pm|\mathbf{K}|\, v,\\&=\pm 2(\omega_0/c)\sin(\theta/2)v.\end{aligned}\tag{2.1}$$

Here $c$ is the velocity of light in the medium; $v$ is the velocity of the sound wave by which the light wave was Bragg-reflected; and $\mathbf{K}=\mathbf{k}-\mathbf{k}_0$ is the change in the wave vector of the light wave, namely, the wave vector of the sound wave. In quantum-mechanical language, Brillouin scattering is often said to correspond to the incident photon creating (Stokes: $\Omega=-Kv$) or destroying a phonon (anti-Stokes: $\Omega=Kv$).

If there are other low-frequency fluctuations with a dispersion relation $\omega(K)$ which can scatter the light, one finds the frequency shift is given by $\Omega=\pm\omega(K)$. In general, the only other modes (excepting sound waves) are of the nonpropagating sort—such as thermal diffusion and mass diffusion (in liquids). In these cases, there is an "unshifted" component of the scattered light with width $\Gamma(K)=2DK^2$ (where $D$ is the appropriate diffusion constant). We omit discussion of ordered systems which also have spin waves or low-frequency optical modes (which occur in ferroelectrics), although these offer a rich field for Brillouin scattering measurements.

In discussing the spectral density of the scattered light for a given scattering angle, it is obviously preferable to separate the dynamical factor related to scattering medium from the essentially kinematical factors which depend on the details of the experimental arrangement. Once this is done, one can then concentrate on the dynamical factor. It is well known[7] that electromagnetic waves couple into the electronic charge density and this in turn affects the motion of the nuclei via the electron–phonon interaction. If we omit all other processes as small, the dynamical factor for light scattering in insulators is directly related to the nuclear displacement–displacement correlation function.

The usual discussions of light scattering do not make a clean separation of the dynamical and kinematical factors, such as is always done in neutron scattering.[31] If one is interested in both the low-energy hydrodynamic region as well as the high-energy region, clearly this separation is especially important. The standard formulation assumes that the light is scattered by the thermally induced fluctuations in the dielectric tensor of the medium. Since the wavelength of light is so large with respect to the spacings between atoms, the electromagnetic wave can be treated classically, although the medium is often treated quantum-mechanically if one is dealing with crystals. (The main effect of quantum mechanics is to introduce Bose–Einstein statistical factors.) The light wave is assumed to induce an oscillating dipole moment, which in turn radiates electromagnetic energy in all directions. We briefly summarize the results of this kind of macroscopic approach in the case of cubic crystals.[32] This is followed by an alternative discussion[7,8] based on an effective photon–phonon interaction valid for insulators.

### A. Macroscopic Approach

The electric field of the incident light wave in the crystal is defined by

$$\mathbf{E}_0(\mathbf{R},t)=\mathbf{E}_0\exp[i(\mathbf{k}_0\cdot\mathbf{R}-\omega_0 t)],\tag{2.2}$$

where $k_0=\omega_0/c$ is the wave number corresponding to the frequency $\omega_0$ and $c=c_0/n$, with $c_0$ the speed of light *in vacuo* and $n$ the index of refraction (assumed to be a scalar for simplicity). One finds that at a point $\mathbf{R}$, far away from the scattering which took place at the origin, the electric field of the scattered light at time $t$ is

$$\mathbf{E}(\mathbf{R},t)=-(\omega_0/c)^2(4\pi R)^{-1}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\exp[i(\mathbf{K}\cdot\mathbf{R}-\omega t)]\;\hat{\mathbf{k}}\times[\hat{\mathbf{k}}\times\mathfrak{E}(\mathbf{K},\omega)\cdot\mathbf{E}_0(\mathbf{R},t)].\tag{2.3}$$

Here the "momentum transfer" is

$$\mathbf{K}=\mathbf{k}-\mathbf{k}_0,\tag{2.4}$$

$\mathbf{k}$ is the momentum along the scattered direction $\|\,\mathbf{R}$, and $\mathfrak{E}(K,\omega)$ is the double Fourier transform of the

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[31] For liquids, however, this has been done by R. Pecora, J. Chem. Phys. **40**, 1604 (1964); L. I. Komarov and I. Z. Fisher, Zh. Eksperim. i Teor. Fiz. **43**, 1927 (1962) [English transl.: Soviet Phys.—JETP **16**, 1358 (1963)]; see also R. D. Mountain, Rev. Mod. Phys. **38**, 205 (1966).

[32] A more complete account has been given by G. Benedek and K. Fritsch, Phys. Rev. **149**, 647 (1966); see also G. Benedek and T. Greytak, Proc. IEEE **53**, 1623 (1965).

dielectric tensor:

$$\mathfrak{E}(\mathbf{r},t)=V\int\frac{d\mathbf{q}}{(2\pi)^3}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\,\mathfrak{E}(\mathbf{q},\omega)\exp\left[i(\mathbf{q}\cdot\mathbf{r}-\omega t)\right],$$

$$\mathfrak{E}(\mathbf{q},\omega)=V^{-1}\int d\mathbf{r}\int_{-\infty}^{\infty}dt\,\mathfrak{E}(\mathbf{r},t)\exp\left[-i(\mathbf{q}\cdot\mathbf{r}-\omega t)\right].\tag{2.5}$$

The volume $V$ will generally be set equal to unity. To an excellent approximation, we may neglect the change in the wavelength of the light in computing the momentum transfer, with the result that

$$K=2(\omega_0/c)\sin\left(\tfrac{1}{2}\theta\right),\tag{2.4'}$$

where $\theta$ is the angle between $\mathbf{k}$ and $\mathbf{k}_0$. The error involved is of order $(k-k_0)/K$.

The light detector at point $\mathbf{R}$ measures $P(\omega;\mathbf{R})$, the average power per unit energy range, per unit solid angle. This is given by

$$P(\mathbf{K},\omega;\mathbf{R})=\frac{c}{4\pi}\lim_{T\to\infty}T^{-1}\times\left\langle\int_0^T dt_1\exp(-i\omega t_1)\mathbf{E}^*(\mathbf{R},t_1)\cdot\int_0^T dt_2\exp(i\omega t_2)\mathbf{E}(\mathbf{R},t_2)\right\rangle_{\mathrm{Av}}.\tag{2.6}$$

The average $\langle\cdots\rangle_{\mathrm{av}}$ is over the states of the system. Introducing the change of variables $t_2=\tau$, $t=t_1-t_2$, we can transform (2.6) to

$$P(\mathbf{K},\omega;\mathbf{R})=\frac{c}{4\pi}\lim_{T\to\infty}T^{-1}\int_0^T d\tau\int_{-T}^{T}dt\exp(-i\omega t)\times\langle\mathbf{E}^*(\mathbf{R},t+\tau)\cdot\mathbf{E}(\mathbf{R},\tau)\rangle_{\mathrm{Av}}.\tag{2.6'}$$

The limit $T\to\infty$ means that the light intensity must be averaged over a macroscopically small but microscopically large time interval. It is generally easier to use the equivalent canonical ensemble average, that is,

$$\langle\mathbf{E}^*(t)\cdot\mathbf{E}(0)\rangle_0\equiv\frac{\mathrm{Tr}\,\{\exp(-\beta\hat{H}_0)\mathbf{E}^*(t)\cdot\mathbf{E}(0)\}}{\mathrm{Tr}\,\{\exp(-\beta\hat{H}_0)\}}=\lim_{T\to\infty}T^{-1}\int_0^T d\tau\langle\mathbf{E}^*(t+\tau)\cdot\mathbf{E}(\tau)\rangle_0,\tag{2.7}$$

where $\beta\equiv1/k_BT$ and $\hat{H}_0$ is the Hamiltonian of the unperturbed crystal. The fields are expressed in Heisenberg representation. Putting (2.3) into (2.7) and (2.6), we find

$$P(\mathbf{K},\omega;\mathbf{R})=(c/4\pi)(\omega_0/c)^4(4\pi R)^{-2}\times\int_{-\infty}^{\infty}dt\exp(-i\Omega t)\langle\mathbf{B}^*(\mathbf{K},t)\cdot\mathbf{B}(\mathbf{K},0)\rangle_0.\tag{2.8}$$

Here $\mathbf{K}$ and $\Omega=\omega-\omega_0$ are the momentum and energy transferred to the crystal, and

$$\mathbf{B}(\mathbf{K},t)\equiv[\hat{\mathbf{k}}\times(\hat{\mathbf{k}}\times\mathfrak{E}(\mathbf{K},t)\cdot\mathbf{E}_0)].$$

Theoretically it is convenient if we express the power in terms of the spectral density of the scattered light, $\tilde{S}(\mathbf{K},\ \omega-\omega_0)$. This quantity may be operationally defined by

$$\tilde{S}(\mathbf{K},\omega-\omega_0)\equiv P(\mathbf{K},\omega;\mathbf{R})\Big/\int_{-\infty}^{\infty}d\omega P(\mathbf{K},\omega;\mathbf{R}),\tag{2.9}$$

which is clearly normalized to unity and independent of $\mathbf{R}$. More explicitly, we have

$$\tilde{S}(\mathbf{K},\Omega)=\int_{-\infty}^{\infty}dt\exp(i\Omega t)\langle\hat{\mathbf{B}}(-\mathbf{K},t)\cdot\hat{\mathbf{B}}(\mathbf{K},0)\rangle_0\Big/2\pi\langle|\hat{\mathbf{B}}(\mathbf{K},0)|^2\rangle_0.\tag{2.9'}$$

The tilde is used in order to distinguish this spectral density from Van Hove's dynamical structure factor

$$M^2S(\mathbf{K},\Omega)\equiv\int_{-\infty}^{\infty}dt\exp(i\Omega t)\langle\hat{\rho}(-\mathbf{K},t)\hat{\rho}(\mathbf{K},0)\rangle_0,\tag{2.10}$$

where $\hat{\rho}(\mathbf{r})$ is the local density operator

$$\hat{\rho}(\mathbf{r})\equiv M\sum_{n=1}^{N}\delta(\mathbf{r}-\hat{\mathbf{r}}_n)=\int\frac{d\mathbf{k}}{(2\pi)^3}\exp(i\mathbf{k}\cdot\mathbf{r})\hat{\rho}(\mathbf{k}).\tag{2.11}$$

The differential cross section for neutron scattering is[6] (where $a$ is the scattering length)

$$d^2\sigma/dEd\Theta=(k/k_0)a^2S(\mathbf{K},\Omega),\tag{2.12}$$

which is the analog of $P(\mathbf{K},\ \omega;\ \mathbf{R})$. Alternatively, the transition probability per unit time for the neutron to go from state $(\mathbf{k}_0,\omega_0)$ to $(\mathbf{k},\omega)$ is given by

$$W(\mathbf{K},\Omega)=|V_0|^2S(\mathbf{K},\Omega),\tag{2.12'}$$

where $V_0$ is the pseudo-potential for neutron–nuclei scattering.

The change in the electronic dielectric tensor is assumed to be linear in the elastic strain components $S_{\alpha\beta}(\mathbf{r},t)$. Following fairly standard notation,[4,32] we have

$$\boldsymbol{\varepsilon}_{\alpha\beta}(\mathbf{r},t)=-\boldsymbol{\varepsilon}_0^2\sum_{\mu,\nu}p_{\alpha\beta\mu\nu}S_{\mu\nu}(\mathbf{r},t),\tag{2.13}$$

where $\boldsymbol{\varepsilon}_0$ is the isotropic, static, dielectric tensor and

$$S_{\mu\nu}(\mathbf{r},t)\equiv\tfrac{1}{2}\{(\partial u_\mu/\partial x_\nu)(\mathbf{r},t)+(\partial u_\nu/\partial x_\mu)(\mathbf{r},t)\},\tag{2.14}$$

where $\hat{\mathbf{u}}(\mathbf{r}, t)$ is the displacement field operator in Heisenberg representation. The elasto-optical coefficients $p_{\alpha\beta\gamma\delta}$ may be obtained from macroscopic measurements, (being of order unity), although they may also be expressed in terms of microscopic theory and are, in principle, calculable (for example, Loudon[7]). For a cubic crystal one has[4]

$$p_{\alpha\alpha,\alpha\alpha}\equiv p_{11}, \qquad p_{\alpha\alpha,\beta\beta}\equiv p_{12} \qquad (\alpha\neq\beta),$$

and

$$p_{\alpha\beta,\alpha\beta}=p_{\beta\alpha,\alpha\beta}=p_{\beta\alpha,\beta\alpha}=p_{\alpha\beta,\beta\alpha}\equiv p_{44} \qquad (\alpha\neq\beta).$$

Thus (2.13) may be reduced to

$$\boldsymbol{\varepsilon}_{\alpha\beta}(\mathbf{r}, t) = -\boldsymbol{\varepsilon}_0^2\{2p_{44}S_{\alpha\beta}(\mathbf{r}, t)$$
$$+(p_{11}-p_{12}-2p_{44})S_{\alpha\alpha}(\mathbf{r}, t)\delta_{\alpha\beta}+p_{12}\boldsymbol{\nabla}\cdot\mathbf{u}(\mathbf{r}t)\delta_{\alpha\beta}\}, \qquad (2.15)$$

where $\boldsymbol{\varepsilon}_0^2=(c_0/c)=n$. In an isotropic (or amorphous) crystal, $p_{11}-p_{12}=2p_{44}$. A nonviscous $(\eta=0)$ liquid is even simpler, since, in addition, $p_{11}=p_{12}$, leaving only the last term in (2.15). In this case, the displacement field fluctuations are due entirely to density oscillations.

The spectral density of the scattered light (2.9′) can now be related to the Fourier transform of the phonon propagator $D(\mathbf{K}, \Omega)$. Using (2.13) and (2.14), we have

$$\mathfrak{E}(\mathbf{K}, t)\cdot\mathbf{E}_0=-inE_0K\sum_j u^j(\mathbf{K}, t)\boldsymbol{\zeta}(\hat{\mathbf{K}}, j), \qquad (2.16)$$

where

$$\mathbf{u}(\mathbf{K}, t)=\sum_{j=1,2,3} u^j(\mathbf{K}, t)\hat{\mathbf{e}}(\mathbf{K}, j) \qquad (2.17)$$

expresses the elastic displacement in terms of components along the three polarization directions (for a given wave vector $\mathbf{K}$). The vectors $\boldsymbol{\zeta}(|\boldsymbol{\zeta}|^2<1)$ are defined by[32]

$$\boldsymbol{\zeta}(\hat{\mathbf{K}}, j)=p_{44}[(\hat{\mathbf{E}}_0\cdot\hat{\mathbf{K}})\hat{\mathbf{e}}(\mathbf{K}, j)+(\hat{\mathbf{E}}_0\cdot\hat{\mathbf{e}}(\mathbf{K}, j))\hat{\mathbf{K}}]$$
$$+(p_{11}-p_{12}-2p_{44})\sum_l(\hat{\mathbf{K}})_l(\hat{\mathbf{E}}_0)_l e_l(\mathbf{K}, j)\hat{\mathbf{l}}$$
$$+p_{12}[\hat{\mathbf{K}}\cdot\hat{\mathbf{e}}(\mathbf{K}, j)]\hat{\mathbf{E}}_0, \qquad (2.18)$$

where $\hat{\mathbf{l}}$ represents one of the unit vectors along the cube axes. Finally if we introduce [keeping (2.4) in mind] another set of real vectors

$$\mathbf{n}(j)\equiv\hat{\mathbf{k}}\times[\hat{\mathbf{k}}\times\boldsymbol{\zeta}(\hat{\mathbf{K}}, j)], \qquad (2.19)$$

we may write the spectral density as

$$\tilde{S}(\mathbf{K}, \Omega)=\frac{\sum_{jj'}\mathbf{n}(j)\cdot\mathbf{n}(j')\int_{-\infty}^{\infty}dt\exp i\Omega t\hat{\mathbf{e}}(\mathbf{K}j)\cdot\langle\hat{\mathbf{u}}(-\mathbf{K}t)\hat{\mathbf{u}}(\mathbf{K}, 0)\rangle_0\cdot\hat{\mathbf{e}}(\mathbf{K}j')}{2\pi\sum_{j,j'}\mathbf{n}(j)\cdot\mathbf{n}(j')\hat{\mathbf{e}}(\mathbf{K}j)\cdot\langle\hat{\mathbf{u}}(-\mathbf{K}0)\hat{\mathbf{u}}(\mathbf{K}0)\rangle_0\cdot\hat{\mathbf{e}}(\mathbf{K}j')}. \qquad (2.20)$$

Once the initial and final directions of the light beam are fixed relative to the cube axes of the crystal, the vectors $\mathbf{n}$ are uniquely determined. They are functions of the elasto-optical constants [here the analog of $a$ in (2.12)] and the polarization of the elastic displacement of interest. All the dynamical factors related to the crystal, on the other hand, are concealed in the displacement–displacement correlation function. The kinematical factors $\mathbf{n}(j)\cdot\mathbf{n}(j')$ depend only on the details of the probing arrangement.

As a special case, let us consider (2.20) for a nonviscous compressible liquid. In this case, we see from (2.18) and (2.19) that

$$\mathbf{n}(j)=\hat{\mathbf{k}}\times(\hat{\mathbf{k}}\times\hat{\mathbf{E}}_0)[\hat{\mathbf{K}}\cdot\hat{\mathbf{e}}(\mathbf{K}j)]p_{11}$$

and hence

$$\mathbf{n}(j)\cdot\mathbf{n}(j')=\delta_{j1}\delta_{j'1}(\sin^2\phi)p_{11}^2,$$

where $\phi$ is the angle between $\mathbf{E}_0$ and $\mathbf{k}$. In addition, if we recall the equation of continuity $(\rho_0=MN/V)$

$$\hat{\rho}(\mathbf{K}t)/\rho_0+i\mathbf{K}\cdot\hat{\mathbf{u}}(\mathbf{K}, t)=0,$$

we may reduce (2.6″) to

$$P(\mathbf{K}, \omega; R)=(c/4\pi)(\omega_0/c)^4(4\pi R)^{-2}\sin^2\phi(E_0np_{11})^2\int_{-\infty}^{\infty}dt\exp(i\Omega t)\frac{\langle\hat{\rho}(-\mathbf{K}, t)\hat{\rho}(\mathbf{K}, 0)\rangle_0}{\rho_0^2}$$

for liquids. For natural unpolarized light, we must average over the direction of $\mathbf{E}_0$ in the plane perpendicular to $\mathbf{k}_0$. In this case, $\sin^2\phi$ is replaced by $\frac{1}{2}(1+\cos^2\theta)$, where $\theta$ is the angle between $\mathbf{k}$ and $\mathbf{k}_0$. According to (2.9), the spectral density of the scattered light is

$$\tilde{S}(\mathbf{K}, \Omega)=\int_{-\infty}^{\infty}dt\exp(i\Omega t)\langle\hat{\rho}(-\mathbf{K}, t)\hat{\rho}(\mathbf{K}, 0)\rangle_0\Big/2\pi\langle\hat{\rho}(-\mathbf{K}, 0)\hat{\rho}(\mathbf{K}, 0)\rangle_0. \qquad (2.22)$$

In our simple version of a liquid, $\tilde{S}(\mathbf{K}, \Omega)$ is directly proportional to Van Hove's density–density correlation function $S(\mathbf{K}, \Omega)$ defined by (2.10). This result does not necessarily imply that all liquids sustain only longitudinal displacements or density oscillations. In fact, liquids with shear viscosity may exhibit damped shear waves.

Phenomenologically, one may describe an isotropic medium in terms of two complex elastic moduli[33] giving the response to isotropic and anisotropic strains,

$$\bar{K}(\omega) = K'(\omega^2) + i\omega\zeta'(\omega^2),$$

$$\bar{\mu}(\omega) = \mu'(\omega^2) + i\omega\eta'(\omega^2). \tag{2.23}$$

In the absence of dispersion, $K'$ and $\zeta'$ are the compression modulus and volume (or bulk) viscosity, respectively; $\mu'$ and $\eta'$ are the shear modulus and shear viscosity, respectively. In terms of linear response theory (which is discussed in Sec. III, Part B), one may interpret the finite value of the rigidity $\mu'$ as a result of the nonlocal response to shearing strains. The complex frequency-dependent shear viscosity is often approximated by

$$\eta(\omega) = \eta/(1 - i\omega\tau) = \tau\bar{\mu}(\omega), \tag{2.23$'$}$$

where $\tau$ is the so-called Maxwellian relaxation time for shear stresses to be damped. We have $\eta' = \eta$ and $\mu' = \eta/\tau$, if we neglect dispersion. For frequencies $\omega \gg 1/\tau$, the viscous liquid behaves like a solid with rigidity $\mu'$ and negligible shear viscosity. In contrast to the situation at low frequencies, the shear waves are not damped in this limit. In any event, in dealing with liquids with large shear viscosity, one must take into account fluctuations in the dielectric tensor due to shearing strains.[33] In terms of the expansion (2.15), this would mean only setting $p_{11} - p_{12} = 2p_{44}$. The coefficient $p_{44}$ is often taken to be proportional to $\mu'(0)$.

In (2.13) we have not included the contribution from thermal fluctuations in the local energy or temperature. This term

$$C_V^{-1} \partial\boldsymbol{\epsilon}_0/\partial T \,|_V \times \hat{\mathcal{E}}(\mathbf{r}, t)\delta_{\alpha\beta} \tag{2.24}$$

is generally neglected[5,33] since the thermo-optical coefficient $\partial\boldsymbol{\epsilon}_0/\partial T\,|_V$ is extremely small compared to the photoelastic coefficients $p_{\alpha\beta,\mu\nu}$. The latter coefficients are defined at constant entropy. No confusion should arise between the dielectric constant $\boldsymbol{\epsilon}_0$ and the local energy deviation operator $\hat{\mathcal{E}}(\mathbf{r}t)$. The importance of the term in (2.24) is discussed in Sec. IV. It appears that it may be more important in crystals than in liquids.

## B. Golden Rule Formulation

In Sec. IIA, calculation of the first-order Raman scattering reduced to calculating the electric moment induced by the electric field $\mathbf{E}$ of the incident light. The scattered intensity was proportional to the absolute square of the radiating dipole

$$|\,\mathbf{M}\,|^2 = |\sum_{\beta,\mu,\nu} \alpha_{\beta\mu}\alpha_{\beta\nu}E_\mu E_\nu\,|^2.$$

The only difference between the classical and quantum calculations is that, in the latter, one has to compute the matrix elements of the moment (i.e., the electronic polarization tensor $\boldsymbol{\alpha}$) and to sum over initial and final states (properly weighted) in the usual fashion. Thus we have

$$I \propto |\,M\,|^2 = \sum_{\beta,\mu,\nu} E_\mu^* E_\nu \times \sum_{n,m} \frac{\langle n\,|\,\alpha_{\beta\mu}\,|\,m\rangle\langle m\,|\,\alpha_{\beta\nu}\,|\,n\rangle \exp(-\beta E_n)}{\sum_n \exp(-\beta E_n)}, \tag{2.25}$$

where $|\,n\rangle$, $|\,m\rangle$ represent the exact electronic states. In homopolar insulators, the electromagnetic perturbation can only lead to virtual electron–hole pairs in the electronic charge density around the atoms. We consider only the one-photon term in the interaction of the radiation with the medium,

$$V_{er} = -c^{-1} \int \mathbf{j}_e(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r})\,d\mathbf{r}. \tag{2.26}$$

The two-photon term

$$-\left(\frac{e}{2mc^2}\right) \int \rho_e(\mathbf{r})\mathbf{A}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r})\,d\mathbf{r}$$

is very small in comparison. The virtual electronic charge density fluctuations produced by (2.26) couple by the electron–phonon interaction to the vibrating nuclei. Thus it is possible to change the vibrational state of the medium through the intermediary of virtual electron–hole excitations, with the real creation or annihilation of "phonons."

If the crystal is polar, the nuclear vibrations can be directly excited by light [due to a perturbation like (2.26) involving the nuclear current density]. However, it seems that such effects give rise to much smaller light scattering than the indirect process through the electrons.[7]

One often expands the electronic polarizability in powers of the nuclear strains, treating the coefficients as constants which can be determined experimentally (the elasto-optical constants). This is the meaning of (2.13), where we use only the linear terms in the expansion, i.e., one-phonon processes. However, one can also carry out the calculation of the light-scattering cross section by standard quantum-mechanical third-

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[33] S. M. Rytov, Zh. Eksperim. i Teor. Fiz. **33,** 166, 514, 671 (1957) [English transl.: Soviet Phys.—JETP **6,** 130, 401, 513 (1958)].

order perturbation theory. Each scattering amplitude for $\mathbf{k}_0\omega_0 \rightarrow \mathbf{k}\omega$ (with the creation or absorption of a vibrational quantum $\mathbf{K}$, $\Omega$) will involve $V_{er}$ (the electron–radiation interaction) twice and $V_{el}$ (the electron–lattice interaction) once.

A clear and complete account of such calculations, as well as references to the work of other authors, has been given by Loudon.[7] One result of his work is the relation of the elasto-optical constants and the Raman tensors, for which microscopic formulas are given. Loudon was mainly interested in the properties of these Raman tensors, and assumed the vibrational states were phonons of infinitely long lifetime. In contrast, we are mainly interested in the detailed nature of these vibrational states. Loudon's work can be used to find a good approximation for the vertex functions involving one incoming photon, one outgoing photon, and one incoming (or outgoing) phonon. The virtual electronic processes are concealed in this vertex function.

Our effective Hamiltonian is

$$H_I = \sum_{\substack{\mathbf{k}\mathbf{k}_0 \\ \lambda\lambda_0}} \sum_{\substack{\mathbf{K} \\ j}} V \left( \begin{array}{cc|c} \mathbf{k}_0 & \mathbf{k} & \mathbf{K} \\ \lambda_0 & \lambda & j \end{array} \right) b_\lambda^*(\mathbf{k}) b_{\lambda_0}(\mathbf{k}_0) [a_{\mathbf{K}j} + a_{-\mathbf{K}j}^*] \delta_{\mathbf{k}_0, \mathbf{k}-\mathbf{K}}, \tag{2.27}$$

which couples the radiation field described by

$$H_r = \sum_{\mathbf{k}, \lambda=1,2} \hbar\omega_k [b_\lambda^*(k) b_\lambda(k) + \tfrac{1}{2}], \tag{2.28}$$

in standard notation ($\omega_q = cq$), and the nuclear displacement field which is given in the phonon representation by (1.1). The matrix elements are defined by

$$V \left( \begin{array}{cc|c} \mathbf{k}_0 & \mathbf{k} & \mathbf{K} \\ \lambda_0 & \lambda & j \end{array} \right) = \left( \frac{2\pi e^2}{m^2} \right) (2MN)^{-1/2} [\omega_k \omega_{k_0} \omega_j(K)]^{-1/2} \sum_{ii', ll'} \epsilon_i(\mathbf{k}_0\lambda_0) \epsilon_{i'}(\mathbf{k}\lambda) e_l(\mathbf{K}j) i K_{l'} R_{ii'}{}^{ll'}, \tag{2.29}$$

where $\epsilon(\mathbf{k}\lambda)$ are the polarization vectors ($\lambda = 1, 2$) corresponding to the two transverse photons and ($i$, $i'$, $l$, $l'$) refer to components along the cubic axes of the crystal. The Raman tensor depends on the energies

$$R_{ii'}{}^{ll'} = R_{ii'}{}^{ll'}[-\omega_{k_0}, \omega_k; \tilde{\omega}_j(K)].$$

However, the interband electronic energies are so large compared to typical phonon energies $\tilde{\omega}_j(K)$ that we may set $\tilde{\omega}_j(K)$ equal to zero in the Raman tensor, and $\omega_{k_0} \simeq \omega_k$. In this approximation the Raman tensor for acoustic phonons is given by Eq. (30) of the first paper in Ref. 7, and is the same for emission or absorption of phonons. This last simplification was already implicitly assumed in (2.27). The explicit relation between the elasto-optical constants and $R$ is

$$p_{i'il'} = (4\pi e^2 / m^2 n^2)(\omega_k^{-2}) R_{ii'}{}^{ll'}(-\omega_k, \omega_k; 0). \tag{2.30}$$

Fetter[8] has recently used an effective Hamiltonian such as (2.27) in discussing intensity correlations in first-order Raman scattering from *optical* phonons. In addition, such Hamiltonians are often used in the field of nonlinear optics.[34] Actually, in our calculations, it is convenient to use the displacement field explicitly:

$$H_I = \sum_{\mathbf{k}_0\mathbf{k}, \lambda_0\lambda} \hat{B} \begin{pmatrix} \mathbf{k}_0 & \mathbf{k} \\ \lambda_0 & \lambda \end{pmatrix} b_\lambda^*(\mathbf{k}) b_{\lambda_0}(\mathbf{k}_0), \tag{2.31}$$

where, using (2.29), we have

$$\hat{B} \begin{pmatrix} \mathbf{k}_0 & \mathbf{k} \\ \lambda_0 & \lambda \end{pmatrix} \equiv \frac{n^2 \omega_{k_0}{}^2}{2(\omega_{k0}\omega_k)^{1/2}} \sum_{i,i',l,l'} \epsilon_i(\mathbf{k}_0\lambda_0) \epsilon_{i'}(\mathbf{k}\lambda) \times p_{ii'll'} \hat{S}_{ll'}(\mathbf{K}) \tag{2.32}$$

and

$$\mathbf{K} = \mathbf{k} - \mathbf{k}_0, \qquad \hat{S}_{ll'}(\mathbf{K}) \equiv \tfrac{1}{2} i [K_{l'} \hat{u}_l(\mathbf{K}) + K_l \hat{u}_{l'}(\mathbf{K})].$$

We can now proceed to compute the scattering cross section for the process $\mathbf{k}_0\lambda_0 \rightarrow \mathbf{k}\lambda$, with the vibrational state of the crystal changing from $E_i \rightarrow E_f$. This is given by standard first-order time-dependent perturbation theory:

$$\sum g(E_i) W(E_i, \mathbf{k}_0\lambda_0 \rightarrow E_f, \mathbf{k}\lambda) = 2\pi \sum_i g(E_i) \mid \langle f; n_k+1, n_{k_0}-1 \mid H_I \mid i; n_k, n_{k_0} \rangle \mid^2 \delta(E_f - E_i - \omega_{k_0} + \omega_k), \tag{2.33}$$

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[34] See, for example, A. Yariv, IEEE J. of Quantum Electron. **1**, 29 (1965); A. Sealer and H. Hsu, *ibid.* **1**, 116 (1965).

where we have introduced a canonical ensemble for the initial state of the crystal,

$$g(E_i) = \exp(-\beta E_i) / \sum_j \exp(-\beta E_j),$$

and the summation is made over the exact eigenstates of the crystal. If we sum over final states as well and substitute (2.31) into (2.33), we easily find that

$$W(\mathbf{k}_0\lambda_0 \rightarrow \mathbf{k}\lambda) = \int_{-\infty}^{\infty} dt \exp[i(\omega_{\mathrm{k}} - \omega_{\mathrm{k}_0})t] \left\langle \hat{B}^+ \begin{pmatrix} \mathbf{k}_0 & \mathbf{k} \\ \lambda_0 & \lambda \end{pmatrix}; t \right) \hat{B} \left( \begin{matrix} \mathbf{k}_0 & \mathbf{k} \\ \lambda_0 & \lambda \end{matrix}; 0 \right) \right\rangle_0, \tag{2.34}$$

using the now classic manipulations.[6] As usual,

$$\hat{B}(t) = \exp(i\hat{H}t) \hat{B}(0) \exp(-i\hat{H}t), \tag{2.35}$$

where $\hat{H}$ is the crystal Hamiltonian.

$$\hat{n}(k\lambda) = 1, \qquad \hat{n}(\mathbf{k}_0\lambda_0) = 0.$$

Using (2.32) and (2.13), the correlation function in (2.34) may be rewritten as

$$(\tfrac{1}{2}n)^2 (\omega_{k0}/\omega_k) \langle \boldsymbol{\varepsilon}(\mathbf{k}, \lambda) \cdot \mathfrak{G}^+(\mathbf{K}, t) \cdot \epsilon(\mathbf{k}_0, \lambda_0) \boldsymbol{\varepsilon}(\mathbf{k}\lambda) \cdot \mathfrak{G}(\mathbf{K}, 0) \cdot \epsilon(\mathbf{k}_0\lambda_0) \rangle_0 = \left\langle B^+ \left( \begin{matrix} \mathbf{k}_0 & \mathbf{k} \\ \lambda_0 & \lambda \end{matrix}; t \right) B \left( \begin{matrix} \mathbf{k}_0 & \mathbf{k} \\ \lambda_0 & \lambda \end{matrix}; 0 \right) \right\rangle_0. \tag{2.36}$$

In Part A of this section we found that the scattering intensity was proportional to [see (2.8)]

$$C(\mathbf{K}t) \equiv \langle \mathbf{B}^+(\mathbf{K}, t) \cdot \mathbf{B}(\mathbf{K}, 0) \rangle_0, \tag{2.37}$$

where $\mathbf{B}(\mathbf{K}, t) \equiv \hat{\mathbf{k}} \times (\mathbf{k} \times \mathfrak{G}(\mathbf{K}t) \cdot \mathbf{E}_0)$. However, $\hat{\mathbf{k}} \times \hat{\mathbf{k}} \times \mathbf{A}$ is equal to the projection of the vector $\mathbf{A}$ onto the plane perpendicular to the unit vector $\hat{\mathbf{k}}$. As a result, we may rewrite (2.37) as

$$C(\mathbf{K}t) = \sum_{\lambda'\lambda''} \langle \epsilon(\mathbf{k}\lambda') \cdot \mathfrak{G}^+(\mathbf{K}, t) \cdot \mathbf{E}_0^* \epsilon(\mathbf{k}\lambda'') \cdot \mathfrak{G}(\mathbf{K}, 0) \cdot \mathbf{E}_0 \rangle_0 \epsilon(\mathbf{k}\lambda') \cdot \epsilon(\mathbf{k}\lambda''). \tag{2.38}$$

Using the orthogonality of the photon polarization vectors and taking the initial light wave to be linearly polarized

$$\mathbf{E}_0 = i(2\pi\omega_{k_0})^{1/2} \epsilon(\mathbf{k}_0, \lambda_0), \tag{2.39}$$

we find that

$$\sum_{\lambda} \left\langle B^+ \left( \begin{matrix} \mathbf{k}_0 & \mathbf{k} \\ \lambda_0 & \lambda \end{matrix}; t \right) B \left( \begin{matrix} \mathbf{k}_0 & \mathbf{k} \\ \lambda_0 & \lambda \end{matrix}; 0 \right) \right\rangle_0$$

$$= (n^2/8\pi\omega_k) \langle \mathbf{B}^+(\mathbf{K}, t) \cdot \mathbf{B}(\mathbf{K}, 0) \rangle_0. \tag{2.40}$$

For natural light, we must average over the direction of $\mathbf{E}_0$, for a fixed value of $\mathbf{k}_0$. The relation (2.40) enables one to relate the polarization-averaged transition probability $W(\mathbf{k}_0 \rightarrow \mathbf{k})$ [see (2.34)] to the scattered power $P(\mathbf{K}, \omega)$ [see (2.8)] and the spectral density $\tilde{S}(\mathbf{K}, \omega_k - \omega_{k_0})$ [see (2.9')].

For notational simplicity, we have generally made no distinction between a local variable and the deviation of a local variable from its equilibrium value. The context should make it clear which is relevant. The deviations give rise to scattering in the nonforward direction and enter into the various correlation functions. (We need not consider elastic Bragg scattering since the momentum transfers of interest are very small.)

According to (2.20), the spectral density for light scattering involves the displacement–displacement correlation function

$$C_{\mu\nu}(\mathbf{K}, \Omega) \equiv \int_{-\infty}^{\infty} dt \exp(i\Omega t) \langle u_\mu(-\mathbf{K}, t) u_\nu(\mathbf{K}, 0) \rangle_0.$$

The dynamical displacement field operator for a crystal is defined by

$$\hat{\mathbf{u}}(\mathbf{r}) = (N)^{-1} \sum_{g=1}^{N} \hat{\mathbf{u}}_g \delta(\mathbf{r} - \mathbf{r}_g), \tag{2.42}$$

and thus

$$\hat{\mathbf{u}}(\mathbf{K}) = (N)^{-1} \sum_{g=1}^{N} \hat{\mathbf{u}}_g \exp(-i\mathbf{K} \cdot \mathbf{r}_g), \tag{2.43}$$

where $\mathbf{r}_g$ represents the equilibrium lattice position and $\hat{\mathbf{u}}_g$ the dynamic displacement from equilibrium of the $g$th atom. In terms of the atomic displacements, we have

$$\mathsf{C}(\mathbf{K}, \Omega) = (1/N^2) \sum_{g,h} \exp[+i\mathbf{K} \cdot (\mathbf{r}_g - \mathbf{r}_h)]$$

$$\times \int_{-\infty}^{\infty} dt \exp(i\Omega t) \langle \hat{\mathbf{u}}_g(t) \hat{\mathbf{u}}_h(0) \rangle_0, \tag{2.44}$$

which might be contrasted with the usual form of Van

Hove's function (2.10)

$$S(\mathbf{K},\Omega)=\sum_{g,h}\exp\left[i\mathbf{K}\cdot(\mathbf{r}_g-\mathbf{r}_h)\right]\int_{-\infty}^{\infty}dt\exp(i\Omega t)$$
$$\times\langle\exp\left[i\mathbf{K}\cdot\hat{\mathbf{u}}_g(t)\right]\exp\left[-i\mathbf{K}\cdot\hat{\mathbf{u}}_h(0)\right]\rangle_0.$$

If we expand $\hat{\rho}(K)$ in powers of the atomic displacements, it is easily verified that to first order one has

$$\delta\rho(\mathbf{K})/\rho_0\equiv\left[\hat{\rho}(\mathbf{K})-\hat{\rho}_0(\mathbf{K})\right]/\rho_0=-i\mathbf{K}\cdot\hat{\mathbf{u}}(\mathbf{K}),$$

where the Fourier component of the density for a rigid lattice is

$$\hat{\rho}_0(\mathbf{K})=M\sum_{g=1}^{N}\exp(-i\mathbf{K}\cdot\hat{\mathbf{r}}_g);\qquad \rho_0=MN.$$

In other words, the continuity equation (2.21) relating the longitudinal displacement and the local density is valid only for wavelengths much larger than the mean displacement of the atoms in a crystal. This condition is well satisfied in light scattering measurements, where one is justified in working in the continuum limit. However, the limited validity of (2.21) can, in principle, make the interpretation of neutron scattering data difficult because $S(\mathbf{K},\Omega)$ may be an involved function of the more fundamental displacement correlation function $\mathbf{C}(\mathbf{K},\Omega)$.

### C. Green's Function Formalism

At this point, we formally introduce the standard thermodynamic Green's function for atomic displacement, or phonon propagator. It is useful to be able to express the spectral density $\tilde{S}(\mathbf{K},\Omega)$ directly in terms of these propagators, since they are the functions used in almost all fundamental studies of the dynamic properties of crystals and thus we can make direct contact with these calculations.[1,9,10,14,35]

The phonon propagator is defined by

$$D_{i_1i_2}(\mathbf{r}_1t_1;\mathbf{r}_2t_2)=i\langle Tu_{i_1}(\mathbf{r}_1t_1)u_{i_2}(\mathbf{r}_2t_2)\rangle_0,\qquad(2.45)$$

where $u_{i_1}(\mathbf{r}_1t_1)$ is the $i$th component of the displacement operator of an atom whose equilibrium position is $\mathbf{r}_1$ in Heisenberg representation. As usual, $T$ orders the operators so that those at largest times are to the left. The spectral density for light scattering $\tilde{S}(\mathbf{K},\Omega)$ involves the displacement–displacement correlation function $\langle u_{i_1}(\mathbf{r}_1t_1)u_{i_2}(\mathbf{r}_2t_2)\rangle_0$. This is related to the time-ordered phonon propagator. Noting that $D_{i_1i_2}$ depends only on the difference $t_1-t_2$ (due to the cyclic invariance of the trace over the canonical ensemble), we first introduce the Fourier transforms of

$$D_{\alpha\beta}(t)\equiv i\langle Tu_\alpha(\mathbf{r}t)u_\beta(\mathbf{r}',0)\rangle_0,$$
$$=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\exp(-i\omega t)D_{\alpha\beta}(\omega),\qquad(2.46)$$

and

$$D_{\alpha\beta}^{>}(t)\equiv i\langle u_\alpha(\mathbf{r},t)u_\beta(\mathbf{r}',0)\rangle_0,$$
$$=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\exp(-i\omega t)D_{\alpha\beta}^{>}(\omega),$$
$$D_{\alpha\beta}^{<}(t)\equiv i\langle u_\beta(\mathbf{r}'0)u_\alpha(\mathbf{r}t)\rangle_0,$$
$$=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\exp(-i\omega t)D_{\alpha\beta}^{<}(\omega).\qquad(2.47)$$

For simplicity, we leave the position variables implicit in the following manipulations. One may easily verify the important periodicity condition

$$D_{\alpha\beta}^{>}(t+\tau)=D_{\alpha\beta}^{<}(t);\qquad \tau\equiv-i\beta,\qquad(2.48)$$

which implies

$$D_{\alpha\beta}^{>}(\omega)=\exp(i\omega\tau)D_{\alpha\beta}^{<}(\omega).$$

If we express $D_{\alpha\beta}^{>}(\omega)$ in terms of a new function $\chi_{\alpha\beta}''(\omega)$,

$$D_{\alpha\beta}^{>}(\omega)=i\chi_{\alpha\beta}''(\omega)/\left[1-\exp(-\beta\omega)\right],\qquad(2.49)$$

then

$$D_{\alpha\beta}^{<}(\omega)=i\chi_{\alpha\beta}''(\omega)/(e^{\beta\omega}-1),\qquad(2.49')$$

and finally

$$\chi_{\alpha\beta}''(\omega)=-i\left[D_{\alpha\beta}^{>}(\omega)-D_{\alpha\beta}^{<}(\omega)\right].\qquad(2.50)$$

There is an elegant way[1,3] of obtaining $\chi_{\alpha\beta}''(\omega)$ and hence $D_{\alpha\beta}^{>}(\omega)$. This takes advantage of the fact that (2.48) makes working along the imaginary time axis convenient. Restricting ourselves to the region Re $t=0$, $-\beta\leq\text{Im }t\leq0$, we can express $D_{\alpha\beta}(t)$ by the Fourier series

$$D_{\alpha\beta}(t)=\tau^{-1}\sum_{l}D_{\alpha\beta}(\omega_l)\exp(-i\omega_lt),\qquad(2.51)$$

where

$$\omega_l=2\pi l/\tau,\qquad l=0,\pm1,\pm2,\cdots.$$

In addition, one may show that

$$D_{\alpha\beta}(\omega_l)=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\frac{\chi_{\alpha\beta}''(\omega)}{\omega_l-\omega}.\qquad(2.52)$$

The Fourier coefficients $D_{\alpha\beta}(\omega_l)$ are the functions most easily found. However, generally one may analytically continue these coefficients to the whole complex plane by the direct substitution $\omega_l\rightarrow z$ and hence find $D_{\alpha\beta}(z)$ for $z=\omega\pm i0^+$. Then we may obtain $\chi_{\alpha\beta}''(\omega)$ as the discontinuity of $D_{\alpha\beta}(z)$ across the real frequency axis, i.e.,

$$\chi_{\alpha\beta}''(\omega)=2\text{ Im }D_{\alpha\beta}(\omega_l)\,\big|_{\omega_l\rightarrow\omega-i0^+}.\qquad(2.53)$$

Finally we explicitly note that

$$\int_{-\infty}^{\infty}dt\exp(i\omega t)\langle u_\alpha(\mathbf{r},t)u_\beta(\mathbf{r}',0)\rangle_0=\frac{2\text{ Im }D_{\alpha\beta}(\omega-i0^+)}{(1-e^{-\beta\omega})}.\qquad(2.54)$$

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[35] G. Baym, Ann. Phys. (N.Y.) **14**, 1 (1961).

The important periodicity condition (2.48) requires that[35]

$$D_{\alpha\beta}{}^{><}(\mathbf{r},\mathbf{r}';t)=D_{\beta\alpha}{}^{><}(\mathbf{r}',\mathbf{r};t), \tag{2.55}$$

which follows from time-reversal and translational symmetry. That

$$D_{\alpha\beta}(\mathbf{r},\mathbf{r}')=D_{\alpha\beta}(\mathbf{r}-\mathbf{r}')$$

may only be true after we average over the positions of impurities in the crystal. Also $\chi_{\alpha\beta}''(\omega)$ is real and odd in $\omega$, and

$$\begin{aligned}\chi_{\alpha\beta}''(\mathbf{r},\mathbf{r}';\omega)&=\chi_{\alpha\beta}''(|\,\mathbf{r}-\mathbf{r}'\,|;\omega)\\&=\int_{-\omega}^{\infty}dt\exp(i\omega t)\langle[u_\alpha(\mathbf{r}t),u_\beta(\mathbf{r}',0)]\rangle_0.\end{aligned} \tag{2.56}$$

For light scattering problems, we can ignore the atomic structure of the medium, and thus we consider the continuum limit. We have, for example,

$$\mathfrak{D}_{i_1i_2}(\mathbf{K},\omega_l)=\int_0^\tau dt\int d\mathbf{r}\exp[-i(\mathbf{K}\cdot\mathbf{r}-\omega_l t)]D_{i_1i_2}(\mathbf{r},t),$$

$$\begin{aligned}D_{i_1i_2}(\mathbf{r},t)=\tau^{-1}\sum_l\int\frac{d\mathbf{K}}{(2\pi)^3}&\\ \times\exp[i(\mathbf{K}\cdot\mathbf{r}-\omega_l t)]\mathfrak{D}_{i_1i_2}(\mathbf{K},\omega_l),&\end{aligned} \tag{2.57}$$

for $t$ in restricted time zone. In general, the space integration would be replaced by sums over the lattice points. We do restrict the momentum integrations in (2.57) to the first Brillouin zone. The reason for introducing a *time-ordered* phonon propagator is that it satisfies Dyson's equation,

$$\mathfrak{D}_{\alpha\beta}{}^{-1}(\mathbf{K},\omega_l)=[\mathfrak{D}_{\alpha\beta}{}^0(\mathbf{K},\omega_l)]^{-1}-\Pi_{\alpha\beta}(\mathbf{K},\omega_l), \tag{2.58}$$

where $\mathfrak{D}_{\alpha\beta}{}^0(\mathbf{K},\omega_l)$ is the phonon propagator for a harmonic lattice and $\Pi_{\alpha\beta}(\mathbf{K},\omega_l)$ is the self-energy or polarization matrix. One may use (2.58) to develop a systematic, self-consistent perturbation scheme. In a harmonic lattice, for each wave vector $\mathbf{K}$, there are three natural frequencies $\omega_j(\mathbf{K})$ with polarization vectors $\mathbf{e}(\mathbf{K}j)$. The matrix phonon propagator for the interacting system can also be diagonalized[10,35]

$$\mathfrak{D}_{\alpha\beta}(\mathbf{K},\omega_l)=M^{-1}\sum_j e_\alpha(\mathbf{K}j)e_\beta(\mathbf{K}j)\mathfrak{D}_j(\mathbf{K},\omega_l), \tag{2.59}$$

where $M$ is the mass of the atoms and

$$\mathfrak{D}_j(\mathbf{K},\omega_l)=\{-(\omega_l)^2+\omega_j{}^2(\mathbf{K})-M^{-1}\Pi_j(\mathbf{K},\omega_l)\}^{-1}. \tag{2.60}$$

The diagonalized polarization is defined by

$$\Pi_j(\mathbf{K},\omega_l)=\sum_{\alpha,\beta}e_\alpha(\mathbf{K}j)\Pi_{\alpha\beta}(\mathbf{K},\omega_l)e_\beta(\mathbf{K},j). \tag{2.61}$$

We have assumed that the interactions contained in $\Pi_{\alpha\beta}(\mathbf{K},\omega_l)$ do not change the eigenvectors $\mathbf{e}(\mathbf{K}j)$, which is only strictly true in an isotropic solid. Completing this summary, we introduce the spectral density of $\mathfrak{D}_j(\mathbf{K},\omega_l)$ [see (2.52)],

$$\mathfrak{D}_j(\mathbf{K},\omega_l)=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\frac{\chi_j''(\mathbf{K},\omega)}{\omega_l-\omega}. \tag{2.62}$$

We now return to the spectral density for light scattering given by (2.20). Using (2.53) and (2.54), we may show that

$$\begin{aligned}\int_{-\infty}^{\infty}dt\exp(i\Omega t)\mathbf{e}(\mathbf{K}j)\cdot\langle\hat{\mathbf{u}}(-\mathbf{K}t)\hat{\mathbf{u}}(\mathbf{K},0)\rangle_0\cdot\mathbf{e}(\mathbf{K}j')&=-\sum_{\alpha\beta}e_\alpha(\mathbf{K}j)\chi_{\alpha\beta}''(\mathbf{K},\Omega)e_\beta(\mathbf{K}j')n(-\Omega)\\&=M^{-1}\sum_{j''}[\mathbf{e}(\mathbf{K}j'')\cdot\mathbf{e}(\mathbf{K}j)][\mathbf{e}(\mathbf{K}j'')\cdot\mathbf{e}(\mathbf{K}j')]\\&\qquad\times\chi_{j''}''(\mathbf{K},\Omega)[n(\Omega)+1]\\&=M^{-1}\chi_j''(\mathbf{K},\Omega)[n(\Omega)+1]\delta_{jj'}.\end{aligned} \tag{2.63}$$

Here $n(\Omega)$ is the Bose–Einstein distribution. We see the $\tilde{S}(\mathbf{K},\Omega)$ can be expressed as a weighted sum of the spectral densities of the three different polarizations, namely

$$\tilde{S}(\mathbf{K},\Omega)=\sum_j|\,\mathbf{n}(j)\,|^2\chi_j''(\mathbf{K},\Omega)[n(\Omega)+1]\Big/2\pi\sum_j|\,\mathbf{n}(j)\,|^2\int_{-\infty}^{\infty}d\omega\chi_j''(\mathbf{K},\omega)[n(\omega)+1]. \tag{2.64}$$

For cubic crystals, the vectors $\mathbf{n}(j)$ are given by (2.18) and (2.19). More generally, we have

$$(\zeta^j)_\alpha=\sum_{\beta,\gamma,\delta}p_{\alpha\beta,\gamma\delta}(\hat{E}_0)_\beta(\hat{K})_\gamma e_\delta(\mathbf{K}j). \tag{2.65}$$

Eq. (2.64) is our basic formal result. In the next section, we discuss $\chi_j''(K,\Omega)$, particularly for low frequencies and long wavelengths. As one special case, though, let us consider (2.64) for a harmonic lattice. In this approximation, we have

$$\begin{aligned}\chi_j''(\mathbf{K},\Omega)&=2\pi\operatorname{sgn}\Omega\delta(\Omega^2-\omega_j{}^2(K)),\\&=[\pi/\omega_j(K)]\{\delta(\Omega-\omega_j(K))-\delta(\Omega+\omega_j(K))\}.\end{aligned} \tag{2.66}$$

This spectral weight satisfies

$$\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\omega\chi_j''(\mathbf{K},\omega)=1. \tag{2.67}$$

In fact, (2.67) is a sum rule which is always valid. It may be considered as an integral form of the commutation relations between position and momentum, and has many guises in terms of other quantities. Using (2.66), one may reduce the numerator of (2.64) to

$$\pi \sum_j \frac{|\mathbf{n}^j|^2}{\omega_j(K)} \{\delta(\Omega-\omega_j(K))[n(\omega_j(K))+1] + \delta(\Omega+\omega_j(K))[n(\omega_j(K))]\}. \quad (2.68)$$

The first term corresponds to the (Stokes) creation of a phonon and the second to the (anti-Stokes) annihilation of a phonon, each having the appropriate quantum-statistical weight.

One of the advantages of introducing thermodynamic Green's functions is that the highly asymmetric statistical weight appears as a separate factor in Eq. (2.64). The spectral density of the diagonalized phonon propagator is a function of the temperature only through the weak temperature dependence of the polarization or self-energy $\Pi_j(K, \Omega)$. In the hydrodynamic region we have $n(\Omega)\simeq k_BT/\Omega \gg 1$. Thus both lines have equal weight and $\tilde{S}(K, \Omega)\simeq\tilde{S}(K, -\Omega)$. Of course, for $T\rightarrow 0$, the anti-Stokes component vanishes as $\exp(-\Omega/k_BT)$, which is the number of thermally excited phonons present.

In a crystal, the spectral density satisfies

$$\tilde{S}(\mathbf{K}, \Omega) = \tilde{S}(\mathbf{K}+2\pi\mathbf{b}, \Omega), \quad (2.69)$$

where $\mathbf{b}$ is an arbitrary vector of the reciprocal lattice. The momentum transfer involved in Brillouin scattering of visible light ($\mathbf{k}-\mathbf{k}_0=\mathbf{K}+2\pi\mathbf{b}$) is so small that Umklapp processes are not possible.[16] They do occur, and are important, in neutron scattering—indeed, it is only through these Umklapp processes that one can study transverse modes by neutrons.

## III. PHONON PROPAGATOR IN THE HYDRODYNAMIC LIMIT

The hydrodynamic region $\mathbf{K}\rightarrow 0$, $\Omega\rightarrow 0$ is discussed in Secs. IIIA and IIIB. First we make some general remarks about the analytic structure of the spectral weight $\chi_j''(\mathbf{K}, \Omega)$, especially for high frequencies. [For more detail, we refer the reader to Refs. 10, 35, and 36.] If we make use of (2.60) in conjunction with (2.62), we find the formally exact result

$$\chi_j''(K, \Omega) = 2 \operatorname{Im} \mathfrak{D}_j(K, \Omega) = \frac{2\Pi_j^I(K, \Omega)}{[\Omega^2-\omega_j^2(K)+\Pi_j^R(K, \Omega)]^2+[\Pi_j^I(K, \Omega)]^2}, \quad (3.1)$$

where the polarization or self-energy for the $j$th polarization has been separated as usual:

$$M^{-1}\Pi_j(\mathbf{K}, \Omega) = \Pi_j^R(\mathbf{K}, \Omega) + i\Pi_j^I(\mathbf{K}, \Omega). \quad (3.2)$$

One may show that $\Pi_j^R(\mathbf{K}, \Omega)$ is an even function of $\Omega$, while $\Pi_j^I(\mathbf{K}, \Omega)$ is odd. In the limit that $\Pi_j\rightarrow 0$, (3.1) goes over into (2.66), which describes the well-defined excitations of a pure, harmonic lattice.

If $\Pi_j^R(\mathbf{K}, \Omega)$ and $\Pi_j^I(\mathbf{K}, \Omega)$ are finite but still "small" compared to $\omega_j(K)$, it makes sense to interpret (3.1) in terms of renormalized, damped quasi-phonons. The energy $\tilde{\omega}_j(K)$ of these quasi-phonons is defined by the real, positive solution $\Omega_0$ of the equation

$$\Omega_0^2-\omega_j^2(K)+\Pi_j^R(K, \Omega_0) = 0. \quad (3.3)$$

If there is only one such solution and, moreover, if $\Pi_j^I(K, \Omega)$ is a smoothly varying function for $\Omega$ in the vicinity of $\Omega_0$, then we can make the approximation $\Pi_j^I(K, \Omega)\simeq\Pi_j^I[K, \tilde{\omega}_j(K)]$ in (3.1). Making use of this simplification and the definition (3.3), one may rewrite (3.1) in the quasi-particle form:

$$\chi_j''(K, \Omega) = 2\pi Z_j(K, \Omega_0)(2\pi\Omega_0)^{-1} \times \left\{ \frac{\frac{1}{2}\Gamma_j(K, \Omega_0)}{(\Omega-\Omega_0)^2+\frac{1}{4}\Gamma_j^2(K, \Omega_0)} - \frac{\frac{1}{2}\Gamma_j(K, \Omega_0)}{(\Omega+\Omega_0)^2+\frac{1}{4}\Gamma_j^2(K, \Omega_0)} \right\}. \quad (3.4)$$

For a given wave number $K$ and polarization $j$, we have a quasi-phonon with the complex energy $E_j(K)\equiv \tilde{\omega}_j(K)+i\Gamma_j(K)/2$. The renormalized energy is

$$\begin{aligned} \Omega_0=\tilde{\omega}_j(K) &= [\omega_j^2(K)-\Pi_j^R(K, \Omega_0)]^{1/2} \\ &\simeq \omega_j(K)-\Pi_j^R(K, \omega_j(K))/2\omega_j(K) \\ &\equiv \omega_j(K)+\Delta_j(K), \end{aligned} \quad (3.5)$$

while the reciprocal lifetime $\{\propto \ln|\exp[iE_j(K)t]|^2\}$ is defined by

$$\begin{aligned} \Gamma_j(K) &\equiv \Gamma_j(K, \Omega_0) \\ &= \{\Pi_j^I(K, \Omega_0)/\Omega_0\} Z_j^{1/2}(K, \Omega_0), \\ &\simeq \Pi_j^I(K, \omega_j(K))/\omega_j(K) \ll \omega_j(K). \end{aligned} \quad (3.6)$$

In addition to the renormalized, damped excitation spectrum of the phonons, the spectral density is also corrected by the so-called wave function renormalization factor

$$Z_j(K, \Omega_0) \equiv |1+(2\Omega_0)^{-1}\cdot \partial\Pi_j^R(K, \Omega_0)/\partial\Omega_0|^2. \quad (3.7)$$

While $Z$ is frequently set equal to unity [as we have done in (3.6)], its effect on the overall weight is sometimes crucial in order that the quasi-particle approximation satisfy certain sum rules.

As discussed in the Introduction, for large wave vectors one may determine $\Delta_j(K)$ and $\Gamma_j(K)$ by simply expanding the polarization function $\Pi_j(K, \Omega)$ in the anharmonic and other perturbations, keeping only the first few diagrams (see Fig. 1). Such calculations have been made by several authors for both pure anharmonic crystals,[10,14,37] as well as for crystals with a random

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[36] R. A. Cowley, Advan. Phys. **12,** 421 (1963).

[37] J. M. Conway, thesis, Cornell University, 1964 (unpublished).

distribution of impurities.[38,39] For low frequencies, no finite subset of self-energy diagrams is good enough—physically this corresponds to the fact that the interactions between the phonons of thermal energies occur sufficiently rapidly that one can no longer treat them as unperturbed phonons between scatterings.

However, Kwok, Martin, and Miller[10] have recently solved Dyson's equation for three-phonon processes using a single bubble diagram, with the true propagators but no vertex corrections. Diagramatically, they solved (C) of Fig. 1 with a bare 3-phonon vertex, using (3.4) as an "ansatz" for the spectral weight of the phonon Green's function to be determined. The result for the damping $\Gamma_j(K)$ [defined by (3.6)] reduced to Akhiezer's result[15] in the low-frequency hydrodynamic region [see (1.5)]. As Kwok has emphasized the use of the approximation (3.4) in place of (3.1) is only justified if one believes that, for a given wave vector and polarization, there is only one excitation. In fact, at low-enough frequencies one may have a second-sound wave associated with the longitudinal hydrodynamic first-sound wave. Kwok *et al.*[10] justified their neglect of this additional mode on the grounds that the propagators occurring in the polarization function are those corresponding to the high-frequency collective modes, and thus the possible existence of the low-frequency second-sound mode need not be taken into account self-consistently.

The existence of lightly damped hydrodynamic modes depends on strong interactions between particles (first sound) or phonons (second sound) but, just as importantly, also on the fact that the various conservation laws (in particular, that of momentum and energy) are obeyed in spite of these collisions. This last requirement is only met if the vertex function is properly treated. For two-body interactions, the necessary conditions on approximations to two-particle Green's functions are discussed in Refs. 2 and 40. While the present author has not completed an investigation of the analogous conditions for three-phonon interactions, it seems highly likely that for a phonon propagator to include collision effects as well as to satisfy the conservation laws will require that the vertex function be treated at least in the ladder approximation.

The successful reproduction[10] (by Kwok *et al.*) of Akhiezer's hydrodynamic result[15] for the damping of *first* sound using only a bare vertex seems closely related to the fact that the long wavelength phonons already exist in the absence of phonon interactions. This is in contrast to low-frequency sound waves in a gas of particles, the very existence of which depends on the momentum-conserving interactions between the particles. Physically, one expects that the diagrams required to give *second* sound in crystals *will* require that the vertex be treated in some "conserving approximation," such as (D) of Fig. 1. This has been proven in detail very recently by Sham.[40a] As far as *first* sound in crystals is concerned, the vertex corrections only change the damping by a numerical factor. However, their inclusion is absolutely necessary if the renormalized first-sound velocity is to be given in terms of the adiabatic elastic constants rather than the high-frequency isothermal constants.

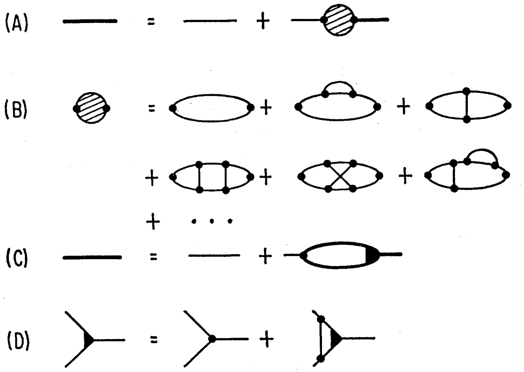

Fig. 1. Dyson's equation for the phonon Green's function is given formally by (A). The polarization function is the sum of all possible irreducible diagrams, the first few being shown in (B) for cubic anharmonicity. These can be summed up by introducing self-consistent propagators and a vertex function, as in (C). The ladder approximation for the vertex function is gifen by (D).

To conclude, we recall the relation[14,41,42] between the scattering function $S(\mathbf{K}, \Omega)$ defined by (2.10) and the more fundamental spectral weight of the matrix phonon propagator $\chi_{\mu\nu}''(\mathbf{K}, \Omega)$ given by (2.53) and (2.54). One can separate out the part of $S(\mathbf{K}, \Omega)$ which is rapidly varying at the one-phonon resonances from the diffuse background, since it can be shown[42] that this part satisfies

$$\int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \omega S_p(\mathbf{K}, \omega) = N[d(\mathbf{K})]^2 \left(\frac{K^2}{2M}\right), \qquad (3.8)$$

where $[d(\mathbf{K})]^2$ is the Debye–Waller form factor. For a general anharmonic crystal, one still has interference effects in $S_p(\mathbf{K}, \Omega)$ between one-phonon processes and two-phonon processes which can complicate the interpretation of neutron scattering data.

In the limit of small wave numbers, one has a more *direct* relation which the excitation spectrum since

$$N^{-1} S_p(\mathbf{K}, \Omega) = \tfrac{1}{2} e^{-W} \mathbf{K} \cdot \chi''(\mathbf{K}, \Omega) \cdot \mathbf{K} [n(\Omega) + 1], \qquad (3.9)$$

where $[d(K)]^2 = \exp(-W)$, with $W \propto K^2$. The equality (3.9) follows from a straightforward expansion of

$$\hat{\rho}(\mathbf{K}) = M \sum_{n=1}^{N} \exp[-i\mathbf{K} \cdot (\mathbf{r}_n + \hat{\mathbf{u}}_n)]$$

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[38] A. A. Maradudin, *Astrophysics and the Many-Body Problem* (W. A. Benjamin, Inc., New York, 1963), Chap. VIII.

[39] E. M. Iolin, Fiz. Tverd. Tela **7**, 1490 (1965) [English transl.: Soviet Phys.—Solid State Phys. **7**, 1198 (1965)].

[40] G. Baym and L. P. Kadanoff, Phys. Rev. **124**, 287 (1961).

[40a] L. J. Sham, Phys. Rev. **156**, 494 (1967); see also W. Götze and K. H. Michel, Phys. Rev. **156**, 963 (1967).

[41] G. Baym, Phys. Rev. **121**, 741 (1961).

[42] V. Ambegaokar, J. Conway, and G. Baym, in *Lattice Dynamics*, R. F. Wallis Ed. (Pergamon Press, Inc., New York, 1965), p.261.

in the atomic displacements $\hat{\mathbf{u}}_n$. It is correct to order $K^2$; more precisely, it omits terms of order $K^4\langle u^4\rangle_{0,L}$, where $\hat{\mathbf{u}}$ is the displacement field and the subscript $L$ refers to a cumulant average.[42] [If the so-called "linear" approximation[41,42] is valid ($\langle u^n\rangle_{0,L}=0$, for $n>2$), then (3.9) is not restricted to small $K$.] One can rewrite (3.9) as

$$N^{-1}S_p(\mathbf{K},\Omega)=(2M)^{-1}\sum_j[\mathbf{e}(\mathbf{K}j)\cdot\mathbf{K}]^2\chi_j''(\mathbf{K},\Omega)\times[n(\Omega)+1]. \quad (3.10)$$

For the small wave numbers of interest in light scattering, the correlation function given by (2.44) of course satisfies

$$\mathbf{e}(\mathbf{K},j)\cdot\mathbf{C}(\mathbf{K},\Omega)\cdot\mathbf{e}(\mathbf{K},j)=\chi_j''(\mathbf{K},\Omega)[n(\Omega)+1]. \quad (3.11)$$

Indeed, this relation holds quite generally. In principle, then, photon scattering is a more direct probe of the structure of $\chi_j''(K,\Omega)$ than is neutron scattering.

Some further discussion of sum rules such as (3.8) is given at the end of Sec. IIIB.

### A. Model Calculations of Kwok and Martin

We now turn to Kwok and Martin's direct evaluation[9] of the phonon propagator for a simple anharmonic isotropic solid in the hydrodynamic region. The Hamiltonian used is reminiscent of one often used in studies of He II as well as quantum hydrodynamics, since it includes only longitudinal phonons which interact by normal phonon processes arising from cubic anharmonicity. The phonons are assumed to have the constant isothermal sound velocity $v$. For the three-phonon process to be possible, it is necessary that one take the finite broadening of the phonons into account[10] self-consistently. While admittedly crude, the model does have all the essential characteristics of a solid in so far as a discussion of first- and second-sound oscillations is concerned.

KM's discussion is based on the well-known Kadanoff–Baym[3] Green's function formulation of non-equilibrium problems. After introducing a driving term into the Hamiltonian of the sort $-\int d\mathbf{r}\mathbf{J}(\mathbf{r})\cdot\hat{\mathbf{u}}(\mathbf{r})$ (where $\mathbf{J}(\mathbf{r})$ is some external source which eventually will be set to zero), one may generate the equations of motion for the perturbed phonon-propagator $D$ by functional differentiation with respect to $J(\mathbf{r}')$. It is convenient to use the relative and center-of-mass coordinates in the displacement correlation functions:

$$\begin{aligned} D^{><}(\mathbf{r}_1t_1;\mathbf{r}_2t_2) &\equiv D^{><}[\mathbf{r}_1-\mathbf{r}_2, t_1-t_2; \tfrac{1}{2}(\mathbf{r}_1+\mathbf{r}_2).\tfrac{1}{2}(t_1+t_2)] \\ &= D^{><}(\mathbf{r},t;\mathbf{R},T) \\ &= \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\int\frac{d\mathbf{P}}{(2\pi)^3}\exp[i(\mathbf{P}\cdot\mathbf{r}-\omega t)]D^{><}(\mathbf{P},\omega;R,T), \end{aligned} \quad (3.12)$$

the dependence on $R$, $T$ coming from the driving term. Once again one has the (local) spectral representation

$$D^{>}(\mathbf{P},\omega;R,T)-D^{<}(\mathbf{P},\omega;R,T)=2\chi''(\mathbf{P},\omega;R,T),$$

and hence

$$D^{>}(\mathbf{P},\omega;R,T)=2\chi''(\mathbf{P},\omega;R,T)[1+N(\mathbf{P},\omega;R,T)],$$

where we may think of $N(\mathbf{P},\omega;R,T)$ as the local phonon distribution function in the perturbed system (similar to a Wigner distribution function). KM then find the Kadanoff–Baym transport equations for

$$D^{><}(\mathbf{P},\omega;R,T),$$

assuming the $R$, $T$ dependence is very slow (hydrodynamic approximation). These equations (which can be considered as the analogue of Peierls' equation) may be reduced to one for $N(\mathbf{P},\omega;R,T)$ and another for $\chi''(\mathbf{P},\omega;R,T)$. The solution of the latter can be approximated by a slightly renormalized version of the spectral density for a harmonic lattice (2.66).

The equation for $N(\mathbf{P},\omega;R,T)$ is solved by considering deviations from local thermal equilibrium in the standard way.[3] Expressing the total energy and momentum densities in terms of $D^{<}(\mathbf{P},\omega;R,T)$, one ends up with the various local conservation equations in terms of the conserved quantities and the local thermodynamic variables (temperature, drift velocity, etc.).

KM's work is simply a Green's function version of the standard discussions of the dynamic properties of crystals starting with Peierls' equation.[13] To be more precise, most discussions (see, for example, Ref. 20) actually start with a truncated relaxation-time approximation for the linearized form of this Boltzmann equation, care being taken to satisfy certain important conservation laws in making these approximations.[43] Peierls' equation (with corrections) has also been derived using Green's function techniques by several other authors.[44,45] However, the precise relation between these papers and KM is somewhat complex. As we have mentioned, KM expand their exact equations of motion in terms of derivatives[3] with respect to $R$ and $T$. In terms of specific diagrammatic approximations to Dyson's equation in the absence of a driving term, the significance of this procedure is not transparent (see, however, Ref. 40). Horie and Krumhansel's analysis, on the other hand, seems to ignore vertex corrections. This is somewhat puzzling, since as discussed earlier, the latter are closely tied up with the "scattering-in" terms of transport equations.

The end result of KM's analysis is a set of coupled hydrodynamic equations for the local energy density

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[43] P. L. Bhatnagar, E. P. Gross, and M. Krook, Phys. Rev. **94**, 511 (1954).

[44] J. S. Langer, A. A. Maradudin, and R. F. Wallis, *Lattice Dynamics*, R. F. Wallis, Ed. (Pergamon Press, Inc., New York, 1965), p. 411.

[45] C. Horie and J. A. Krumhansel, Phys. Rev. **136**, A1397 (1964).

$\langle \mathcal{E}(\mathbf{R}, T)\rangle$ and the local displacement $\langle \mathbf{u}(\mathbf{R}, T)\rangle$ in the ensemble driven by the source $\mathbf{J}(\mathbf{r})$. Following the classic paper of Kadanoff and Martin,[46,47] one can then use these equations to find the equilibrium correlation functions of the conserved quantities. The Fourier transform of the response function for two local operators $\hat{A}(\mathbf{r})$ and $\hat{B}(\mathbf{r})$ is defined by

$$\chi_{AB}(k, \omega) \equiv \int d\mathbf{r} \int_{-\infty}^{\infty} dt \exp[i(\mathbf{k}\cdot\mathbf{r} - \omega t)] \times i\theta(t) \langle [\hat{A}(\mathbf{r}, t), \hat{B}(\mathbf{0}, 0)] \rangle_0, \qquad (3.13)$$

which involves the retarded commutator. The so-called absorptive response function is defined by

$$\chi_{AB}''(k, \omega) \equiv \int d\mathbf{r} \int_{-\infty}^{\infty} dt \exp[i(\mathbf{k}\cdot\mathbf{r} - \omega t)] \times \langle [\hat{A}(\mathbf{r}t), \hat{B}(\mathbf{0}, 0)] \rangle_0 \qquad (3.14)$$

and is the spectral density of $\chi_{AB}(k, \omega)$,

$$\chi_{AB}(k, \omega) = \int \frac{d\Omega}{2\pi} \frac{\chi_{AB}''(k, \Omega)}{\Omega - \omega}. \qquad (3.15)$$

If one considers the linear response to a mechanical perturbation of the form

$$\delta\hat{H}(t) = -\lim_{\epsilon \to 0^+} \int d\mathbf{r} e^{\epsilon t} \theta(t) [\mathbf{J}(\mathbf{r}) \cdot \hat{\mathbf{u}}(\mathbf{r}, t) + (T(\mathbf{r})/T_0) \hat{\mathcal{E}}(\mathbf{r}, t)], \qquad (3.16)$$

one can compute by standard techniques the deviation of the expectation value of $\hat{A}_i(\mathbf{r})$ in the perturbed ensemble from its value in equilibrium:

$$\delta\mathbf{A}_j(\mathbf{r}, t) = \langle \hat{\mathbf{A}}_j(\mathbf{r}, t) \rangle - \langle \hat{\mathbf{A}}_j(\mathbf{r}) \rangle_0.$$

For times greater than zero, one has

$$\delta\mathbf{A}_i(\mathbf{k}, \omega) \equiv \int_0^{\infty} dt \int d\mathbf{r} \exp[-i(\mathbf{k}\cdot\mathbf{r} - \omega t)] \delta\mathbf{A}_i(\mathbf{r}, t)$$

$$= \sum_j \int_{-\infty}^{\infty} \frac{d\omega'}{2\pi} \frac{\chi_{\mathrm{A}_i\mathrm{A}_j}''(\mathbf{k}, \omega')}{\omega'(\omega' - \omega)} \cdot \delta\mathbf{b}_j(\mathbf{k}), \qquad (3.17)$$

where

$$\delta\mathbf{b}_j(\mathbf{k}) \equiv \int d\mathbf{r} \exp(i\mathbf{k}\cdot\mathbf{r}) \delta\mathbf{b}_j(\mathbf{r}) = \begin{Bmatrix} \mathbf{J}(\mathbf{k}) \\ \\ T(\mathbf{k})/T_0 \end{Bmatrix}.$$

We do not write down the value of $\delta\mathbf{A}_j(\mathbf{r}, t)$ for times less than zero, except to remark that it is possible to show that the result is consistent (for sufficiently small values of $\mathbf{k}$) with the interpretation of $\mathbf{J}(\mathbf{r})$ and $T(\mathbf{r})$ as the local thermodynamic variables. That is, we have

$$\delta\mathbf{A}_i(\mathbf{r}, t=0) = (\partial\mathbf{A}_i/\partial T)|_J T(\mathbf{r}) + (\partial\mathbf{A}_i/\partial\mathbf{J})|_T \cdot \mathbf{J}(\mathbf{r}), \qquad (3.18)$$

where the coefficients are those appropriate to complete thermal equilibrium.

Since we may compute $\delta A_j(\mathbf{r}, t)$ from some appropriate set of hydrodynamic equations, one may obtain the spectral density using

$$\sum_j \chi_{\mathrm{A}_i\mathrm{A}_j}''(\mathbf{k}, \omega) \cdot \delta\mathbf{b}_j(\mathbf{k}) = \omega \operatorname{Re} \delta A_i(k, z)|_{z=\omega+i0^+}.$$

This whole procedure[46] is simply a systematic way of incorporating the information contained in the differential equations involving conserved dynamical quantities and their associated thermodynamic parameters into the structure of the various correlation functions.

The displacement–displacement spectral density found by KM using the above method is

$$M^{-1}\chi_{\mathrm{long}}''(k, \omega) = \frac{W(vk)^4 \omega \Gamma(k)}{[(\omega^2 - v^2k^2)(\omega^2 - v^2k^2/3) - W\omega^2v^2k^2]^2 + \omega^2\Gamma^2(k)[\omega^2 - v^2k^2]^2}, \qquad (3.19)$$

where $W \equiv (C_P/C_V - 1) > 0$, $C_{V,P}$ being the specific heats per unit volume at constant volume and pressure, respectively. Some terms proportional to the coupling of thermal and mechanical variables are not included in (3.19), although this approximation [see (4.19) of Ref. 9] can be removed. The damping parameter is found to be

$$\Gamma(k) = \tau v^2k^2 + (\tau_d)^{-1}, \qquad (3.20)$$

where $\tau$ is the phonon relaxation time due to normal phonon processes. No momentum-destroying processes ($\tau_d$) were actually considered, but it is clear that, in the usual approximations,[20] they would enter in the way indicated in (3.20). One may interpret the two terms in (3.20) as the damping from the viscosity (or internal friction) and thermal resistivity of the interacting, dissipative phonon gas.

In terms of the time-ordered phonon propagator for longitudinal phonons, (3.19) corresponds to a polarization function or self-energy of the form

$$M^{-1}\Pi_l(k, \omega) = \frac{W(vk)^4}{\omega^2 - v^2k^2/3 + i\omega\Gamma(k) - Wv^2k^2}, \qquad (3.21)$$

where the subscript $l$ denotes longitudinal vibrational modes. Equations (3.19) and (3.21) have been derived on the assumption that

$$\omega\tau \ll 1. \qquad (3.22)$$

For a given value of $\tau$, this defines the hydrodynamic

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[46] L. P. Kadanoff and P. C. Martin, Ann. Phys. (N.Y.) 24, 419 (1963).

[47] P. C. Martin, *Statistical Mechanics of Equilibrium and Non-Equilibrium*, J. Meixner, Ed. (North-Holland Publ. Co., Amsterdam, 1965), p. 100.

region of low energies where the results are valid. The inequality (3.22) represents the sort which always arises in the hydrodynamic domain. At high frequencies, one has a quite different expression for the polarization function. There the imaginary part would be

$$M^{-1}\Pi_l{}^I(k,\omega)=2\omega(1/\tau+1/\tau_d), \qquad (3.21')$$

which is the standard sort of Golden Rule result [$\tau$, $\tau_d$ are defined following (3.20)]. The self-energy given by (3.21) is due entirely to low-frequency energy density oscillations which couple into the particle density with weight $(C_P/C_V-1)$.

To see this more clearly, let us consider the spectral density of the energy–energy response function

$$\chi_{\mathcal{E}\mathcal{E}}''(k,\omega)=\frac{TC_V(v^2k^2/3)\omega\Gamma(k)(\omega^2-v^2k^2)^2}{[(\omega^2-v^2k^2/3)(\omega^2-v^2k^2)-Wv^2k^2\omega^2]^2+\omega^2\Gamma^2(k)[\omega^2-v^2k^2]^2}. \qquad (3.23)$$

Clearly this is the spectral density related to a two-phonon Green's function, since the local energy density is bilinear in the displacement field. Setting $W=0$ for simplicity, (3.23) reduces to

$$\chi_{\mathcal{E}\mathcal{E}}''(k,\omega)=\frac{TC(v^2k^2/3)\omega\Gamma(k)}{(\omega^2-v^2k^2/3)^2+\omega^2\Gamma^2(k)}. \qquad (3.23')$$

Clearly the spectral density of the polarization function $\Pi_l(k,\omega)$, given by (3.19), is related to $\chi_{\mathcal{E}\mathcal{E}}''(k,\omega)$,

$$\operatorname{Im}\Pi_l(k,\omega)=-3W\omega^2\chi_{\mathcal{E}\mathcal{E}}''(k,\omega)/C_VT. \qquad (3.24)$$

More generally, we can always express the polarization function in terms of an irreducible four-vertex function (sum of diagrams with two incoming and two outgoing phonons). This four-vertex function[43] is directly related to $\chi_{\mathcal{E}\mathcal{E}}''(k,\omega)$.

In this regard, we might recall the identity

$$\chi_{\mathcal{E}\mathcal{E}}(k,\omega)=-(k^2/i\omega)TK(k,\omega), \qquad (3.25)$$

where

$$K(k,\omega)=\left(\frac{1}{3VT}\right)\int_0^\infty dte^{i\omega t}$$
$$\times\int_0^\beta d\lambda\langle\hat{\mathbf{Q}}(-k,0)\cdot\hat{\mathbf{Q}}(k,t+i\lambda)\rangle_0 \qquad (3.26)$$

might be thought of as a nonlocal form of Kubo's well-known expression for the thermal conductivity. The heat current operator $\hat{\mathbf{Q}}(\mathbf{r})$ is defined by the energy conservation equation

$$(\partial/\partial t)\hat{\mathcal{E}}(\mathbf{r},t)+\nabla\cdot\hat{\mathbf{Q}}(\mathbf{r},t)=0. \qquad (3.27)$$

The author has suggested[21] that, in the adiabatic hydrodynamic region ($\omega\tau\ll1$), one has

$$K(k,\omega)=\left(\frac{K(0,\omega)}{1-(k^2/i\omega)K(0,\omega)/C}\right). \qquad (3.28)$$

In crudest approximation for the decay of heat currents, one has

$$K(0,\omega)=\tfrac{1}{3}Cv^2\tau_d(1-i\omega\tau_d)^{-1}, \qquad (3.29)$$

which brings us back to (3.23′), if we set $\Gamma(k)\simeq\Gamma(0)$. [We discuss (3.28) in more detail in the next subsection.]

If $\Gamma(k)$ is small, (3.23′) predicts a resonance at

$$\omega=\pm(1/\sqrt{3})vk=\pm v_{II}k, \qquad (3.30)$$

which corresponds to second sound (a low-frequency oscillation in the energy density). On the other hand, if there are too many momentum-destroying phonon interactions, we have

$$\omega\tau_d\ll1, \qquad (3.31)$$

and hence $\Gamma(k)\gg\omega$. In this case (which is the usual one except under very special conditions), we have

$$\chi_{\mathcal{E}\mathcal{E}}''(k,\omega)\simeq TC\omega(D_Tk^2)/[\omega^2+(D_Tk^2)^2], \qquad (3.32)$$

where $D_T\equiv v_{II}{}^2\tau_d$ is the thermal diffusion constant. In terms of the single relaxation-time approximation KM used, the static thermal conductivity is given by the Debye expression,

$$K=K(0,0)=\tfrac{1}{3}Cv^2\tau_d=CD_T. \qquad (3.33)$$

In contrast to the weakly damped propagating mode which arises when $\omega\tau_d\gg1$ [(3.22) is always assumed], (3.32) exhibits the usual damped mode corresponding to thermal diffusion.

Under certain conditions, one can decompose $\chi_l''(k,\omega)$ in (3.19) into a sum of two distinct resonances.[9] Such approximations are most easily made in $\chi_l(k,\omega)$, which is given by

$$M^{-1}\mathfrak{D}_l(k,\omega)=$$
$$-\frac{\omega^2-\frac{1}{3}v^2k^2-Wv^2k^2+i\omega\Gamma(k)}{[\omega^2-v_I{}^2k^2+i\Gamma_I(k)\omega][\omega^2-v_{II}{}^2k^2+i\Gamma_{II}(k)\omega]} \qquad (3.34)$$

for $\omega$ in the upper-half plane. The denominator has been written in a symmetric manner, with

$$(v_Iv_{II})^2=v^4/3; \qquad v_I{}^2+v_{II}{}^2=(\tfrac{4}{3}+W)v^2 \qquad (3.35)$$
$$\Gamma(k)=\Gamma_I(k)+\Gamma_{II}(k);$$
$$\Gamma(k)v^2=\Gamma_Iv_I{}^2+\Gamma_{II}v_{II}{}^2-\omega\Gamma_I\Gamma_{II}/k^2. \qquad (3.36)$$

Making use of the fact that $W\ll1$ in crystals, (3.35) may be solved to give

$$v_I=v(1+\tfrac{3}{4}W),$$
$$v_{II}=(v/\sqrt{3})(1-\tfrac{3}{4}W). \qquad (3.35')$$

If the inequality

$$W\Gamma(k)\omega \ll (vk)^2 \tag{3.37}$$

is also satisfied, the solutions of (3.36) are

$$\Gamma_{\mathrm{I}} \approx (9/4)W\Gamma,$$
$$\Gamma_{\mathrm{II}} \approx [1-(9/4)W]\Gamma. \tag{3.36$'$}$$

If we neglect $Wv^2k^2$ in the numerator of (3.34), we may easily express it in terms of partial fractions, with the result that

$$M^{-1}\chi_l''(k,\omega)=\frac{(1-\frac{3}{4}W)\omega\Gamma_{\mathrm{I}}}{(\omega^2-v_{\mathrm{I}}^2k^2)^2+(\omega\Gamma_{\mathrm{I}})^2}+\frac{\frac{3}{4}W\omega\Gamma_{\mathrm{II}}}{(\omega^2-v_{\mathrm{II}}^2k^2)^2+(\omega\Gamma_{\mathrm{II}})^2}+\frac{3(\omega\Gamma)W(\omega^2-v_{\mathrm{I}}^2k^2)(\omega^2-v_{\mathrm{II}}^2k^2)}{[(\omega^2-v_{\mathrm{I}}^2k^2)^2+(\omega\Gamma_{\mathrm{I}})^2][(\omega^2-v_{\mathrm{II}}^2k^2)^2+(\omega\Gamma_{\mathrm{II}})^2]}. \tag{3.38}$$

The third antiresonance term is clearly of negligible importance. The second-sound resonance width is considerably larger than that of first-sound (by a factor $\sim 1/W$), while its relative weight is smaller (by a factor $\sim W$).[9,48] Second sound in He II couples into the longitudinal displacement correlation function in a similar fashion.[49]

### B. Nonlocal Hydrodynamic Equations

In principle, it is straightforward to generalize KM's discussion to a more realistic crystal with phonons of transverse and mixed polarization, as well as momentum-destroying interactions. However, this general approach[3] to nonequilibrium phenomena in crystals suffers from the same kind of defect that any Chapman–Enskog method does. Namely, one is led to a specific set of transport equations which involve various thermodynamic derivatives and transport coefficients; but these are already given *explicitly* in terms of the properties of the interacting elementary excitations.

In recent years, considerable interest has developed in an alternative way of dealing with slow irreversible processes. In the Kubo formulation, one first tries to derive from microscopic theory the various equations of irreversible thermodynamics relating currents and forces. The proportionality constants (or transport coefficients), however, are given by formally exact time integrals of current–current correlation functions in an equilibrium ensemble. As one example, the static thermal conductivity is given by $K(\mathbf{0},0)$ defined in (3.26). One is still faced with the problem of actually evaluating these formal expressions—a not entirely trivial task. In any event, it is very convenient to be able to separate *this* question from the derivation of the equations describing the response to weak, slowly varying perturbations. In the Chapman–Enskog approach, one does not have this separation. To be more specific, this separation involves deriving a generalized version of irreversible thermodynamics with transport coefficients depending on position and time. Several people have begun such a formulation.[47,50,21,51] These nonlocal constitutive equations, in conjunction with the various local conservation equations, form a closed set and should be completely sufficient to formally describe all hydrodynamic modes. The dispersion equations of such modes will involve various nonlocal transport coefficients $\bar{L}(\mathbf{q},\omega)$ (which are a generalization of the Kubo formulas used in the limit $\mathbf{q}\rightarrow 0$, $\omega\rightarrow 0$) as well as thermodynamic derivatives. The evaluation of these quantities is a separate problem.

In this subsection, we discuss the question of second sound in realistic crystals in the spirit of the above approach.

We begin by writing down the *usual* set of conservation and constitutive equations for the local hydrodynamic variables which are sufficient to describe the slowly varying properties of a crystal. We consider an isotropic medium, although qualifying remarks will be made at certain points as to how the results would be altered for more restrictive crystal symmetries. The conservation equations for local energy, number, and momentum densities are, respectively,

$$(\partial\mathcal{E}/\partial t)(\mathbf{r},t)+\boldsymbol{\nabla}\cdot\mathbf{Q}(\mathbf{r},t)=0, \tag{3.39}$$

$$(\partial/\partial t)\rho(\mathbf{r},t)+\boldsymbol{\nabla}\cdot(\partial/\partial t)[\rho_0\mathbf{u}(\mathbf{r}t)]=0, \tag{3.40}$$

$$\rho_0(\partial^2\mathbf{u}(\mathbf{r},t)/\partial t^2)+\boldsymbol{\nabla}\cdot\boldsymbol{\tau}(\mathbf{r},t)=0 \tag{3.41}$$

where $\mathbf{Q}(\mathbf{r},t)$ is the heat current and $\boldsymbol{\tau}(\mathbf{r},t)$ is the stress tensor. Since we take the volume to be unity, $\rho_0$ is the average density. For a fixed number of particles, constant density is equivalent to constant volume.

The stress tensor is taken to be the usual local approximation, in which case (3.41) may be reduced to[12,47]

$$\rho_0\partial^2\mathbf{u}(\mathbf{r},t)/\partial t^2=-\boldsymbol{\nabla}p(\mathbf{r},t)+(\mu+\eta\partial/\partial t)\nabla^2\mathbf{u}(\mathbf{r},t)+[\tfrac{1}{3}\mu+(\tfrac{1}{3}\eta+\zeta\partial/\partial t)]\boldsymbol{\nabla}[\boldsymbol{\nabla}\cdot\mathbf{u}(\mathbf{r},t)]. \tag{3.41$'$}$$

The proportionality constants $\eta$, $\zeta$, and $\mu$ are the shear viscosity, bulk viscosity, and modulus of rigidity, respectively, and $p(\mathbf{r},t)$ is the local pressure (the diagonal part of the stress tensor). The part of the

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[48] R. A. Guyer, Phys. Letters **17**, 208 (1965); see also R. A. Guyer, Phys. Rev. **148**, 789 (1966).

[49] P. C. Hohenberg and P. C. Martin, Phys. Rev. Letters **12**, 69 (1964); see also V. L. Ginzburg, Zh. Eksperim. i Teoret. Fiz. **13**, 243 (1943).

[50] C. P. Enz, Phys. Letters **20**, 442 (1966); C. P. Enz, Ann. Phys. (N.Y.) (to be published).

[51] J. A. MacLennan, *Advances in Chemical Physics*, I. Prigogine, Ed. (John Wiley & Sons, Inc., New York, 1963), Vol. 5; D. N. Zubarev, Doklady Akad. Nauk S.S.S.R. **162**, 532 (1965)]; [English transl.: Soviet Phys.—Doklady **10**, 452 (1965)]; H. Mori, Progr. Theoret. Phys. (Kyoto) **28**, 763 (1962).

stress tensor which is proportional to the time derivatives of the strain (i.e., the terms involving the viscosities) gives rise to damping. The viscosity coefficients are given by the static limit of appropriate Kubo correlation functions—their evaluation requires a separate dynamical discussion. The terms proportional to the strain involve thermodynamic derivatives. Again, their determination, although considerably simpler than the dissipative terms, requires a discussion of the high-frequency excitations of the system, or equivalently, the ground state properties of the crystal.

Before discussing the form of the energy flux, it is useful to analyze (3.41′) a little further in conjunction with (3.40). Taking the divergence of (3.41′), we find an equation for the longitudinal displacement $\mathbf{u}_l(\mathbf{r}, t)$. Since

$$\rho(\mathbf{r}t) = -\rho_0 \nabla\cdot\mathbf{u}_l(\mathbf{r}t), \tag{3.42}$$

it will be convenient to work in terms of the density,

$$(\partial^2/\partial t^2)\rho(\mathbf{r}t) - \nabla^2 p(\mathbf{r}, t) = (\tfrac{4}{3}\eta+\zeta)/\rho_0)\,(\partial/\partial t)\,\nabla^2\rho(\mathbf{r}t) + (\tfrac{4}{3}\mu/\rho_0)\,\nabla^2\rho(\mathbf{r}t). \tag{3.43}$$

Now we can express the local pressure in terms of the local density and temperature:

$$p(\mathbf{r}t) = \partial p/\partial\rho\,|_T\,\rho(\mathbf{r}t) + \partial p/\partial T\,|_V\,T(\mathbf{r}t), \tag{3.44}$$

or, in terms of the local density and entropy $s(\mathbf{r}t)$,

$$p(\mathbf{r}t) = \partial p/\partial\rho\,|_s\,\rho(\mathbf{r}t) + \partial p/\partial s\,|_V\,s(\mathbf{r}t). \tag{3.45}$$

As usual, we assume the constant part of the local variables has been subtracted out. For crystals, we may take $s(\mathbf{r}t) = \mathcal{E}(\mathbf{r}t)/T$. Substituting this expansion into (3.43), we find that

$$(\partial^2/\partial t^2)\rho(\mathbf{r}t) - c_l^2\nabla^2\rho(\mathbf{r}t) = D_l(\partial/\partial t)\,\nabla^2\rho(\mathbf{r}t) + T^{-1}\partial p/\partial s\,|_V\,\nabla^2\mathcal{E}(\mathbf{r}t). \tag{3.46}$$

We have introduced abbreviations for the longitudinal sound velocity

$$c_l^2 \equiv (\tfrac{4}{3}\mu/\rho_0) + c_A^2, \tag{3.47}$$

where the adiabatic thermodynamic sound velocity is

$$c_A^2 \equiv \partial p/\partial\rho\,|_s \tag{3.48}$$

and the longitudinal diffusion constant is

$$D_l = (\tfrac{4}{3}\eta+\zeta)/\rho_0. \tag{3.49}$$

If we neglect the two terms on the right-hand side of (3.46), [that is, neglect the damping effects due to viscosity and thermal conduction], we are left with a density oscillation moving with velocity $c_l$ defined in (3.47). One often assumes that $\partial p/\partial s\,|_V = 0$, so that the density oscillation is uncoupled from the local energy (or entropy) fluctuations. In terms of (3.45), this is equivalent to limiting oneself to an adiabatic pressure wave. We have chosen to treat the local energy as the basic thermal variable since eventually we want to use hydrodynamic equations [such as (3.46)] to derive expressions for the energy–energy correlation function. However, we could equally well make use of the local temperature. Finally, $\partial p/\partial s\,|_V$ is directly related to the thermal expansion, which is zero in a harmonic crystal.

Next we turn to the transverse oscillations. Taking the curl of (3.41′), we are left with

$$\rho_0(\partial^2/\partial t^2)\,\nabla\times\mathbf{u}_t(\mathbf{r}t) = (\mu+\eta\partial/\partial t)\,\nabla\times\nabla^2\mathbf{u}_t(\mathbf{r}t) \tag{3.50}$$

Thus the transverse displacement $\mathbf{u}_t$ is completely uncoupled from the local density and temperature. This crucial fact has already been used in discussing (3.43). That is, we have assumed that any one of the three local quantities (pressure, density, and energy) could be expressed in terms of the other two. The equation of motion for $\mathbf{u}_t$ can be written as

$$(\partial^2/\partial t^2)\mathbf{u}_t(\mathbf{r}t) - c_t^2\nabla^2\mathbf{u}_t(\mathbf{r}t) = D_t(\partial/\partial t)\,\nabla^2\mathbf{u}_t(\mathbf{r}t), \tag{3.51}$$

where the transverse velocity is defined by

$$c_t^2 = \mu/\rho_0 \tag{3.52}$$

and the transverse diffusion constant is simply the viscosity,

$$D_t = \eta/\rho_0. \tag{3.53}$$

In an anisotropic (cubic, for example) crystal, there are sound waves of mixed polarization and the situation is more complicated. In particular, the nonlongitudinal elastic displacements may couple to the local temperature (or energy).

We are faced with solving (3.46) in conjunction with (3.39) for $\rho(\mathbf{r}t)$ and $\mathcal{E}(\mathbf{r}t)$. The usual step in solids (and liquids) is to use a local form of Fourier's law of heat conduction

$$\mathbf{Q}(\mathbf{r}, t) = -K\nabla T(\mathbf{r}t) \tag{3.54}$$

to reduce (3.39) to

$$(\partial/\partial t)\mathcal{E}(\mathbf{r}, t) = K\partial T/\partial\epsilon\,|_V\,\nabla^2\epsilon(\mathbf{r}t) + K\partial T/\partial\rho\,|_s\,\nabla^2\rho(\mathbf{r}, t). \tag{3.55}$$

If we can neglect the last term, we are left with the famous partial differential equation governing heat conduction at constant density.

The simultaneous solution of (3.55) and (3.46) has been exhaustively discussed in the literature, especially for liquids. [Formally, the only difference between liquids and crystals is in the velocity defined by (3.47)]. Often the local pressure and temperature are used as basic variables. It is a straightforward matter to transform (3.55) and (3.46) for comparison. A very succinct discussion of the weakly damped pressure waves and heavily damped temperature waves is given on page 303 of Ref. 18. At low frequencies, the pressure wave propagates with the adiabatic sound velocity given by (3.47). At high frequencies ($\omega \gg 1/\tau_d$, where $\tau_d$ is the relaxation time for heat currents to decay), one finds that the sound velocity involves the isothermal compressibility. Strictly speaking, the local temperature and the attendent concept of a thermal conductivity coefficient requires that $\omega\tau_d \ll 1$ (unless there is a frequency window). For this reason, it seems unphysical to solve the usual local hydrodynamic equations in the limit $\omega\tau_d \gg 1$ (high thermal conductivity) and use the results to describe the damping of isentropic sound waves. Moreover, at high frequencies the thermal diffusion mode should cease to exist entirely [rather than be given by $\omega = -i(K/C_V)q^2$].

Let us next sketch the general formulation of *nonlocal* hydrodynamics as given by Martin[47] and others.[52,53] We apply a dynamical perturbation of the form

$$\delta \hat{H}(t) = -\sum_j \int d\mathbf{r}\,\delta\mathbf{b}_j^*(\mathbf{r}t)\cdot\hat{\mathbf{B}}_j(\mathbf{r}t), \tag{3.56}$$

a *specific* form of which is (3.16). This gives rise to nonzero expectation values of the various current operators $\mathbf{J}_j(\mathbf{r}t)$, defined by

$$(\partial/\partial t)\mathbf{B}_j(\mathbf{r}, t) + \nabla\cdot\mathbf{J}_j\mathbf{r}(t) = 0. \tag{3.57}$$

If $\mathbf{B}$ is a vector, $\mathbf{J}$ will be a tensor. To lowest order, the well-known calculation of the current response gives

$$\delta\mathbf{J}_i(k, \omega) = -\sum_j \mathfrak{L}_{\mathbf{J}_i\mathbf{J}_j}(k, \omega)\cdot\nabla\delta b_j^*(k, \omega), \tag{3.58}$$

where the response function is given by the usual Kubo formula

$$\mathfrak{L}_{\mathbf{J}_i\mathbf{J}_j}(k, \omega) = \int_0^\infty dt \exp(i\omega t) \times \int_0^\beta d\lambda \langle \mathbf{J}_i(-k, 0)\cdot\mathbf{J}_j(k, t+i\lambda)\rangle_0. \tag{3.59}$$

A similar calculation of the perturbed values of the conserved quantities gives

$$\delta B_i(k, \omega) = \sum_j \chi_{B_iB_j}(k, \omega)\delta b_j^*(k, \omega), \tag{3.60}$$

(3.17) being an example for a slowly turned-on perturbation, beginning at $t = -\infty$ and removed at $t = 0$.

Martin next argues that a reasonable definition of the local thermodynamic variable $\delta b_j(r)$ conjugate to the dynamical variable $\hat{B}_j(r, t)$ is

$$\delta B_i(\mathbf{k}t) = \sum_j \chi_{B_iB_j}(k, \omega=0)\delta b_j(\mathbf{k}t). \tag{3.61}$$

This definition is not unique but is consistent with the usual definition of thermodynamic variables in the limit $\omega \to 0$, and then $k \to 0$, namely,

$$\delta B_i(k, \omega) = \sum_j \partial B_i/\partial b_j|_{\mathrm{eq}}\cdot\delta b_j(k, \omega). \tag{3.62}$$

This distinction between the true local hydrodynamic variables (which are what one measures with local probes) and the external variables $b_j^*(\mathbf{r})$ [which take on values determined by us] is quite natural, although it is not often made in the extensive literature on the response to so-called "thermal" perturbations. It is convenient to give the current response in terms of the true local hydrodynamic variables:

$$\delta\mathbf{J}_i(\mathbf{r}, t) = -\sum_j \int_{-\infty}^{\infty} dt' L_{J_iJ_j}(\mathbf{r}-\mathbf{r}', t-t')\cdot\nabla\delta b_j(\mathbf{r}', t'), \tag{3.63}$$

where $L_{J_iJ_j}(\mathbf{r}, t)$ is the nonlocal *transport* coefficient. One may consider that $L$ is phenomenologically defined by (3.63). Combining (3.63) and (3.58), we may express the response correlation functions $\mathfrak{L}$ in terms of the transport coefficients $L$,

$$\mathfrak{L}_{J_iJ_j}(k\omega) = \sum_l L_{J_iJ_j}(k\omega)(\delta b_l/\delta b_j^*)(k\omega). \tag{3.64}$$

Next we assume that the perturbation (3.56) is turned on slowly and then removed, i.e.,

$$\delta b_j^*(\mathbf{r}, t) = \lim_{\epsilon\to 0^+} e^{\epsilon t}\theta(-t)\delta b_j^*(\mathbf{r}). \tag{3.65}$$

It is convenient to introduce the one-sided Fourier transform

$$\delta A^>(\mathbf{r}, \omega) \equiv \int_0^\infty dt \exp(i\omega t)\delta A(\mathbf{r}t). \tag{3.66}$$

Thus the basic conservation equation (for $t > 0$)

$$(\partial/\partial t)\delta B_i(\mathbf{r}t) + \nabla\cdot\delta\mathbf{J}_i(\mathbf{r}t) = 0 \tag{3.67}$$

reduces to

$$-i\omega\delta B_i^>(k\omega) + i\mathbf{k}\cdot\delta\mathbf{J}_i^>(k, \omega) = \delta B_i(k). \tag{3.68}$$

Here the initial value of the observables,

$$\delta B_i(k) \equiv \int d\mathbf{r} \exp(-i\mathbf{k}\cdot\mathbf{r})\delta B_i(\mathbf{r}, t=0),$$

is assumed to be known. Rewriting (3.61), we have

$$\delta b_i^>(k, \omega) = \sum_j \chi_{B_iB_j}^{-1}(k, 0)\delta B_j^>(k, \omega), \tag{3.69}$$

where the inverse matrix is defined by

$$\sum_j R_{J_iJ_j}^{-1}R_{J_jJ_l} = \delta_{J_iJ_l}. \tag{3.70}$$

Combining (3.69) with the alternate form of (3.63), we find

$$\delta\mathbf{J}_i^>(k, \omega) = -i\sum_j L_{\mathbf{J}_i\mathbf{J}_j}(k, \omega)\cdot\mathbf{k}\delta b_j^>(k, \omega) - \omega^{-1}\sum_j [L_{\mathbf{J}_i\mathbf{J}_j}(k, \omega) - L_{\mathbf{J}_i\mathbf{J}_j}(k, 0)]\cdot\mathbf{k}\delta b_j^>(k). \tag{3.71}$$

Equations (3.68) and (3.71) are our basic equations. One can eliminate the currents $\delta\mathbf{J}_i^>(k\omega)$ and express

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[52] G. P. de Vault and J. A. McLennan, Phys. Rev. **137**, A724 (1965).

[53] B. U. Felderhof and I. Oppenheim, Physica **31**, 1441 (1965).

the densities $\delta B_i^{>}(k\omega)$ in terms of the initial values $\delta B_i(k)$:

$$-i\omega\delta B_i^{>}(k,\omega)+\sum_{j,l}\mathbf{k}\cdot L_{\mathbf{J}_i\mathbf{J}_j}(k,\omega)\cdot\mathbf{k}\chi_{B_jB_l}{}^{-1}(k,0)\delta B_l^{>}(k,\omega)$$
$$=\delta B_i(k)+(i\omega)^{-1}\sum_{j,l}\mathbf{k}\cdot[L_{\mathbf{J}_i\mathbf{J}_j}(k,\omega)-L_{\mathbf{J}_i\mathbf{J}_j}(\mathbf{k},0)]\cdot\mathbf{k}\chi_{B_jB_l}{}^{-1}(k,0)\delta B_l(k). \quad (3.72)$$

These linear algebraic equations play the role of hydrodynamic equations. The existence of the macroscopic conservation Eqs. (3.67) restricts the discussion to slowly varying disturbances, where the response of the system is limited to a small number of collective oscillations in the conserved quantities $B_i(\mathbf{r})$.

Finally by comparing (3.68) and (3.71), after some manipulation, one finds[47]

$$\frac{\delta b_l}{\delta b_j^*}(k,\omega)=\left[\delta_{lj}-\sum_r\frac{(\mathbf{k}\cdot L_{\mathbf{J}_l\mathbf{J}_r}(k,\omega)\cdot\mathbf{k})}{i\omega}\chi_{B_rB_j}{}^{-1}(k,0)\right]^{-1}. \quad (3.73)$$

This result may be viewed as an implicit dispersion relation for collective modes since the zeros of the denominator correspond to an infinite response of the local hydrodynamic variables to a finite external disturbance. These collective modes are related to the poles of the response correlation function $\mathcal{L}$, as is clear from (3.64). Moreover, the form of (3.64) and (3.73), as well as some specific examples, suggests that the nonlocal transport coefficients $L(\mathbf{k},\omega)$ will be smooth, well-behaved functions of $\mathbf{k}$, even near the poles of $\mathcal{L}(\mathbf{k},\omega)$. Thus one might make the approximation $L_{J_lJ_r}(\mathbf{k},\omega)\simeq L_{J_lJ_r}(\mathbf{k}=0,\omega)$ in the denominator of (3.73). On the other hand, (3.64) implies that

$$\lim_{k\to 0}(\delta b_i/\delta b_j^*)(k,\omega)=\delta_{ij} \quad (3.74)$$

and

$$\lim_{k\to 0}L_{\mathbf{J}_i\mathbf{J}_j}(k,\omega)=\mathcal{L}_{\mathbf{J}_i\mathbf{J}_j}(k=0,\omega). \quad (3.75)$$

Combining this approximation with the one made in going from (3.61) to (3.62), the dispersion relation of the hydrodynamic modes

$$\omega=-i\mathbf{k}\cdot L_{\mathbf{J}_i\mathbf{J}_j}(k,\omega)\cdot\mathbf{k}/\chi_{B_iB_j}(k,0) \quad (3.76)$$

reduces to the more useful result

$$\omega=-\frac{i\mathbf{k}\cdot\mathcal{L}_{\mathbf{J}_i\mathbf{J}_j}(0,\omega)\cdot\mathbf{k}}{\partial B_i/\partial b_j\,|_{\text{eq}}}. \quad (3.77)$$

The preceding formulation is a valid description of the evolution of a many-particle system only in the hydrodynamic region of frequencies much less than collision frequencies between the elementary excitations of the system. Felderhof and Oppenheim[53] have given a useful analysis of the physical validity and implicit assumptions involved. For a specific system, one has a whole set of different relaxation times associated with the decay of the various correlation functions. Some of these relaxation times may be much larger than the "collision times" describing the rate at which energy and momentum are transferred between the excitations. One often refers to collective modes involving nonlocal transport coefficients as including "memory" or non-Markovian effects.

Equations (3.58) and (3.60) are valid even for a noninteracting system of quasi-particles, at any frequency and wave vector, assuming one is clever enough to construct the appropriate driving term (3.56). For large $\omega$ (by "large," one always means large relative to some reciprocal relaxation time), the response functions reduce to

$$\mathcal{L}_{\mathbf{J}_i\mathbf{J}_j}(k,\omega)\to(-i\omega)^{-1}\int_0^\beta d\lambda\langle\mathbf{J}_i(-k,0)\mathbf{J}_j(k,i\lambda)\rangle_0$$
$$+O(1/\omega^2). \quad (3.78)$$

Inserting this into (3.76) gives an undamped mode One can include damping by keeping the next terms in the high-frequency expansion of $\mathcal{L}_{J_iJ_j}(k,\omega)$. The consistency of such high frequency expansions and the whole low-frequency hydrodynamical scheme must always be kept in mind. As a pertinent example, $\mathcal{L}_{QQ}(k,\omega)$ is given exactly by (3.78) for *all* frequencies in a harmonic crystal. While such a crystal will clearly exhibit infinite "thermal conductivity," it does not have any hydrodynamic modes satisfying (3.76).

The local version of the hydrodynamic equations which we originally wrote down [see (3.46), (3.55), and (3.51)] may be derived from (3.72) by using local transport coefficients. This is justified in the hydrodynamic region of low frequencies and long wavelengths because the difference between $L(\mathbf{q},\omega)$ and $L(\mathbf{0},0)$ is small. Thus, in a single relaxation-time approximation to an appropriate current–current correlation function, one expects that

$$\mathcal{L}(\mathbf{q}=0,\omega)\simeq\mathcal{L}(\mathbf{q}=0,\omega=0)/(1-i\omega\tau_d). \quad (3.79)$$

However, in general, this result is only physically significant for $\omega\tau_d\ll 1$, since $\tau_d$ is essentially the same relaxation time as $\tau$, the one which describes the rate at which the local conjugate hydrodynamic variable (pressure, temperature, etc.) varies. To simplify matters in the following discussion we could stick to local viscosities and a local rigidity modulus, since there is no reason to expect any significant nonlocal behavior for pure monatomic crystals.[54] However, the thermal

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[54] G. P. de Vault and J. A. McLennan, Phys. Rev. **138**, A856 (1965).

conductivity is quite different since it is well known from studies on the static case that there are many phonon processes which do not lead to any dissipation of the heat current.[13] Using the notation of Sec. IIIA, one expects that it is possible to satisfy[20]

$$\omega \ll 1/\tau \tag{3.80}$$

and

$$\omega \gg 1/\tau_d \tag{3.81}$$

simultaneously [see discussion following Eq. (3.30)]. If $\omega$ is in this "frequency window," then one can expect to find significant nondissipative behavior arising from the nonlocal nature of the energy current response to a change in the temperature gradient. The crucial condition is that the relaxation time $\tau$ which determines the validity of the hydrodynamic domain (crudely speaking, where the concept of local temperature has a well-defined meaning) can be much smaller than the relaxation time $\tau_d$ which governs how rapidly heat currents decay. This situation seems to require that the high frequency elementary excitations have an acoustic dispersion relation, although the necessity for this condition is not clear at the present time. The possibility of a frequency window in an interacting spin-wave system seems unlikely.

One can use (3.72) to give a systematic discussion of hydrodynamic modes. Details of this somewhat complicated task are deferred to a future publication, where we shall apply it to systems undergoing phase transitions. Here we only discuss some results for isotropic crystals and liquids when we neglect the $k$ dependence of the various transport coefficients, as we did in (3.75), and in going from (3.76) to (3.77).

The spectral density of the displacement–displacement correlation may be split into a longitudinal and transverse part in an isotropic system [see also (2.59)]:

$$M\chi_{u_\alpha u_\beta}''(k\omega) = (k_\alpha k_\beta/k^2)\chi_l''(k,\omega) + [\delta_{\alpha\beta} - (k_\alpha k_\beta/k^2)]\chi_t''(k,\omega). \tag{3.82}$$

We might also note that

$$\chi_{v_\alpha v_\beta}''(k,\omega) = \omega^2 \chi_{u_\alpha u_\beta}''(k,\omega) \tag{3.83}$$

and

$$M\chi_{\rho\rho}''(k,\omega) = \rho_0^2 k^2 \chi_l''(k,\omega). \tag{3.84}$$

Let us first discuss the transverse part $\chi_t''(k,\omega)$, which is decoupled from both longitudinal displacements and the local energy. We find

$$M^{-1}\chi_t''(k,\omega) = \frac{D_t^R(\omega)k^2\omega}{[\omega^2 - v_t^2k^2]^2 + [D_t^R(\omega)k^2\omega]^2}, \tag{3.85}$$

where the frequency-dependent transverse diffusion constant is given by

$$D_t(\omega) \equiv D_t^R(\omega) + iD_t^I(\omega) = (\eta/\rho_0)[(1 - i\omega\tau_\eta)^{-1}], \tag{3.86}$$

in a single relaxation-time approximation. The transverse sound velocity is now

$$v_t^2 = (\mu/\rho_0) + \omega D_t^I(\omega), \tag{3.87}$$

instead of (3.52). For an excellent discussion of the physical meaning of a frequency-dependent shear viscosity, we once again refer to Landau and Lifshitz (see p. 130 of Ref. 12). We note that a liquid ($\mu = 0$) may exhibit undamped shear waves for $\omega\tau_\eta \gg 1$, with an effective rigidity coefficient $\mu' = \eta/\tau_\eta$ [see (2.23′)]. Formally, these high-frequency shear waves are the close analogs of undamped temperature waves as derived from a nonlocal thermal conductivity [see (3.23) and (3.28)]. While bulk viscosity and thermal conduction may exist, they play no role in $\chi_t''(k,\omega)$.

We next turn to the spectral density for longitudinal modes. To begin with, we consider sufficiently high frequencies such that the density oscillations are isothermal. We find

$$M^{-1}\chi_l''(k,\omega) \simeq \frac{D^R(\omega)k^2\omega}{[\omega^2 - v_l^2k^2]^2 + [D^R(\omega)k^2\omega]^2}, \tag{3.88}$$

where

$$D(\omega) \equiv D_l(\omega) + \tfrac{4}{3}D_t(\omega) \equiv D^R + iD^I, \tag{3.88′}$$

and the velocity is now

$$v_l^2 = v_0^2 + \omega D^I(\omega).$$

Here $v_0$ is the isothermal sound velocity. In the notation introduced in (3.88′), we have $D(\omega = 0) = D_l$, where $D_l$ is given by (3.49).

We have included the effect of a nonlocal bulk (or second) viscosity

$$D_l(\omega) = \tau_\zeta(v_\infty^2 - v_0^2)/(1 - i\omega\tau_\zeta), \tag{3.89}$$

as well as a nonlocal shear viscosity, although the latter is generally small in comparison. We assume that the shear viscosity can be treated in the local approximation (i.e., $\omega\tau_\eta \ll 1$). In contrast, the nonlocal bulk viscosity involves some relatively slow relaxation process. The classic case is the slow transfer of energy from the translational degrees of freedom to internal atomic or molecular degrees of freedom (rotation, vibrations, etc.) It is a well-studied phenomena in liquids and gases, but should be also of interest in crystals. (We refer the reader to pp. 305 and 527 of Ref. 18 for a more detailed discussion.) The two velocities which enter into this problem are the low-frequency ($\omega\tau_\zeta \ll 1$) sound velocity

$$v_0^2 \equiv \partial p/\partial\rho\,|_T + \tfrac{4}{3}\mu/\rho_0$$

and the high-frequency sound velocity

$$v_\infty^2 \equiv \partial p/\partial\rho\,|_A + \tfrac{4}{3}\mu/\rho_0.$$

Here $A$ denotes the additional quantity of interest which is weakly coupled to the local density. Its relaxation rate is usually approximated by

$$dA/dt = -A/\tau_\zeta,$$

which is consistent with the single relaxation-time expression given by (3.89).

It is useful to relate (3.88) to the result of Kwok and Martin discussed in the preceding subsection [see (3.19) and (3.21)]. First of all, it is important to remember that in the model of a crystal used by KM (also by Guyer and Krumhansel), both the rigidity and the shear viscosity are zero. In addition, the bulk viscosity involves the rapid exchange of momentum between the phonons ($\omega\tau_\zeta \ll 1$) and hence

$$D_l^R(\omega) \simeq \tau_\zeta(v_\infty^2 - v_0^2). \tag{3.89'}$$

Here $v_0$ is the isothermal thermodynamic sound velocity and (since $\mu = 0$)

$$v_\infty^2 = v_{\mathrm{ad}}^2 = (C_P/C_V)v_{\mathrm{iso}}^2.$$

Rewriting (3.89'), we have

$$D_l^R k^2 = ((C_P/C_V) - 1)\tau_\zeta v_0^2 k^2. \tag{3.89''}$$

This, in conjunction with (3.88), is in essential agreement with the first term in (3.38). As we noted following (3.20), the bulk viscosity in the phonon gas with $\mu = \eta = 0$ arises from the coupling of *density* fluctuations to energy fluctuations.

We might emphasize here that (3.20) has been derived on the assumption that conditions (3.80) and (3.81) are valid. Other limits can be approximately found using (3.88'). For the case of an interacting phonon gas, $\tau_\zeta$ is the time required to reach local thermal equilibrium—thus one is limited to the local region $\omega\tau_\zeta \ll 1$. In molecular crystals (such as solid hydrogen and methane), one may have other contributions to the bulk viscosity which exhibit considerable dispersion.

A more detailed study of $\chi_l''(k, \omega)$ indicates that even if we neglect the thermal conductivity, (3.88) predicts the existence of a damped diffusion mode (i.e., a peak in the spectral density $\chi_l''(k, \omega)/\omega$ at $\omega = 0$). Approximating $D(\omega) \simeq D_l(\omega)$ in (3.88'), one can rewrite (3.88) as

$$\frac{1}{M}\frac{\chi_l''(k, \omega)}{\omega} = \frac{\tau_\zeta}{1+\omega^2\tau_\zeta^2} \times \frac{k^2(v_\infty^2 - v_0^2)}{[\omega^2 - k^2(v_0^2 + \omega^2\tau_\zeta^2 v_\infty^2)/1+\omega^2\tau_\zeta^2]^2 + [\omega\tau_\zeta k^2(v_\infty^2 - v_0^2)/1+\omega^2\tau_\zeta^2]^2}. \tag{3.90}$$

The first factor suggests that the diffusive mode will have a width of order $1/\tau_\zeta$. One can express $\chi_l''(k, \omega)$ explicitly as the sum of this diffusion mode and the two sound wave resonances. This has been done by Mountain,[55] who was the first to notice that the use of a frequency-dependent bulk viscosity implies the existence of a damped density fluctuation as well as the usual modification of propagating sound waves. (We refer to Mountain's work for detailed calculations of the relative weights of the various modes.) Probably the simplest way of proving that there is an unshifted central peak is to compute the second frequency derivative of $\chi_l''(k, \omega)/\omega$ at $\omega = 0$. One finds that a peak occurs only when

$$(kv_0\tau_\zeta)^2 > 2/(1 + v_\infty^4/v_0^4) \lesssim 1.$$

If the momentum transfer is too small to satisfy this condition, the Brillouin peaks are so close in that they effectively wash out Mountain's mode and the spectral density $\chi_l''(k, \omega)/\omega$ has a minimum at $\omega = 0$. In discussing experimental results, it is probably just as well to use (3.90) directly, rather than various approximations to it.

It should be clear that a discussion similar to that of Mountain for a nonlocal bulk viscosity applies also to a nonlocal shear viscosity. The effect of the latter is to give rise to extra longitudinal and transverse diffusive modes with width $\simeq 1/\tau_\eta$.

The damping of all these modes (independent of the momentum transfer and proportional to collision rate) indicates that they are *not* hydrodynamic collective modes (such as first sound and thermal diffusion or second sound). Rather, they can be related to the motion of some additional nonhydrodynamic degree of freedom (the internal energy of molecules, local order, etc.), which is damped exponentially due to collisions between the particles of the system.

The spectral density for longitudinal modes given by (3.88) does not contain the effect of temperature fluctuations. Let us consider the effect of a local thermal conductivity $K(\omega) \simeq K(0) \simeq C_V v^2 \tau_d$ (i.e., $\omega\tau_d \ll 1$) in conjunction with the nonlocal bulk viscosity given by (3.89). Now $v_0$ is the adiabatic sound velocity $v_a$. The limit $\omega\tau_\zeta \ll 1$ corresponds to the case worked out in great detail by Kadanoff and Martin.[46] One finds

$$\frac{v_a^2\chi_{\rho\rho}''(k, \omega)}{\omega} = \frac{\chi_l''(k, \omega)(v_a k)^2}{\omega} \simeq \frac{WD_2k^2}{\omega^2 + (D_2k^2)^2} + \frac{D_2 v_a k^4}{(\omega^2 - v_a^2k^2)^2 + (\omega D_2 k^2)^2} + \frac{(\omega^2/v_a^2)(D_1 - D_2)}{\omega^2 + (D_2k^2)^2} - \frac{(\omega^2 - v_a^2k^2) \times \{D_2k^2W + [(\omega^2 - v_a^2k^2)/v_a^2] \times (D_1 - D_2)\}}{(\omega^2 - v_a^2k^2)^2 + (\omega D_1 k^2)^2}, \tag{3.90'}$$

where $W \equiv (C_P/C_V - 1)$. One finds $D_1 \simeq D_l + D_P W$ and

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[55] R. D. Mountain, J. Res. Natl. Bur. Std. **70A**, 207 (1966). The diffusion mode predicted by Mountain was recently observed by W. S. Gornall *et al.*, Phys. Rev. Letters **17**, 297 (1966). For further details, see G. I. A. Stegeman, M. Sc. thesis, University of Toronto, 1966 (unpublished).

$D_2 \simeq D_P \equiv K/C_P$ under the assumptions $\omega\tau_d \ll 1$ and $\omega\tau_\zeta \ll 1$. The first term in $\chi_{\rho\rho}''(k\omega)$ may be identified with the thermal fluctuations which couple into the density fluctuations due to the finite thermal expansion coefficient. This result is essentially equivalent to Eq. (87a) of KM.[46] Actually all but the first term in (3.90′) should be multiplied by the factor

$$\{v_a^4/[v_a^4+\omega^2(D_1-D_2)^2]\}\simeq 1,$$

which is related to the damped mode of Mountain previously mentioned.

Next we consider the case $\omega\tau_\zeta \gg 1$, $\omega\tau_d \ll 1$. After more lengthy algebra, we obtain

$$\frac{v_a^2\chi_{\rho\rho}''(k,\omega)}{\omega}\simeq\left\{\frac{r^4D_Pk^2W}{\omega^2+(D_2k^2)}\right\}+\left(\frac{v_\infty^4}{v_\infty^4+\omega^2(D_2-D_1)^2}\right)\left\{\frac{r^2\omega^2D_1k^2}{(\omega^2-v_\infty^2k^2)^2+(\omega D_1k^2)^2}\right\}, \tag{3.90″}$$

with $r \equiv v_a/v_\infty$ and

$$D_1 \simeq (D_l/\omega^2\tau_\zeta^2)+r^2WD_P,$$

$$D_2 \simeq D_V - r^2WD_P.$$

We have omitted the antiresonance terms in (3.90″) [the analog of the last two terms in (3.90′)]. If we set $C_P=C_V$, the second term in (3.90″) reduces to (3.90) in the limit $\omega\tau_\zeta \gg 1$, as it should.

The idea of generalizing low-frequency hydrodynamic theories by using frequency and wave-number-dependent response functions is of course quite old.[33,56] Generally this has been limited to dealing with frequency-dependent shear and bulk viscosities. These basically phenomenological theories have been quite successful in explaining high-frequency sound propagation (as well as Brillouin light scattering experiments) in liquids. More recent versions of this approach have considered the $\omega \to \infty$ limit of all kinds of nonlocal response coefficients. The reactive parts which are left [see (3.78)] are easily evaluated and one is led to predict the existence of various new propagating modes (see, for example, Ref. 57). In general the physical significance of such extrapolations is not too clear, since the validity of any hydrodynamical approximation is always restricted to $\omega \ll 1/\tau_H$, where $\tau_H$ represents the relaxation time for the various local thermodynamic variables. Physically significant nonlocal behavior only arises when the associated transport coefficients are characterized by relaxation times $\tau_d \gg \tau_H$.

Recently a Cornell group[58] has made a serious attempt to compute the density–density correlation function using various Boltzmann transport equations appropriate to dilute as well as dense gases. Their work reproduces the usual hydrodynamic expressions for $S(k,\omega)$ in the appropriate limit, but, more importantly, numerical calculations show in a very detailed way how the shape of $S(k,\omega)$ changes as one goes over from the low-energy region to the high-energy region.

It would be of great interest to derive from the appropriate transport equation for dense gases the hydrodynamical equations involving frequency-dependent volume and shear viscosities, since the domain of validity of such descriptions would then be manifest. In essence, this justification has been given for the frequency-dependent thermal conductivity[23,9] in the case of an interacting phonon gas. Whether a liquid is best viewed as a dense gas or as a crystal with highly mobile atoms is an old question.[56] In this connection, the reproduction of a frequency-dependent shear viscosity from microscopic theory would add much to our understanding. Experimentally, light-scattering studies of the damping of high-frequency shear waves in simple liquids would be useful.

The dynamical properties of real liquids are much more difficult to calculate than those of crystals and dilute gases. The only exceptions are the quantum liquids formed by the two isotopes of Helium. The spectral density $\chi_{\rho\rho}''(k,\omega)$ for He II and He$^3$ has been computed using Landau's phenomenological theories.[49,59]

The thermal collective mode [which appears most clearly in $\chi_{\varepsilon\varepsilon}''(k,\omega)$ given by (3.23) but which also enters into $\chi_{\rho\rho}''(k\omega)$ with a small residue] is often discussed[20] in terms of the simply understood hydrodynamic equation

$$\tau_d\times[(\partial/\partial t)\mathbf{Q}(\mathbf{r},t)]+\mathbf{Q}(\mathbf{r},t)=-K\nabla T(\mathbf{r},t). \tag{3.91}$$

When this is combined with (3.39), one finds the modified form of Fourier's differential equation

$$\tau_d\times(\partial^2T/\partial t^2)(\mathbf{r},t)+(\partial T/\partial t)(\mathbf{r},t)=(K/C_P)\nabla^2T(\mathbf{r},t).$$

If we limit ourselves to the problem of isobaric thermal waves, one finds that [compare (3.28)]

$$K(k,\omega)=\bar{K}(k,\omega)\bigg/\left[1-\frac{k^2}{i\omega}\frac{\bar{K}(k,\omega)}{C_P}\right]. \tag{3.92}$$

For the reasons discussed following (3.73), we expect a good approximation lies in using $\bar{K}(k=0,\omega)$ in the denominator. Using (3.75), one thus has the following dispersion relation for thermal waves in an isotropic media:

$$(\omega/k)^2=-i\omega\cdot[K(k=0,\omega)]/C_P,$$

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[56] J. Frenkel, *Kinetic Theory of Liquids* (Clarendon Press, Oxford England, 1946), particularly Chap. IV.

[57] H. L. Frisch, Physics **2**, 209 (1966); N. S. Gillis and R. D. Puff, Phys. Rev. Letters **16**, 606 (1966).

[58] S. Yip and M. Neklin, Phys. Rev. **135**, A1241 (1964); S. Yip and S. Ranganathan, Phys. Fluids **8**, 1956 (1965); M. Nelkin and S. Yip, Phys. Fluids **9**, 380 (1966); see also T. G. Greytak and G. B. Benedek, Phys. Rev. Letters **17**, 179 (1966).

[59] A. A. Abrikosov and I. M. Khalatnikov, Zh. Eksperim. i Teor. Fiz. **41**, 544 (1961) [English transl.: Soviet Phys.—JETP **14**, 389 (1962)].

which is a natural generalization of the standard thermal diffusion mode. If we make use of (3.25), an equivalent form of (3.92) is

$$\bar{\chi}_{\varepsilon\varepsilon}(k,\omega)=\bar{\chi}_{\varepsilon\varepsilon}(k,\omega)/[1+\bar{\chi}_{\varepsilon\varepsilon}(k,\omega)],$$

where $\bar{\chi}_{\varepsilon\varepsilon}(k,\omega)$ plays the role of a polarization function.[47] It would be useful to understand more clearly the distinction between $\bar{\chi}_{\varepsilon\varepsilon}(k,\omega)$ and $\chi_{\varepsilon\varepsilon}(k,\omega)$ in terms of diagrammatic perturbation theory.[43,59a]

As a specific example of (3.92), Kwok and Martin's calculation gives (setting $C_P=C_V$ for simplicity)

$$K(k,\omega)=i\omega Cv^2/3/[\omega^2-v^2k^2/3+i\omega\Gamma(k)]. \qquad (3.93)$$

Inserting this into (3.92), we find

$$\bar{K}(k,\omega)=i\omega Cv^2/3/[\omega^2+i\omega\Gamma(k)]. \qquad (3.93')$$

This clearly shows how the second-sound pole is removed from $\bar{K}(k,\omega)$, the remaining weak $\mathbf{k}$ dependence now being from the damping.

In the spectral densities we have discussed [(3.85), (3.88), and (3.90)], we have used the $\mathbf{k}=0$ limit of the various nonlocal transport coefficients. This means that we are only considering the correlation between fluctuations at different points in time. The spatial correlations are completely neglected. Certainly one expects the $\mathbf{k}$ dependence to be important near second-order phase transitions. Moreover, the case of $\bar{K}(k,\omega)$ for the interacting phonon gas [see (3.93′)] suggests that it may be important in other cases as well, especially in the region where hydrodynamics is breaking down ($\omega\tau_H\gtrsim 1$).

In Appendix A, we evaluate $K(\mathbf{q}=0,\omega)$ from first principles for the simple case of a harmonic crystal which is isotopically disordered. It is argued that the crucial normal phonon interactions have little effect in the limit $\mathbf{q}\rightarrow 0$. A direct computation of $K(\mathbf{q},\omega)$ near the second-sound resonance for a cubically anharmonic crystal is much more complicated, since it involves the finding of appropriate solutions of an integro-differential equation with a structure similar to Peierls' transport equation[43,59a] (more or less). As we have tried to emphasize, the actual frequency and wave-number dependence of transport coefficients of an anharmonic crystal is probably very poorly described by the single relaxation-time approximation we have used for illustration in this subsection. (We refer the reader to the work of Guyer and Krumhansel[23] for a detailed study of Peierls' transport equation.) We restrict ourselves to a brief discussion of the special effects arising when the mean free path $\lambda$ (due to quasi-momentum conserving three-phonon processes) is much smaller than the typical cross-sectional diameter of the specimen (denoted by $R$). If the quasi-momentum-destroying phonon processes (apart from boundary scattering) give rise to bulk mean free path $\lambda_z$, one finds that the damping of heat currents depends very much on whether $\lambda_z\gg\lambda$ or $\lambda_z\ll\lambda$. In particular, if $\lambda_z\gg\lambda$, the phonons reach the boundary (where they dissipate their momentum) by a sort of Brownian motion due to the strong normal phonon processes. Such a condition corresponds to a convective heat flow on a local scale, and is referred to as Poiseuille flow. One expects (and indeed finds) that the effective heat relaxation time $\tau_d$ is of the "random walk" type:

$$\tau_d\simeq(R/\lambda)^2\tau=(R/v)^2\tau^{-1}\gg R/v,$$

where $v$ is some mean sound velocity.

In terms of hydrodynamical equations for an interacting phonon gas, one finds in a natural way that the local heat current has a contribution proportional to the local drift velocity (local convection) as well as a term proportional to the local temperature gradient [such as assumed in (3.54)]. Under Poiseuille flow conditions ($\lambda\ll R$, $\lambda\times\lambda_z\gg R^2$), the former contribution is dominant. The local drift velocity of phonons may be proportional[9] to the local temperature gradient to the extent that the phonon heat current is proportional to the total quasi-momentum.

Recent work by Enz[50] has clarified in what way one can treat convective effects such as Poiseuille flow in terms of the correlation function method used in this subsection. Roughly speaking, $\Gamma(k)$ is once more given by (3.20) but now[23]

$$\tau_d=\tfrac{5}{8}(R/v)^2\tau^{-1}, \qquad \text{if } \lambda\times\lambda_z\gg R^2 \qquad (3.94)$$

$$=\tau_z, \qquad \text{if } \lambda\times\lambda_z\ll R^2. \qquad (3.94')$$

It is clear that the minimum frequency for undamped second sound ($\omega\gg 1/\tau_d$) is much smaller if Poiseuille flow conditions exist than what one would expect from simple boundary scattering ($1/\tau_d\simeq v/R$). Moreover, in this region the damping of second sound is proportional to the inverse of the specimen's cross-sectional area.

In Sec. IA, we noted briefly that, in a harmonic crystal, a sound wave such as excited by ultrasonic methods corresponds more truly to a coherent (or Glauber) state.[60] Since the displacement and momentum operators of the $n$th atom [see (1.1) and (1.6)] are linear in the phonon creation and annihilation operators, the thermal averages of $\hat{\mathbf{u}}_n$ and $\hat{\mathbf{p}}_n$ clearly vanish in a harmonic crystal. Let us now consider (1.2) in conjunction with the perturbation

$$\begin{aligned} V&=-\sum_n \mathbf{J}_n(t)\cdot\hat{\mathbf{u}}_n \\ &=-\sum_{\mathbf{k}} \mathbf{J}(-\mathbf{k},t)\cdot\hat{\mathbf{u}}(\mathbf{k}), \end{aligned} \qquad (3.95)$$

where $\hat{\mathbf{u}}(\mathbf{k})$ is defined by (2.43) and $\mathbf{J}(\mathbf{r},t)$ is some "classical" driving force (a real $c$ number). If we calculate the expectation value of $\hat{\mathbf{u}}_n$ in the perturbed

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[59a] In computing $\bar{K}(\mathbf{q},w)$, we need only consider irreducible diagrams. See L. J. Sham, Phys. Rev. (to be published).

[60] P. Carruthers and M. N. Nieto, Am. J. Phys. **33**, 537 (1965); further references are given there.

ensemble, the linear response to the driving term is given by

$$\mathbf{u}(\mathbf{k},\omega)=M^{-1}\sum_j \mathbf{e}(\mathbf{k}j)\mathfrak{D}_j(\mathbf{k},\omega)\times[\mathbf{e}(kj)\cdot\mathbf{J}(k\omega)], \tag{3.96}$$

where $\mathfrak{D}_j(k\omega)$ is given by (2.60) generally. In a harmonic crystal, all higher-order terms vanish and thus (3.96) is exact, with

$$\mathfrak{D}_j(k,\omega)=1/[\omega_j^2(k)-\omega^2].$$

Similarly the expectation value of the momentum operator in the perturbed harmonic crystal can be shown to be given by

$$M^{-1}\mathbf{p}(k,\omega)=-i\omega\mathbf{u}(k,\omega).$$

The simplicity of these exact results simply mirrors the fact that the effect of (3.95) is to generate coherent states of the harmonic crystal. These may be represented by

$$(a_{\mathbf{k}j}^{+}-\alpha_{\mathbf{k}j}^{*})\mid 0\rangle',$$

where the ground state is defined by

$$a_{\mathbf{k}j}\mid 0\rangle'=\alpha_{\mathbf{k}j}\mid 0\rangle'$$

for all modes $(\mathbf{k},j)$. Explicit calculation[60] gives

$$\alpha_{\mathbf{k}j}=-i[2MN\omega_j(k)]^{-1/2}[\mathbf{J}(-k,\omega_j(k))\cdot\mathbf{e}(kj)]. \tag{3.97}$$

Fourier-transforming (3.96), one easily finds that result may be expressed as

$$\mathbf{u}(\mathbf{k},t)=\sum_j \mathbf{e}(kj)[2/M\omega_j(k)]^{1/2}\mid\alpha_{kj}\mid \times\cos[\omega_j(k)t-\phi(kj)], \tag{3.98}$$

where $\alpha_{kj}\equiv\mid\alpha_{kj}\mid\exp i\phi(kj)$. We recall that $\mid\alpha_{kj}\mid^2$ gives the number of phonons in mode $(k,j)$ in a coherent state $\mid 0\rangle'$.

In the general case of an anharmonic crystal, the linear response result (3.96) is no longer exact and, in addition, $\mathfrak{D}_j(k,\omega)$ contains self-energy effects. Working to first order in $V$, one finds that, in contrast with (3.98), $\mathbf{u}(\mathbf{k},t)$ now corresponds to a oscillatory wave of finite lifetime. In the absence of a driving force such as (3.95), it is not obvious that $\langle\hat{\mathbf{u}}_n\rangle_0=\langle\hat{\mathbf{p}}_n\rangle_0=0$ for a general anharmonic crystal. However these results follow if one has inversion symmetry (such as exists in a monoatomic, Bravais lattice). This completes our discussion of coherent states in crystals.

The various spectral densities which we have discussed obey certain exact sum rules, some of which were mentioned or used in passing. Such sum rules play two very important roles in many-body problems.[11,42,46] Firstly, they provide a check on the validity of specific dynamical approximations. Secondly, they sometimes enable one to circumvent approximate calculations completely, especially as to the relative weight of the various collective modes.

If we denote the quantum-mechanical operator corresponding to some conserved quantity by $\hat{\mathbf{B}}$, one may show

$$\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\omega^n\chi_{\mathrm{BB}}''(k,\omega)$$
$$=(i^n/2V)\langle[(\partial^n/\partial t^n)\hat{\mathbf{B}}(-k,t),\hat{\mathbf{B}}(k,0)]\rangle_0\big|_{t=0} \tag{3.99}$$

for $n>0$ (see Appendix B of Ref. 46, for example). Clearly the R.H.S. is an ensemble average of $n$ equal-time commutators, and is related to the short-time dynamical evolution of the operator $\hat{\mathbf{B}}$. The left-hand side obviously gives extra weight to high frequencies. If $\mathbf{B}$ is the local displacement $\hat{\mathbf{u}}(\mathbf{r})$, the first moment $(n=1)$ is easily worked out, giving the well-known result[41]

$$\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\omega\chi_{u_\alpha u_\beta}''(k,\omega)=\delta_{\alpha\beta}/M. \tag{3.100}$$

Here $\chi_{\mu\nu}''$ is defined by (2.56). Recalling (2.56), we have

$$\chi_j''(k,\omega)=M\mathbf{e}(kj)\cdot\chi_{\mathrm{uu}}''(k,\omega)\cdot\mathbf{e}(kj),$$

and thus easily verify (2.67) as a special case of (3.100).

The equivalent sum rule for the density–density correlation function is

$$\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\omega\chi_{\rho\rho}''(k,\omega)=\rho_0^2(k^2/M). \tag{3.101}$$

$\chi_{\rho\rho}''(k,\omega)$ is closely related to Van Hove's function defined in (2.10):

$$\chi_{\rho\rho}''(k,\omega)=2\rho_0^2[N^{-1}S(k,\omega)](1-e^{-\beta\omega}).$$

Substitution of this result into (3.101) enables us to derive the famous Placzek sum rule

$$\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\omega S(k,\omega)=N(k^2/2M),$$

where we have used

$$S(-\mathbf{k},-\omega)=e^{-\beta\omega}S(\mathbf{k},\omega).$$

These relations should be compared with (3.9) and (3.8), respectively.

For $n=1$, the right-hand side of (3.99) is proportional to $k^2$, with a factor involving only the mass of the atoms. Higher moments involve relatively sensitive functions of the interparticle potential,[61] and for this reason are not used very often.

There is another kind of frequency sum rule which makes contact with thermodynamic derivatives. These give more weight to the low frequencies, and are only true for sufficiently long wavelengths. As a result, they are often referred to as hydrodynamic sum rules. For

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[61] R. D. Puff, Phys. Rev. **137**, A406 (1965).

the energy spectral density, we have

$$\lim_{k\to 0}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\frac{\chi_{\mathcal{E}\mathcal{E}}''(k,\omega)}{\omega}=\lim_{k\to 0}\chi_{\mathcal{E}\mathcal{E}}(k,0)$$
$$=C_PT. \tag{3.102}$$

Due to the use of the harmonic approximation in Kwok and Martin's computation of certain equilibrium parameters, (3.23) satisfies (3.102) only to the extent that $C_V \simeq C_P$. The other important example is probably the "compressibility" sum rule, which for liquids is

$$\lim_{k\to 0}\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\frac{\chi_{\rho\rho}''(k,\omega)}{\omega}=\lim_{k\to 0}\chi_{\rho\rho}(k,0),$$
$$=\rho(d\rho/dp)\,|_T,$$
$$=\rho/c_I^2. \tag{3.103}$$

The isothermal and adiabatic thermodynamic sound velocities satisfy the identity

$$c_I^2/c_A^2=K_I/K_A=C_V/C_P, \tag{3.104}$$

the last relation holding for isotropic solids as well. Such low-frequency sum rules as (3.103) may be derived by comparing the coefficients of the local variables in (3.18) with the theoretical result

$$\delta\mathbf{B}_i(\mathbf{k},t=0)=\sum_j\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\frac{\chi_{\mathrm{B}_i\mathrm{B}_j}''(k,\omega)}{\omega}\cdot\mathbf{b}_j(k),$$

which is the analog of (3.17) for times $t\leq 0$. A more general version of (3.103) which is valid for crystals has been discussed by several authors recently. If one specializes Stillinger's general result[62] to an isotropic crystal, one finds

$$\lim_{k\to 0}\chi_{\rho\rho}(k,0)=\rho/E, \tag{3.105}$$

where $E$ is the isothermal Young's modulus defined by[12]

$$E^{-1}=\tfrac{1}{9}[(K_I)^{-1}+(3/\mu)]. \tag{3.106}$$

Clearly (3.105) is in disagreement with the hydrodynamic results previously discussed. A more satisfactory derivation of the "elastic" sum rule has been given by Götze.[62a] He has shown that, for long wavelengths, the main effect of the anharmonic self-energy is to replace the isothermal elastic constants by their adiabatic values. The elastic sum rule is then simply another way of writing down Dyson's equation for the phonon propagator $\mathfrak{D}_{\alpha\beta}(k,\omega=0)$ in the limit $\mathbf{k}\to 0$. For an isotropic medium, the transverse and longitudinal displacements completely decouple and thus we find the two sum rules

$$\lim_{k\to 0}(\rho_0k)^2\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\frac{\chi_j''(k,\omega)}{\omega}=\rho_0/c_j^2, \tag{3.107}$$

where the two isothermal sound velocities are

$$c_l=[(\tfrac{4}{3}\mu+K_I)/\rho_0]^{1/2},\qquad c_t=(\mu/\rho_0)^{1/2}. \tag{3.108}$$

A cubic crystal is described by three isothermal elastic constants $c_{11}$, $c_{12}$, and $c_{44}$. An isotropic medium requires the further restriction $2c_{44}=c_{11}-c_{12}$. In this case one usually introduces the Lame constants, $\lambda=c_{12}$ and $\mu=c_{44}$, in terms of which we have $K_{\mathrm{I}}=\lambda+(\tfrac{2}{3})\mu$. If the atoms in the crystal interact only by central forces, one has the Cauchy relation $\mu=\lambda$. This implies that $c_l=\sqrt{3}c_t$ and, in addition, the adiabatic longitudinal sound velocity is given by $c_{Al}^2=(C_P/C_V)c_{Il}^2$, as in liquids.

The hydrodynamic results for $\chi_l''(k\omega)$ and $\chi_t''(k\omega)$ satisfy (3.107), as we should expect. One may in fact use the sum rules for $\chi_{\rho\rho}''(k\omega)$ given by (3.99) and (3.107) to estimate the relative weights of collective oscillations if there are only two; this is often done[11] in He II. If we make the ansatz [compare with (2.66)]

$$\chi_{\rho\rho}''(k,\omega)=(\rho_0^2k^2/M)2\pi(\operatorname{sgn}\omega)$$
$$\times\{Z_{\mathrm{I}}\delta(\omega^2-v_{\mathrm{I}}^2k^2)+Z_{\mathrm{II}}\delta(\omega^2-v_{\mathrm{II}}^2k^2)\}, \tag{3.109}$$

the sum rules give the following results:

$$Z_{\mathrm{I}}=1-Z_{\mathrm{II}},$$
$$Z_{\mathrm{II}}=\left(\frac{(v_{\mathrm{I}}^2/c_l^2)-1}{(v_{\mathrm{I}}^2/v_{\mathrm{II}}^2)-1}\right). \tag{3.110}$$

At low hydrodynamic frequencies, it is reasonable to take $v_{\mathrm{I}}$ to be equal to the adiabatic sound velocity. With this assumption, we have

$$Z_{\mathrm{II}}\simeq[(C_P/C_V)-1]. \tag{3.111}$$

Baym[35] has shown how one can express each of the elastic constants in terms of the phonon propagator. These relations are sum rules of a kind similar to (3.107).

## IV. GENERALIZATIONS AND SUGGESTIONS FOR EXPERIMENTS

The second sound or thermal diffusion mode in solids scatters light very weakly compared to the ordinary sound waves. The relative weight is $W\simeq(C_P/C_V-1)$, which even at room temperature is only of the order of 0.1. Beautiful confirmation of the line shape of the Landau–Placzek unshifted resonance has been recently reported for liquids using Brillouin scattering.[63,64] As a first step, similar measurements should be done on crystals. This should be possible at sufficiently high temperatures. Care must be taken to

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[62] F. H. Stillinger, Phys. Rev. **142**, 237 (1966).

[62a] W. Götze, Phys. Rev. **156**, 951 (1967).

[63] N. C. Ford, Jr., and G. B. Benedek, Phys. Rev. Letters **15**, 649 (1965). The relative intensity had been verified for a long time; for a recent reference, see H. Z. Cummins and R. W. Gammon, J. Chem. Phys. **44**, 2785 (1966).

[64] See, for example, *Physics of Quantum Electronics*, P. L. Kelley, B. Lax, and P. E. Tannenwald, Eds. (McGraw-Hill Book Co., Inc., New York, 1966), Part 2, p. 137.

subtract out the Rayleigh scattering of light directly from impurities in the crystal. This is easy enough since this spurious scattering is temperature independent and gives rise to a Lorentzian central peak with a width proportional to $\omega_0{}^4$, independent of $q$ (see p. 388 of Ref. 5).

Unfortunately, very low temperatures are needed for the appearance of a significant "frequency window." Presumably the most suitable temperature region[20] is somewhat above the point of maximum thermal conductivity (which usually occurs at around 1/20 of the Debye temperature). At higher temperatures, the scattered light might still disclose significant differences from the simple Landau–Placzek behavior even in the absence of a well-defined second-sound doublet. Deviations from the Landau–Placzek result must occur when the momentum transfer $q$ becomes of the order of $v/3D_T$ or somewhat larger. Here $v$ is some average high-frequency phonon velocity and $D_T=K/C_P$ is the thermal diffusion constant. Either hydrodynamics breaks down *or* there is a frequency window. If there is, the broad central peak goes over smoothly into a "second-sound" doublet. The higher the temperature, the smaller the frequency window becomes.

Since the scattered power increases as the fourth power of the initial photon frequency [see (2.8)], naturally it is advantageous to work with the largest frequency which is consistent with the above conditions.

Direct time-dependent thermal studies do not have to contend with the smallness of $W$. Very recently, for example, a group at Duke[65] has verified that temperature pulses in a single crystal of isotopically pure He$^4$ move with the expected second-sound velocity (with negligible diffusion) when the typical frequency component of the pulse is in the frequency window. This positive result should spur attempts to excite directly a temperature wave by rapidly varying the temperature of one end of the specimen. However, it seems that the available thermometry is not yet good enough to measure temperature oscillations with a frequency $\sim 10^7$ sec$^{-1}$, which is a typical value needed for weakly damped thermal waves. Light scattering methods seem potentially superior because the spectral density of the scattered light is a more direct probe of the excitation spectrum, and hence is more easily compared to theory.

In recent years, several ways of enhancing ordinary Brillouin scattering have been developed.[64] In theory, similar tricks may be used to overcome the smallness of $W$ and make second-sound waves more easily observable. Thus one might apply a longitudinal sound wave (of frequency $\omega^*$) to the crystal from which the light is being scattered. We assume the frequency $\omega^*$ is in the region where the temperature waves are weakly damped. If the scattering angle $\theta$ is such that the momentum transfer $q$ is equal to the wave number of the temperature wave ($\omega^*/v_{\text{II}}$), we should expect a strong "second-sound" doublet at $\Omega=\pm\omega^*$. This arrangement will also enhance the doublet corresponding to first sound by the same amount. (In an isotropic crystal, the transverse sound-wave doublet will be uneffected.)

Throughout this paper, we have neglected nonlinear effects arising from the coupling between the light waves and the medium. The usual discussions[34] work with a *harmonic* phonon field (1.12) coupled to the radiation field (2.28) by the nonlinear interaction given by (2.27). To deal with the low-energy hydrodynamic region, the displacement field, of course, must be dealt with more adequately. (Probably the simplest procedure would be to use Kwok and Martin's Hamiltonian.[9]) As a first step in the problem at hand, one might proceed even more phenomenologically by simply including electrostrictive terms ($\propto \mathbf{E}^2$) in the stress tensor in (3.41).

However, it would seem that stimulated Brillouin scattering[64] will not be very useful in overcoming the small second-sound scattering cross section. The threshold would occur when the average power fed into the second-sound mode is greater than the rate at which second-sound decays. However it is known from studies of other systems that if there are two or more types of boson excitations in a medium, the excitation with the smallest width gives rise to almost all the stimulated Brillouin scattering. (Consider the example of crystals with acoustical and optical phonons.[7]) When we recall that the second-sound resonance has a much larger width than first-sound (by a factor $W^{-1}$, in fact), the situation does not justify much optimism. Recently it has been suggested[65a] that in addition to electrostriction, one should include an energy source on the right-hand side of (3.39) due to electric field heating. It then obtains that thermal waves may have a lower threshold for stimulated emission than sound waves if the ratio of $C_P$ to the thermal expansion coefficient is small enough.

Brillouin light scattering from crystals at temperatures near a phase transition[66] is often quite strong. Such transitions occur in quartz, as well as in solid hydrogen and methane. The effect is the analogue of "critical opalescence" in liquids.[67] In liquids, the isothermal compressibility diverges at a second-order phase transition, and so does $C_P$ (the specific heat at constant pressure). In contrast, $C_V$ is essentially uneffected. As a result, the coupling between the energy and density fluctuations is greatly enhanced near the transition temperature.[63]

The existence of long-range correlations in crystals

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[65] C. C. Ackerman, B. Bertman, H. A. Fairbank, and R. A. Guyer, Phys. Rev. Letters **16,** 789 (1966).

[65a] R. H. Herman and M. A. Gray, Phys. Rev. Letters **19,** 825 (1967).

[66] V. L. Ginzburg, Usp. Fiz. Nauk **77,** 621 (1962) [English transl.: Soviet Phys.—Usp. **5,** 649 (1963)]; V. L. Ginzburg and A. P. Levanyuk, J. Phys. Chem. Solids **6,** 51 (1958); R. W. Gammon and H. Z. Cummins, Phys. Rev. Letters **17,** 193 (1966).

[67] A discussion in the same spirit as Part B of Sec. III is given by B. U. Felderhof, J. Chem. Phys. **44,** 602 (1966).

means that the limit $k\rightarrow 0$ must be done with more care, and the hydrodynamic mode dispersion relation given by (3.76) cannot be simply approximated by (3.77). Moreover the description of the new phase in crystals below $T_c$ involves specification of the appropriate "order" parameter.[66] This observable and its fluctuations must be included and thus one finds the possible existence of new low-frequency, long wavelength collective modes, as well as anomalous dispersion in the original hydrodynamic sound waves. The fluctuations in the dielectric constant related to those in the order parameter give rise to intense light scattering. In a future paper, we shall give a detailed discussion of the intensity and damping of temperature waves near second-order phase transitions.

While the phenomenon is not restricted to the hydrodynamic region, one expects anomalies[39,68] in Brillouin scattering from crystals with two-level scattering systems (energy separation $\Delta$) when the phonon involved has energy $\Delta$. Examples include donor impurities in semiconductors and paramagnetic impurities in dielectrics. The question of how the phonon interacts with the two-level system is somewhat subtle, depending as it does on whether or not the impurities interact with each other. The phonon width will not be proportional to the difference in population of the two levels (as argued in Ref. 68) if a resonance fluorescence calculation[39] is more appropriate.

Several sources of light scattering have been neglected here. First of all, thermally induced diffusion of atoms from site to site will produce density fluctuations in crystals and liquids with short range crystalline order. These fluctuations decay very slowly and hence give rise to a strong narrow undisplaced line, with width $\Delta\Omega\sim 1/\tau_0$. Here $\tau_0$ is the mean time that it takes for a given atom to move to another site.[56] Such processes must be sufficiently rapid to produce an observable line. This condition may be satisfied in crystals near the melting point, as well as in quantum crystals of solid helium, where diffusion is due to the large zero-point energy (see Introduction).

Apart from a remark at the end of Part B of Sec. II, we have also ignored the direct light scattering from thermal fluctuations. If we include this contribution, the spectral density of scattering light is proportional to [compare with (2.64)]

$$\begin{aligned}\Bigg\{&\boldsymbol{\varepsilon}_0{}^4k^2\sum_j|\mathbf{n}(j)|^2\frac{\chi_j''(k,\omega)}{M}+\left(C_V{}^{-1}\frac{\partial\boldsymbol{\varepsilon}_0}{\partial T}\bigg|_{\mathrm{eq}}\right)^2\\&\times\sin^2\phi\,\chi_{\varepsilon\varepsilon}''(k,\omega)+2p_{12}\left(C_V{}^{-1}\frac{\partial\boldsymbol{\varepsilon}_0}{\partial T}\bigg|_{\mathrm{eq}}\right)\boldsymbol{\varepsilon}_0{}^2\\&\times\sin^2\phi\,\chi_{\rho,\varepsilon}''(k,\omega)/\rho_0\Bigg\}[n(\omega)+1].\end{aligned}\tag{4.1}$$

As before, $\phi$ is the angle between the propagation direction of the scattered light and the initial electric field vector $\mathbf{E}_0$. In writing down the cross terms in the local energy and strain, we have for simplicity used the approximation[46]

$$\chi_{-iu,\varepsilon}''(k,\omega)\simeq\mathbf{k}\chi_{\rho,\varepsilon}''(k,\omega)/\rho_0k^2.\tag{4.2}$$

For an isotropic crystal, this result is exact since the transverse displacements do not involve local energy fluctuations. One may obtain $\chi_{\rho,\varepsilon}''(k,\omega)$ from the hydrodynamic equations discussed by Kwok and Martin.[9] We find

$$\begin{aligned}\mathbf{k}\cdot\chi_{-iu,\varepsilon}''(k,\omega)&=(3C_VW/T)^{1/2}\omega k\\&\times\mathrm{Im}\left(\frac{+\frac{1}{3}v^2k^2}{[\omega^2-u_{\mathrm{I}}{}^2k^2+i\omega\Gamma_{\mathrm{I}}][\omega^2-u_{\mathrm{II}}{}^2k^2+i\omega\Gamma_{\mathrm{II}}]}\right),\end{aligned}\tag{4.3}$$

where the notation is the same as was introduced in Sec. IIIA. In the limit $\Gamma\rightarrow 0$, we find

$$\begin{aligned}\chi_{\rho,\varepsilon}''(k,\omega)&=T\partial\rho/\partial T\,|_P(\tfrac{3}{4})^{1/2}(\omega v\,|\,k\,|)\\&\times[\pi\delta(\omega^2-u_{\mathrm{II}}{}^2k^2)-\pi\delta(\omega^2-u_{\mathrm{I}}{}^2k^2)].\end{aligned}\tag{4.4}$$

Use was made of the well-known thermodynamic relation

$$\alpha^2\equiv\left(\rho_0{}^{-1}\frac{\partial\rho_0}{\partial T}\bigg|_P\right)^2=\frac{C_P-C_V}{TK_I},\tag{4.5}$$

where $K_I$ and $\alpha$ are the isothermal bulk modulus and thermal expansion, respectively. For the case of liquids where the thermal waves are strongly damped, $\chi_{\rho,\varepsilon}''(k,\omega)$ is given by Eq. (87c) of Kadanoff and Martin.[46] It also satisfies a hydrodynamic-type sum rule given by Eq. (77b) of the same reference.

We see that the thermal diffusion mode (or second sound in the case of small damping) contributes to each of the correlation functions in (4.1). The part from the *first two terms* in (4.1) can be reduced to (for $p_{11}=p_{12}$)

$$\left(\boldsymbol{\varepsilon}_0\rho_0\times\frac{\partial\boldsymbol{\varepsilon}_0}{\partial\rho}\bigg|_T\right)^2\times K_I{}^{-1}\times\left(1-\frac{C_V}{C_P}\right)\times\left[1+R\frac{C_P{}^2}{C_V{}^2}\right],\tag{4.6}$$

where

$$R\equiv\left(\alpha^{-1}\times\frac{\partial\boldsymbol{\varepsilon}_0}{\partial T}\bigg|_\rho\right)^2\bigg/\left(\rho_0\frac{\partial\boldsymbol{\varepsilon}_0}{\partial\rho}\bigg|_s\right)^2.\tag{4.7}$$

The coefficient $R$ is a measure of the strength of direct light scattering from fluctuations in the local energy, relative to the part which couples into the local density. The combined strength given in (4.6) is proportional to $(C_P-C_V)$, while the last term in (4.1) is proportional to $(C_P-C_V)^{1/2}$. Since $W$ is very small, this means that insofar as we are interested in light scattering as a probe of temperature waves, the major contribution may be from the cross terms involving $\chi_{\rho,\epsilon}''(k,\omega)$ if

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[68] S. A. Al'tschuler and B. I. Kochelaev, Zh. Eksperim. i Teor. Fiz. **49**, 862 (1965) [English transl.: Soviet Phys.—JETP **22**, 600 (1966)].

the electronic dielectric constant is fairly temperature-dependent. The application of an external temperature wave to the specimen might be used to overcome the smallness of the thermo-optical coefficient and hence enhance the importance of the last two terms in (4.1).

Finally, we have always assumed that the light waves scatter off the collective modes of an infinite medium. Actually, there is much to learn from Brillouin light scattering from the surface of condensed systems. As is well known, crystals exhibit surface sound oscillations called Rayleigh waves (see p. 105ff of Ref. 12). Introducing a free surface as a perturbation in an otherwise harmonic crystal (by setting the interactions across a plane equal to zero), Maradudin and co-workers[69] have discussed such surface oscillations in some detail. The spectral density of scattered light is given by (2.20) once again, or

$$\tilde{S}(\mathbf{k},\Omega)\propto\sum_{jj'}\mathbf{n}(j)\cdot\mathbf{n}(j')\times\frac{\operatorname{Im}G(-\mathbf{k}j;\mathbf{k}j';\Omega-i0^{+})}{[\omega(k,j)\omega(k,j')]^{1/2}}\times[n(\Omega)+1],\quad(4.8)$$

where the retarded phonon Green's function $G(\mathbf{k}j, \mathbf{k}'j'; \omega)$ for a harmonic crystal with a free surface is given explicitly by Eq. (16) of a paper by Maradudin and Melngalis.[69] It has a pole corresponding to Rayleigh surface waves, in addition to those for the bulk phonons. Brillouin scattering is a very direct way of studying the dispersion relation of these surface oscillations. Surface thermal diffuse scattering[69] of x rays is much more indirect. Liquids also sustain surface capillary waves[18] (third sound in He II), which can be studied in the same way as Rayleigh waves.[69a] In surface scattering, the angle $\theta$ in (2.4′) is measured with respect to the elastically reflected beam.

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## APPENDIX A. COMPUTATION OF THE NONLOCAL THERMAL CONDUCTIVITY

In Sec. IIIB, we suggested that a good approximation to the dispersion relation for thermal waves is

$$(\omega/q)^2=-i\omega[K(\omega)/C_P],\qquad(\mathrm{A1})$$

where

$$K(\omega)\equiv K(q=0,\omega)=(3VT)^{-1}\int_0^\infty dt\times\exp(i\omega t)\int_0^\beta d\lambda\langle\hat{\mathbf{Q}}(0)\cdot\hat{\mathbf{Q}}(t+i\lambda)\rangle_0.\qquad(\mathrm{A2})$$

This approximation was expected to be valid in the region where damping effects due to second viscosity ($\tau v^2k^2$) were much smaller than those arising from thermal conduction ($1/\tau_d$). This is the region of direct physical interest, even though the momentum-destroying processes are much slower than momentum-conserving phonon interactions. If $\tau$ is not very much smaller than $\tau_d$, we can only expect to find deviations from the standard result of damped thermal waves

$$(\omega/q)^2=-i\omega\{K(q=0,\omega=0)/C_P\},\qquad(\mathrm{A3})$$

rather than weakly damped second-sound waves.

In this appendix, we compute $K(\omega)$ in two different examples. We do not include the decay of $\langle\mathbf{Q}(0)\cdot\mathbf{Q}(t)\rangle_0$ from anharmonic phonon interactions. Although there may exist relatively strong normal phonon processes, we make use of the fact that their role in the decay of heat currents is small. This procedure is justified by detailed theoretical calculations[23] of the lattice thermal conductivity in the static limit $\omega\rightarrow0$.

Normal phonon interactions play a direct role in $\langle\hat{\mathbf{Q}}(-q,0)\cdot\hat{\mathbf{Q}}(q,t)\rangle_0$, which occurs in the expression for $K(q,\omega)$. Physically speaking, this is obvious. The Fourier component $\mathbf{Q}(q)$ is no longer proportional to the total quasi-momentum, and hence momentum-conserving processes will lead to damping. The effect of umklapp phonon interactions on $\langle\hat{\mathbf{Q}}(0)\cdot\mathbf{Q}(t)\rangle_0$ is qualitatively similar to any other momentum-destroying scattering process.

It is convenient to have $K(\omega)$ in terms of a single time integral,

$$K(\omega)=\frac{-2}{3VT}\int_0^\infty dt\left(\frac{\exp(i\omega t)-1}{i\omega}\right)\operatorname{Im}\langle\hat{\mathbf{Q}}(t)\cdot\hat{\mathbf{Q}}(0)\rangle_0,\qquad(\mathrm{A4})$$

as Langer and others have noted. By expanding the heat-current correlation function in eigenstates of the total Hamiltonian, one may show that the real part of $K(\omega)$ is given by

$$K_R(\omega)=(\pi/3VT)\cdot[(e^{\beta\omega}-1)/\omega]\rho(\omega),\qquad(\mathrm{A5})$$

where

$$\rho(\omega)\equiv Z^{-1}\sum_{m,n}\exp(-\beta E_m\,|\,\langle m\,|\,\mathbf{Q}(0)\,|\,n\rangle\,|^2\times\delta(\omega-[E_m-E_n]).$$

As discussed in Sec. IIC, the method of thermodynamic

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[69] A. A. Maradudin and J. Melngalis, Phys. Rev. **133**, A1188 (1964); R. F. Wallis and A. A. Maradudin, Phys. Rev. **148**, 962 (1966).

[69a] A preliminary experiment of this kind has been recently reported: R. H. Katyl and V. Ingard, Phys. Rev. Letters **19**, 64 (1967).

Green's functions is concerned with *time-ordered* Green's functions, such as

$$F(t)\equiv\langle T\mathbf{Q}(t)\cdot\mathbf{Q}(0)\rangle_0. \tag{A6}$$

As with the phonon propagator, the evaluation of $F(t)$ is most easily done for "times" on the negative imaginary axis. Defining $t=iu$ and noting that $F(u+\beta)=F(u)$ for $-\beta<u<0$, we have the Fourier series expansion

$$F(u)=\tau^{-1}\sum_{l=-\infty}^{\infty}F(\omega_l)\exp(\omega_l u);\qquad \omega_l=2\pi li/\beta,$$

where the coefficients are given by

$$F(\omega_l)=\int_0^{\tau}F(u)\exp(-\omega_l u)\,du.$$

The discontinuity of the analytic continuation of these coefficients is what we need, since

$$\begin{aligned}\pi^{-1}\operatorname{Im}F(z)\,|_{z=\omega+i0^+}&\equiv\bar{F}(\omega),\\&=(e^{\beta\omega}-1)\rho(\omega),\end{aligned} \tag{A7}$$

which, upon insertion into (A5), gives

$$K_R(\omega)=(\pi/3VT)[\bar{F}(\omega)/\omega]. \tag{A8}$$

Thus the evaluation $K_R(\omega)$ boils down to finding the spectral density of the Fourier transform of $F(t)$ for $t$ on the negative imaginary axis. The imaginary part of $K(\omega)$ is probably most easily obtained by noting that the transport coefficient $K(\omega)$ satisfies causality. As a result, the real and imaginary parts are related by the well known Kramers–Kronig dispersion relation

$$\operatorname{Im}K(\omega)=-P\int_0^{\infty}\frac{d\omega'}{\pi}\cdot\frac{\operatorname{Re}K(\omega')}{\omega'-\omega}, \tag{A9}$$

where $P$ stands for principal part. In particular, (A9) shows that if

$$K_R(\omega)=B[1+(\omega\tau_d)^2]^{-1},$$

then

$$K_I(\omega)=\omega\tau_d K_R(\omega).$$

Maradudin[70] has made a careful study of the static ($\omega\rightarrow0$) thermal resistance of isotopically disordered cubic Bravais crystal, in the harmonic approximation and to lowest-order in the "impurity" concentration. His work can be extended to the frequency-dependent thermal conductivity. This is easily done since Maradudin explicitly computed $\bar{F}(\omega)$, with the result

$$\begin{aligned}\langle\bar{F}(\omega)\rangle_{\mathrm{A}}=\sum_{\substack{\mathbf{k}\\ j_1j_2}}\sum_{\substack{\mathbf{k}'\\ j_3j_4}}&\mathbf{S}(\mathbf{k}j_1j_2)\cdot\mathbf{S}(\mathbf{k}'j_3j_4)\\&\times\int_{-\infty}^{\infty}d\omega_1[\theta(\omega_1)+\theta(\omega-\omega_1)]\\&\times\{\langle\Delta^{+\,+}(\mathbf{k}j_1;\mathbf{k}'j_2;\omega_1)\rangle_{\mathrm{A}}\langle\Delta^{-\,-}(\mathbf{k}j_3;\mathbf{k}'j_4;\omega-\omega_1)\rangle_{\mathrm{A}}\\&+\langle\Delta^{+\,-}(\mathbf{k}j_1;\mathbf{k}'j_4;\omega_1)\rangle_{\mathrm{A}}\langle\Delta^{-\,+}(\mathbf{k}j_2;\mathbf{k}'j_3;\omega-\omega_1)\rangle_{\mathrm{A}}\}.\end{aligned} \tag{A10}$$

The brackets $\langle\cdots\rangle_{\mathrm{A}}$ represent impurity (or isotope) position averaging. For this *particular* problem, the vertex corrections do not enter—the average of the product of two phonon Green's functions is effectively equal to the product of two averaged phonon propagators. The usual transformation of the infinite sum over discrete frequencies $\omega_l$ to an integral is the origin of the factors $\theta(\omega)$, defined by

$$\theta(\omega)\equiv(\beta^2/2)\coth(\beta\omega/2). \tag{A11}$$

Finally, $\Delta^{\pm\,\pm}(\omega)$ is the spectral density of the Fourier coefficient

$$\mathfrak{D}^{\pm\,\pm}(\omega_l)=\int_{-\infty}^{\infty}d\omega\left(\frac{\Delta^{\pm\,\pm}(\omega)}{\omega-\omega_l}\right) \tag{A12}$$

related to the ionic displacement propagator

$$\mathfrak{D}^{\pm\,\pm}(\mathbf{k}j;\mathbf{k}'j';t)\equiv\langle T\hat{d}_{\mathbf{k}j}{}^{\pm}(t)\hat{d}_{\mathbf{k}'j'}{}^{\pm}(0)\rangle_0, \tag{A13}$$

where we have defined

$$\begin{aligned}\hat{d}_{\mathbf{k}j}{}^{\pm}&=a_{\mathbf{k}j}+a_{-\mathbf{k}j}{}^*\\&=a_{\mathbf{k}j}{}^*-a_{-\mathbf{k}j}\end{aligned} \tag{A14}$$

in terms of the usual phonon-field operators. For convenience, we follow some of Maradudin's notation and conventions, although they are somewhat different than those used in the main body of this paper.

The homogeneous energy-current operator for a lattice in the harmonic approximation is

$$\mathbf{Q}\equiv\sum_{\mathbf{k},jj'}S(\mathbf{k}jj')\hat{d}_{\mathbf{k}j}{}^{+}\hat{d}_{\mathbf{k}j'}{}^{-}, \tag{A15}$$

with (in standard notation)

$$\mathbf{S}(\mathbf{k}jj')=\tfrac{1}{2}\omega_{j'}(k)[\delta_{jj'}\mathbf{v}(\mathbf{k}j)+\mathbf{v}(\mathbf{k}jj')], \tag{A16}$$

$$\begin{aligned}v_\nu(kjj')&\equiv\frac{\omega_j{}^2(k)-\omega_{j'}{}^2(k)}{[\omega_j(k)\omega_{j'}(k)]^{1/2}}(4\pi)^{-1}\sum_{\mu}\frac{\partial e_\mu(\mathbf{k}j)}{\partial k_\nu}e_\mu(\mathbf{k}j')\\&=v_\nu(kj'j),\\v_\nu(\mathbf{k}j)&\equiv[\partial\omega_j(k)/\partial k_\nu]=-v_\nu(-\mathbf{k}j);\qquad \mu,\nu=x,y,z.\end{aligned} \tag{A17}$$

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[70] A. A. Maradudin, J. Am. Chem. Soc. **86,** 3405 (1964).

The existence of the second term in (A16), which depends on "polarization mixing," has been noted by several authors in recent years.[71] Since it is phase-dependent, (being nondiagonal in the phonon number representation), one cannot deal with it easily using ordinary transport theory based on simple distribution functions. While this oscillating term in the energy flux of a harmonic lattice is probably of little importance when one considers the time-averaged transport of energy, it is obviously of potential interest in the propagation of high frequency waves. For notational simplicity, however, we consider only the first or "Peierls'" term of (A16) in our reduction of (A10). Later we discuss the nondiagonal term in a *pure* harmonic lattice and show that, quite generally, its major effect is to alter slightly the velocity of second sound.

Inserting the spectral densities $\Delta^{\pm\pm}$ Maradudin found and keeping only the diagonal heat current operator as mentioned, we may rewrite (A10) as

$$\langle\bar{F}(\omega)\rangle_{\mathrm{A}}=\sum_{\mathbf{k}j}\int_{-\infty}^{\infty}d\omega_1[\theta(\omega_1)+\theta(\omega-\omega_1)](2\omega_1^2-\omega_1\omega)$$

$$\times\left(\frac{\epsilon p}{\pi\beta}\right)^2\omega_j^6(k)v^2(\mathbf{k}j)\,\frac{b(\omega_1)b(\omega-\omega_1)}{P(\mathbf{k}j;\omega_1)P(\mathbf{k}j;\omega-\omega_1)},\qquad\text{(A18)}$$

where $\epsilon=[(M-M')/M]$, $M'$ being the impurity mass; $p$ is the fractional impurity concentration; and

$$P(\mathbf{k}j;\omega)\equiv[\omega_j^2(k)-\omega^2+\epsilon p\omega_j^2(k)a(\omega)]^2+[\epsilon p\omega_j^2(k)b(\omega)]^2,\qquad\text{(A19)}$$

$$a(\omega)=\frac{1-\epsilon\omega^2G_R(\omega^2)}{[1-\epsilon\omega^2G_R(\omega^2)]^2+[\epsilon\omega^2G_I(\omega^2)]^2},$$

$$b(\omega)=\frac{(\operatorname{sign}\omega)\epsilon\omega^2G_I(\omega^2)}{[1-\epsilon\omega^2G_R(\omega^2)]^2+[\epsilon\omega^2G_I(\omega^2)]^2},\qquad\text{(A20)}$$

with

$$G(\omega^2)=(3N)^{-1}\sum_{\mathbf{k}j}[\omega^2-\omega_j^2(k)-i0]^{-1}\equiv G_R(\omega^2)+iG_I(\omega^2).\qquad\text{(A21)}$$

If we approximate the denominators $P(\mathbf{k}j;\omega)$ using the quasi-particle approximation discussed in the beginning of Sec. III, we may do the $\omega_1$ integration by standard contour integral methods, with the result that

$$\langle F(\omega)\rangle_{\mathrm{A}}=\sum_{\mathbf{k}j}v^2(\mathbf{k}j)(2\pi)^{-1}\left(\frac{2\bar{\omega}}{\beta}\right)^2[\theta(\bar{\omega})+\theta(\omega-\bar{\omega})]\left\{\left[\frac{2\Gamma(\mathbf{k}j)}{\omega^2+[2\Gamma(\mathbf{k}j)]^2}+\frac{2\Gamma(\mathbf{k}j)}{(2\bar{\omega}-\omega)^2+[2\Gamma(kj)]^2}\right]+O\left(\frac{\omega}{\bar{\omega}}\right)\right\}.\qquad\text{(A22)}$$

Here

$$\Gamma(\mathbf{k}j)\simeq\epsilon p\omega_j^2(k)b(\bar{\omega})/2\omega_j(k),\qquad\text{(A23)}$$

where $\bar{\omega}$ is the solution of

$$\omega_j^2(k)-\bar{\omega}^2-\epsilon p\omega_j^2(k)a(\bar{\omega})=0.\qquad\text{(A24)}$$

We neglect the phonon energy shift and hence set $\bar{\omega}\simeq\omega_j(k)$. Furthermore, as a result of the coth factors, the typical phonon entering the sum in (A22) has energy $\sim k_BT$. Since $k_BT\gg\omega$ (by a factor of $10^2$–$10^3$ in the best of cases), we may omit the remainder in the last factor in (A22), since it is of order $(\omega/k_BT)$ relative to the first. Making further use of $\omega_j(k)\gg\omega$ in (A22) and inserting the result into (A8), we have

$$K_R(\omega)\simeq\tfrac{1}{3}\sum_{\mathbf{k}j}v^2(kj)C_V(\omega_j(k),T)\tau(\mathbf{k}j)$$

$$\times\{[1+(\omega\tau(\mathbf{k}j))^2]^{-1}+[1+(\omega_j(k)2\tau(\mathbf{k}j))^2]^{-1}\}.\qquad\text{(A25)}$$

Following Maradudin, we have introduced abbreviations for the specific heat per mode per unit volume in the harmonic approximation

$$C_V(\bar{\omega},T)\equiv(k_B/V)(\tfrac{1}{2}\beta\bar{\omega})^2\operatorname{csch}^2(\tfrac{1}{2}\beta\bar{\omega})\qquad\text{(A26)}$$

and the phonon lifetime

$$\tau(kj)^{-1}\equiv2\Gamma(kj)=\epsilon p\omega_j(k)b[\omega_j(k)].\qquad\text{(A27)}$$

Actually we may omit the second term in the bracket of (A25), since, for the low temperatures of interest,

$$\omega_j(k)\gg[\tau(kj)]^{-1}.\qquad\text{(A28)}$$

Indeed, (A28) is the condition for the quasi-particle approximation to be good in the first place.

To summarize, we have

$$K_R(\omega)\simeq\tfrac{1}{3}\sum_{\mathbf{k}j}v^2(\mathbf{k}j)C_V(\omega_j(k),T)\tau(\mathbf{k}_j)$$

$$[1+(\omega\tau(kj))^2]^{-1}\qquad\text{(A29)}$$

and, using (A9),

$$K_I(\omega)=\tfrac{1}{3}\sum_{\mathbf{k}j}v^2(\mathbf{k}j)C_V(\omega_j(k),T)\tau(kj)$$

$$\times\left(\frac{\omega\tau(kj)}{[1+(\omega\tau(kj))^2]}\right).\qquad\text{(A30)}$$

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[71] R. J. Hardy, Phys. Rev. **132,** 168 (1963); Ph. Choquard, Hel. Phys. Acta **36,** 415 (1963); A. A. Maradudin, Scientific paper 63-129-103-P1, Westinghouse Research Laboratory, Pittsburgh (1963).

In the static limit ($\omega \rightarrow 0$), (A29) reduces to the usual Debye-type formula, as discussed by Maradudin. However the preceding derivation gives more insight into the correctness of a relaxation time approximation than the usual kinetic-equation approach. The phonon lifetime appearing in (A29) is identical to the one found when using time-dependent perturbation theory in conjunction with the $T$ matrix of scattering theory.

While Maradudin's calculation was specifically for an isotopically disordered crystal, the perturbation is of the form

$$V=\sum_{\mathbf{k}_1 j_1}\sum_{\mathbf{k}_2 j_2} V\left(\begin{array}{c|c}\mathbf{k}_1 & \mathbf{k}_2 \\ & \\ j_1 & j_2\end{array}\right)[\hat{d}_{\mathbf{k}_1 j_1}{}^{+}\hat{d}_{-\mathbf{k}_2 j_2}{}^{-}],$$

which typifies a wide class of phonon-impurity interactions.

In a certain rough sense, we expect (A29) and (A30) to be generally valid. Under fairly weak conditions, we have

$$K(\omega)=(3VT)^{-1}\int_0^\infty dt \exp(i\omega t)\int_{-\infty}^{\infty} dt'\Gamma(t-t') \times \tfrac{1}{2}\langle \hat{\mathbf{Q}}(0)\cdot\hat{\mathbf{Q}}(t)+\hat{\mathbf{Q}}(t)\cdot\hat{\mathbf{Q}}(0)\rangle_0, \quad \text{(A31)}$$

where $\Gamma(t)\equiv(2/\pi\hbar)\times\log\coth(\pi|t|/2\beta\hbar)$. Actually the equivalence of (A4) and (A31) is just another way of stating well known fluctuation–dissipation theorem. The symmetric function $\Gamma(t)$ is strongly peaked at $t=0$ and thus one might replace it by $\beta\delta(t)$. This is only true in the limit $\hbar\rightarrow 0$ and thus the result

$$K(\omega)=(3Vk_BT^2)^{-1}\int_0^\infty dt \exp(i\omega t)\langle\{\hat{\mathbf{Q}}(0), \hat{\mathbf{Q}}(t)\}\rangle_0 \quad \text{(A32)}$$

is essentially a classical approximation. Indeed such expressions were first derived by Green several years before the work of Kubo and others on quantum systems. Now the simplest sort of dynamical approximation to $\langle\{\hat{\mathbf{Q}}(0), \hat{\mathbf{Q}}(t)\}\rangle_0$ is that of exponential decay due to dissipative phonon interactions. Thus we might use

$$\langle\{\hat{n}_{\mathbf{k}'j'}(0), \hat{n}_{\mathbf{k}j}(t)\}\rangle_0=\langle\{\hat{n}_{\mathbf{k}'j'}(0), \hat{n}_{\mathbf{k}j}(0)\}\rangle_0 \times\exp[-t/\tau'(\mathbf{k}j)], \quad \text{(A33)}$$

where $\tau'(\mathbf{k}j)$ is an "appropriate" relaxation time per mode and $\hat{n}_{\mathbf{k}j}$ is the number operator for phonons. By taking the thermal average on the right-hand side of (A33) with respect to $H_0$ (the harmonic lattice Hamiltonian), one easily finds that

$$K(\omega)=(\tfrac{1}{3})\sum_{\mathbf{k}j} v^2(\mathbf{k}j)C_V(\omega_j(k), T)\frac{\tau'(\mathbf{k}j)}{1-i\omega\tau'(\mathbf{k}j)}. \quad \text{(A34)}$$

In the static limit, one would get the Debye-type result with $\tau'(\mathbf{k}j)$ as the phonon lifetime appropriate to the decay of lattice heat flow.

Having found $K(\omega)$, it is a simple matter[21] to use the second-sound dispersion relation to find in what way the frequency of a temperature wave depends on the propagation vector $q$. Using (A34) in (A1), one finds, to lowest-order in $[\omega\tau'(\mathbf{k}j)]^{-1}$, that second sound in an anharmonic crystal has a group velocity

$$v_{ss}\simeq\frac{1}{\sqrt{3}}\left\{\frac{1/v(1)+2/v(2)}{1/v^3(1)+2/v^3(2)}\right\}^{1/2}. \quad \text{(A35)}$$

The lifetime $\tau_{ss}$ is, to the same order, given by

$$\tau_{ss}{}^{-1}\simeq\sum_{\mathbf{k}j}\frac{[\tau'(\mathbf{k}j)]^{-1}v^2(j)C_V(\omega_j(k))}{\sum_{\mathbf{k}j} v^2(j)C_V(\omega_j(k))}. \quad \text{(A36)}$$

(A35) involves a different combination of $v(1)$ and $v(2)$ than the usual result found from simple Boltzmann-type transport equations.[20] This difference has been clarified to some extent by Enz.[50] Numerically, (A35) gives extra weight to $v(2)$ [as does the older result[20,65]], and $v_{ss}\simeq v(2)/\sqrt{3}$ is a good approximation in most cases.

The nondiagonal heat current operator $Q^{\mathrm{nd}}$ in a harmonic crystal is given by the second term in (A16). For simplicity we compute $K(\omega)$ for a pure harmonic crystal; as we shall see, the effect of dissipation is generally very small. Using (A32), we find, after some straightforward calculations, that

$$K^{\mathrm{nd}}(\omega)=(3Vk_BT^2)^{-1}(\tfrac{1}{4})\sum_{\mathbf{k}}\sum_{jj'} v^2(\mathbf{k}jj') \times i\omega\left\{\frac{[\omega_j(k)+\omega_{j'}(k)]^2}{[\omega_j(k)-\omega_{j'}(k)]^2-\omega^2}\langle\hat{n}_{\mathbf{k}j}\rangle_0 -\frac{\omega_j(k)\omega_{j'}(k)}{[\omega_j(k)+\omega_{j'}(k)]^2-\omega^2}(2\langle\hat{n}_{\mathbf{k}j}\rangle_0+1)\right\}. \quad \text{(A37)}$$

We note that $\langle\hat{n}_{\mathbf{k}j}\hat{n}_{\mathbf{k}j'}\rangle_0=\langle\hat{n}_{\mathbf{k}j}{}^2\rangle_0\delta_{jj'}$ and hence such terms do not contribute since $v(kjj)=0$. In the harmonic approximation, there is no contribution to $K(\omega)$ due to cross terms such as $\langle\hat{\mathbf{Q}}^{\mathrm{d}}\cdot\hat{\mathbf{Q}}^{\mathrm{nd}}\rangle_0$. If we had included a dissipative mechanism, we would expect that the denominators in (A37) would contain extra terms of order $\tau^{-2}$, where $\tau$ is the phonon lifetime such as in (A27). However, these corrections are negligible if the phonons are well defined excitations [see (A28)]. Finally, the $\omega^2$ terms in the denominators of (A37) may be omitted. The possibility of resonances at $\omega_{\pm}=[\omega_j(k)\pm\omega_{j'}(k)]$ is of only academic interest, since the important thermal phonons have frequencies in the range $10^{11}$–$10^{13}$ sec$^{-1}$.

Since $K^{\mathrm{nd}}(\omega)$ in (A37) is purely reactive, adding it to (A34) will simply alter the second-sound velocity predicted by the latter. We may reduce (A37) to

$$K^{\mathrm{nd}}(\omega)\simeq(12Vk_BT^2)^{-1}i\omega\sum_{\mathbf{k}}D(\hat{\mathbf{k}})(4\pi)^{-2}$$

$$\times\left\{-2(v_l-v_t)^2+\left[\frac{(v_l+v_t)^4}{v_lv_t}-2(v_l-v_t)^2\right]\right.$$

$$\left.\times(\langle n_{\mathbf{k}l}\rangle_0+\langle n_{\mathbf{k}t}\rangle_0)\right\},\quad\text{(A38)}$$

where

$$D(\hat{\mathbf{k}})\equiv(u^2(12)+u^2(13));$$

$$u_\nu(jj')\equiv\sum_\mu\left(\frac{\partial e_\mu(\mathbf{k}j)}{\partial k_\nu}e_\mu(\mathbf{k}j')\right)|\,\mathbf{k}\,|.\quad\text{(A39)}$$

The average of $D(\hat{\mathbf{k}})$ over the orientation of **k** is found to be $\langle D(\hat{\mathbf{k}})\rangle=(\frac{1}{2}+\frac{3}{2})=2$, and hence

$$\sum_{\mathbf{k}}D(\hat{\mathbf{k}})\langle n_{\mathbf{k}j}\rangle_0=2\cdot(V/2\pi^2)\cdot(k_sT/v_j)^3J(2)\quad\text{(A40)}$$

at low temperatures, with

$$J(2)=\int_0^{x_D}\frac{dxx^2}{e^x-1}=2\zeta(3)=2.404.$$

Using these results, (A38) reduces to

$$K^{\mathrm{nd}}(\omega)\simeq\frac{i\omega}{k_B}(3\times2^6\pi^2)^{-1}\left(\frac{v_l}{T}\right)^2$$

$$\times\left\{[\eta^{-1}(1+\eta)^4-2(1-\eta)^2](1+\eta^{-3})\frac{2\zeta(3)}{\pi^2}\left(\frac{k_BT}{v_l}\right)^3\right.$$

$$\left.-4(1-\eta)^2N\right\},\quad\text{(A41)}$$

with $\eta\equiv v_t/v_l<1$.

Let us now consider how $K^{\mathrm{nd}}(\omega)$ given by (A41) affects the solution of the dispersion relation for temperature waves. For simplicity, we shall approximate $K^{\mathrm{d}}(\omega)$ in (A34) by

$$K^{\mathrm{d}}(\omega)\simeq\tfrac{1}{3}C_Vv^2[\tau'/(1-i\omega\tau')],\quad\text{(A42)}$$

where

$$C_V\equiv(2\pi^2/15)k_B(k_BT/v_l)^3(1+2\eta^{-3}).\quad\text{(A43)}$$

Inserting $K(\omega)=K^{\mathrm{d}}(\omega)+K^{\mathrm{nd}}(\omega)$ into (A1), we find

$$\omega\simeq i(\tfrac{1}{3}v^2\tau')[q^2/(1-bq^2)];\qquad\omega\tau'\ll1,\quad\text{(A44)}$$

$$\omega\simeq(1/\sqrt{3})vq(1-bq^2)^{-1/2};\qquad\omega\tau'\gg1,\quad\text{(A45)}$$

where, for $\eta=1/\sqrt{3}$ (a typical ratio),

$$b(T)=K^{\mathrm{nd}}(\omega)/i\omega C$$

$$=(v_l/k_BT)^2 5.24\times10^{-4}[1-7.5\times10^{-4}(\omega_0/k_BT)^3].\quad\text{(A46)}$$

Even if we are in the region of "nonpropagating" thermal waves, the nondiagonal heat current alters the behavior of temperature waves as given by Fourier's law of heat diffusion. However, it is clear that even under the best conditions ($\omega_D$, $q$ large; $T$ small), $|\,b\,|\,q^2\ll1$. Thus it would seem that the nondiagonal heat current is on the borderline of observability.

## APPENDIX B. SECOND SOUND IN SUPERFLUID SYSTEMS

We have discussed second sound as a hydrodynamic collective mode in an interacting phonon gas. A reasonable question to ask is about the relation between this interpretation and the usual one in superfluids, where second sound seems tied up with the movement of the condensate. While not directly related to the subject of this paper, we should like to make some remarks (historical, pedagogic, and speculative) about this question. For an excellent resume of our theoretical understanding of He II, we refer the reader to Hohenberg and Martin.[24] References to the original literature can be found there. Unfortunately, these studies make no attempt to understand the velocity and damping of second sound on the basis of microscopic theory.

Around 1940, both Landau and Tisza developed a generalization of classical hydrodynamics which was appropriate to a two-fluid model. The equations predicted that if the "superfluid" and "normal" fluids were set in out-of-phase oscillation, the local density (or pressure) would not vary but the local temperature would. This new mode (second sound) was thus closely related to the extra degree of freedom introduced by the independent motion of the superfluid relative to the normal fluid. Thermal conduction in He II could be thought of as a limiting case of second sound of infinitely long wavelength—thus one has a natural explanation of the large static thermal conductivity of He II. An important feature of the movement of the superfluid is that it does not carry any entropy.

The microscopic justification of the two-fluid model as appropriate to He II is necessary before one can compute the various thermodynamic parameters entering in the hydrodynamical equations. Moreover the evaluation of the dissipative coefficients requires an understanding of the elementary excitation spectrum, although these damping effects (clearly related to the normal fluid) can be introduced phenomenologically, as one does in classical hydrodynamics. Tisza clearly identified the superfluid as the analog of the condensate formed in an ideal Bose–Einstein gas. However, his interpretation of the normal fluid as composed of weakly interacting atoms excited out of the condensate had little contact with reality. Landau quickly realized that the normal fluid should be expressed in terms of excited states of the whole liquid, namely, weakly interacting excitations of true momentum **k**. Landau concluded that, for wavelengths even of the order of the interatomic spacing $a_0$ between atoms, the only excitations were simple density oscillations ($\omega\propto k$).

For very long wavelengths ($\lambda \gtrsim 10^4 a_0$) one might expect that the excitations would be acoustic for a variety of general arguments. The key feature of Landau's spectrum was that even the relatively high-frequency excitations were phonons. Landau also used the specific heat data to suggest the existence of a "roton" dip in the dispersion relation at $\lambda \simeq 1$ Å. In the light of later work, it is probably unfortunate that the label "roton" was ever introduced.

For all of Landau's brilliance in dealing with the normal fluid, the background superfluid plays a somewhat mysterious role in his work. His reluctance to identify it with a sort of Bose–Einstein condensate occurs once again in his work on superconductors. It is interesting to recall that Landau's famous condition for the undamped relative motion of the condensate followed directly from the phonon nature of the low-lying excitations forming the normal fluid. This example shows that it is very misleading to separate the discussion of the superfluid aspects of He II and superconductors from the "normal" properties.

In a certain sense, Bogoliubov's fundamental work after the war justified the viewpoint of Tisza (in regard to the superfluid) and Landau (in regard to the normal fluid). Working with a gas of weakly coupled atoms obeying Bose statistics and with a repulsive interaction, Bogoliubov introduced the condensate by approximating the zero-momentum creation and annihilation operators as $c$ numbers. The condensate acted as the reservoir or vacuum from which one could excite well-defined elementary excitations. The dispersion relation was linear in $k$ for small $k$, and quadratic in $k$ (particle-like) for large $k$. While this model calculation is clearly not very relevant to the observed spectrum of He II, it is of obvious theoretical importance since it does reproduce many properties of the two-fluid model.

Almost all of the detailed calculations of the properties of a dilute Bose gas which have followed Bogoliubov's original work, however, have been restricted to absolute zero (see, however, Ref. 24). This is unfortunate since the phenomenological two-fluid model description of He II worked out in great detail by Landau and Khalatnikov[72] is, after all, a hydrodynamic theory appropriate to local equilibrium. There has been some recent progress in deriving the simple two-fluid model in terms of thermal Green's functions,[73] but little discussion is given to the damping of the normal fluid by various transport coefficients.[73a] This latter aspect of the problem is of greatest interest to us. The dependence of the attenuation of second sound on the various relaxation processes between the elementary excitations gives graphic insight into the true nature of this collective mode.

In an interacting gas of phonons, the second-sound mode was given by [see (3.20) of text]

$$\omega \simeq vk/\sqrt{3} - i(\tau v^2 k^2 + 1/\tau_d), \tag{B1}$$

for $1/\tau_d \ll \omega \ll 1/\tau$. If $\omega \lesssim 1/\tau_d$, one finds simple thermal diffusion:

$$\omega \simeq -i(K/C)k^2 \simeq -(i/3)v^2 k^2 \tau_d. \tag{B2}$$

In the case of He II, the only available theory of the attenuation of second sound is that developed by Landau and Khalatnikov.[72] They generalized the two-fluid hydrodynamics to include the effects of various viscosities and thermal conduction, in analogy to ordinary fluids. To evaluate these transport coefficients, they needed to know how the elementary excitations interacted. This coupling was introduced phenomenologically by expanding the Hamiltonian appropriate to a quantized hydrodynamical field around the equilibrium density. The successive terms in this expansion may be interpreted in terms of anharmonic coupling between the elementary excitations.

The Landau–Khalatnikov theory predicts that the damping of first and second sound is proportional to the various transport coefficients. Thus second sound satisfies

$$\omega^2 = v_{\mathrm{II}}^2 k^2 (1 - i\omega\alpha_{\mathrm{II}}), \tag{B3}$$

where

$$v_{\mathrm{II}}^2 = (\rho_s/\rho_n)(Ts^2/C) \tag{B4}$$

$$\alpha_{\mathrm{II}} = (\rho_s/\rho_n)(1/\rho)(\tfrac{3}{4}\bar{\eta}_n + \bar{\zeta}_n) + (\bar{K}_n/C). \tag{B5}$$

Here $\rho_s$ and $\rho_n$ are the usual superfluid and normal fluid density, respectively. The phonon thermal conductivity (which seems to be the main source of damping) is found to be

$$\bar{K}_n \simeq \tfrac{1}{3} C_V v^2 \tau_{pr} [1 - (\rho/\rho_n)(sT/v^2)], \tag{B6}$$

where $s$ is the entropy per unit mass. At low temperatures ($\lesssim 1$°K), the relaxation time $\tau_{pr}$ is that for phonon–roton scattering. There is strong phonon–phonon scattering, the corresponding relaxation time $\tau_{pp}$ being much smaller than any other, but these momentum-conserving processes do not effect the thermal conductivity $\bar{K}_n$. They are crucial in so far as they enable rapid energy exchange between phonons, which is necessary for local thermal equilibrium.

There is no easy comparison of (B3) with (B1) or (B2), although, in a rough sense, $\tau_d$ is the analog of $\tau_{pr}$ and $\tau$ is similar to $\tau_{pp}$. The damping of second sound in He II according to (B3) and (B6) is proportional to $\tau_{pr}$, which is similar to (B2). However in the latter case, one has nothing but a heavily damped oscillation, in disagreement with (B3). We emphasize that the transport properties of a gas of Landau excitations is somewhat more complex than that of a simple model

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[72] I. M. Khalatnikov, *An Introduction to the Theory of Superfluidity* (W. A. Benjamin, Inc., New York, 1965).

[73] J. Kane and L. P. Kadanoff, J. Math. Phys. **6**, 1902 (1965) and references given here.

[73a] Bogoliubov's school has recently derived and solved the hydrodynamic equations for a dilute Bose gas and explicitly exhibited first and second sound as poles of the Green's function. See Li Cheng-Chung, Dokl. Akad. Nauk USSR **169**, 1054 (1967) [English transl: Soviet Phys.—Doklady **11**, 714 (1967)].

of an interacting phonon gas used by Kwok and Martin.[9] However, these differences do not explain the completely opposite behavior of the attenuation given by the Landau–Khalatnikov two-fluid model and the interacting phonon gas.

The explanation of this puzzling state of affairs is that the interacting phonon gas calculation does not include the possible free motion of the condensate. In crystals, the analog of the condensate is the center of mass (or, equivalently, the rigid lattice background[24]). This is fixed by external constraints. In He II, however, the condensate can move—and indeed the second sound mode first discussed by Landau (and Tisza) appears to be directly related to the out-of-phase motion of the condensate with respect to the gas of excitations. Its physical origin is thus quite different from the oscillatory mode in a gas of phonons discussed in this paper. To express this in terms of a nonlocal thermal conductivity coefficient, we are suggesting that in He II one has[47]

$$\bar{K}(\omega) = -(C v_{\mathrm{II}}^2/i\omega) + \bar{K}_n(\omega), \qquad \text{(B7)}$$

where in a single relaxation time approximation, one might use

$$\bar{K}_n(\omega) \simeq \bar{K}_n/(1-i\omega\tau_{pr}). \qquad \text{(B8)}$$

Here $\bar{K}_n$ is given by (B6) and $v_{\mathrm{II}}$ by (B4). We emphasize that the actual form of $\bar{K}_n(\omega)$ may be much more complicated than (B8); however, the latter illustrates the basic physical conjecture in the simplest possible form with the expected limiting behavior for $\omega\tau_{pr} \gg 1$ and $\omega\tau_{pr} \ll 1$. The thermal conductivity coefficient $\bar{K}_n(\omega)$ is given by (3.26), where now $Q$ is the entropy current operator

$$\mathbf{Q} = \mathbf{J}_\epsilon - \mu \mathbf{J}. \qquad \text{(B9)}$$

Here $\mathbf{J}_\epsilon$ is the energy current, $\mathbf{J}$ is the matter current, and $\mu$ is the chemical potential. The local expectation value of the entropy current in He II is given by (for $\omega \to 0$)

$$\langle \mathbf{Q} \rangle = \langle \mathbf{v}_n \rangle \rho s T - \bar{K}_n \nabla T, \qquad \text{(B10)}$$

where

$$\mathbf{J} = \rho_n \mathbf{v}_n + \rho_s \mathbf{v}_s, \qquad \rho = \rho_s + \rho_n. \qquad \text{(B11)}$$

Under the usual conditions of thermal conduction experiments, there is zero matter flow $\langle J \rangle = 0$. This implies that

$$\langle \mathbf{v}_n \rangle = -(\rho_s/\rho_n) \langle \mathbf{v}_s \rangle, \qquad \text{(B12)}$$

where $\langle v_s \rangle$ is fixed by the external constraint. The convective term in (B10) gives rise to the singular term in (B7). An alternate but equivalent form of (B10) is (for $\omega \to 0$)

$$\langle \mathbf{J}_\epsilon \rangle = (\mu + Ts)\rho \langle \mathbf{v}_n \rangle + \mu \rho_s \langle \mathbf{v}_s - \mathbf{v}_n \rangle - \bar{K}_n \nabla T.$$

The analogy of (B7) to the better-understood case of the frequency-dependent electrical conductivity in the case of superconductors is important:

$$\bar{\sigma}(\omega) = -(\rho_s e^2/mi\omega) + \bar{\sigma}_n(\omega), \qquad \text{(B13)}$$

where $\rho_s$ is now the number of "superconducting" electrons. The first term in (B13) is due to the diamagnetic term in the current response to the transverse part of an external magnetic vector potential. The analog of (B10) is London's equation. As is well known, there is a completely satisfactory, self-consistent derivation of (B13) for a wide class of superconductors from microscopic theory, the dissipative term (at $\omega = 0$) being due to electrons scattering from phonons or random impurities. The actual form of $\bar{\sigma}_n(\omega)$ is considerably more complex than a simple Drude-type form [the analog of (B8)], most of this difference being due to the presence of an energy gap $\Delta$ in the excitation spectrum.[74]

The electronic thermal conductivity of superconductors is less than in the normal state. While it is undoubtedly true that the current theory of thermal (and thermoelectric) effects in superconductors is still not at the stage of theory of electromagnetic effects, some progress has been made in recent years.[75,76] In discussing this question, one generally aims at the theoretical reproduction of some sort of two-fluid picture with corrections. That this is relevant to superconductors is still a controversial question,[77] since in most cases the electrons come to local thermal equilibrium with the lattice (via impurity and phonon interactions) rather than with themselves. Indeed, these external interactions are often the only ones considered in proving that the normal fluid does not freely accelerate (in contrast to the condensate) under the application of an external field. In the work of Stephen,[76] one is led to the following nonlocal thermoelectric equations:

$$\langle J_n \rangle_\omega = K_1(\omega)(X_1)_\omega + K_2(\omega)(-\nabla T/T)_\omega; \qquad \text{(B14)}$$

$$\langle \mathbf{Q} \rangle_\omega = -K_2(\omega)(X_1)_\omega + K_4(\omega)(-\nabla T/T)_\omega, \qquad \text{(B15)}$$

where $X_1 \equiv (eE + \nabla\mu)/m$. In the single relaxation-time approximation discussed by Stephen,[76] the various transport coefficients for the BCS-type excitations all involve momentum integrals with

$$\tau_s(k)/[1 - i\omega\tau_s(k)] \qquad \text{(B16)}$$

in the integrand. Here $\tau_s(k)$ is the usual relaxation time which is appropriate to impurity potential scattering $1/\tau_s(k) = [v_s(k)/v_F] \times (1/\tau_n)$, with $\tau_n$ the normal state relaxation time and $v_s(k)$ the group velocity for BCS excitations of wavevector $\mathbf{k}$.

The important point is that the entropy current response given by (B15) does not involve a convective term in the same way as (B10) does. Under the condition $\langle J \rangle = 0$, one has

$$-\rho_s \langle \mathbf{v}_s \rangle_\omega = K_1 (X_1)_\omega + K_2 (-\nabla T/T)_\omega, \qquad \text{(B17)}$$

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[74] See J. R. Schrieffer, *Theory of Superconductivity* (W. A. Benjamin, Inc., New York, 1964), Chap. 8. See also Chap. 7 of Ref. 1 for effect of impurity scattering on $\bar{\sigma}_n(\omega)$.

[75] J. M. Luttinger, Phys. Rev. **136**, A1481 (1964).

[76] M. J. Stephen, Phys. Rev. **139**, A197 (1965).

[77] See discussion in *Quantum Fluids*, D. F. Brewer, Ed. (North-Holland Publ. Co., Amsterdam, 1966).

and thus

$$\langle \mathbf{J}_\epsilon \rangle_\omega = (K_2/K_1)\{\rho_s \langle \mathbf{v}_s \rangle_\omega + K_2(-\nabla T/T)_\omega\} + K_4(-\nabla T/T)_\omega. \quad \text{(B18)}$$

Under steady-state conditions ($\omega \rightarrow 0$), we have $X_1 = 0$ and hence

$$\langle \mathbf{J}_\epsilon \rangle_{\omega=0} = K_4(\omega=0) \times (-\nabla T/T)_{\omega=0}. \quad \text{(B19)}$$

On the other hand, there is a convective contribution to the energy current for finite $\omega$ because

$$\langle \mathbf{J}_\epsilon \rangle_\omega = \rho s T \langle \mathbf{v}_n \rangle_\omega - (\rho s T)^2 (1/\rho_n) \langle \tau_s/(1-i\omega\tau_s) \rangle \times (-\nabla T/T)_\omega + K_4(\omega)(-\nabla T/T)_\omega. \quad \text{(B20)}$$

Here we have used the single relaxation-time approximation of Stephen to estimate $K_1$ and $K_2$. The average value $\langle \cdots \rangle$ denotes an appropriate integral over momentum.[76] We expect that the first two terms of (B20) will tend to cancel each other until $\omega\tau_s \gg 1$. The work of Luttinger[75] and others[78] *suggests* that the conclusions we draw from (B20) are much more general than the specific model calculation of Stephan. If this is so, then we see that the occurrence of second sound in superconductors will only come from the possible reactive behavior of the nonsingular transport coefficients $K_i(\omega)$, just as in crystals. However, there is no more reason to expect that a "frequency window" will occur in superconductors than in water. Hence the hydrodynamic region is limited by some such condition as $\omega\tau_s \ll 1$.

While qualitative, the preceding discussion does indicate that a quantitative understanding of the thermal transport properties of superconductors is almost within our reach. No anomalous static thermal conductivity is expected, nor are weakly damped thermal waves. In contrast, the discussion of the transport properties of superfluid He II is still at a very phenomenological (albeit very successful) level. Clearly a first step would be to try to compute the entropy-current correlation function $\bar{K}_n(\omega)$ in (B7) using a dilute Bose gas model. Recalling the case of superconductors in Gor'kov's approximation, one expects that the Kubo-type formulas for transport coefficients for He II will provide the most natural way of understanding the role of typical "coherence" factors.

It is clear that (B7) is in essential agreement with (B3), since insertion of the former into the dispersion relation for second sound gives

$$\omega^2/k^2 = v_{\mathrm{II}}^2 - i\omega \bar{K}_n(\omega)/C. \quad \text{(B21)}$$

The highest frequencies used in second-sound propagation experiments up to the present ($\omega \lesssim 10^7$ sec$^{-1}$) are just below what we need for the frequency dependence of $\bar{K}_n(\omega)$ to be significant. Thus for $T \simeq 0.8$°K, comparison of the experimentally observing damping of second-sound waves with $\alpha_{\mathrm{II}} = \bar{K}_n(0)/v_{\mathrm{II}}^2 C_V$ gives a value $\tau_{pr} \simeq 5 \times 10^{-7}$ sec$^{-1}$ (see review article by de Boer in Ref. 6). If one could get into the frequency window

$$1/\tau_{pr} \ll \omega \ll 1/\tau_{pp}, \quad \text{(B22)}$$

one might expect a second-sound velocity to be given by an expression similar to

$$\tilde{v}_{\mathrm{II}}^2 \simeq (v_{\mathrm{II}}^2 + (\tfrac{1}{3})v^2 - \rho s T/3\rho_n). \quad \text{(B23)}$$

The attenuation will be proportional to $1/\tau_{pr}$. At very low temperatures, we have

$$v_{\mathrm{II}}^2 = (\rho_s/\rho_n) \times (s^2 T/C) \simeq (\tfrac{1}{3})v^2, \quad \text{(B24)}$$

but, in addition, $\rho \cdot s \cdot T \simeq \rho_n \cdot v^2$, and thus $\tilde{v}_{\mathrm{II}} = v/\sqrt{3}$ once again. The quantitative significance of this result should not be taken too seriously since it depends fairly sensitively on the simple form (B8).

The singular term in (B7) due to reversible relative motion of the two fluids gives rise to high thermal conductivity and weakly damped temperature waves for all frequencies satisfying $\omega\tau_{pp} \ll 1$. No lower limit on $\omega$ is required, as with second sound in crystals. The fact that He II sustains second-sound waves with frequencies much less than a kilocycle is naturally explained. In this connection, the anomalous properties of second-sound propagation for temperatures $\lesssim 0.5$°K seem to be (among other things) closely related to the inability to satisfy $\omega\tau_{pp} \ll 1$ necessary for local thermal equilibrium.

We felt it was simpler not to complicate the discussion in the main part of this paper with the anomalous aspects of second sound in He II arising from the reversible out-of-phase motion of the gas of excitations and the condensate.

Actually, our present understanding of second sound in a gas of phonons seems to be on a much firmer microscopic basis than in He II. In this connection, we recall our brief remarks about Poiseuille flow in Part B of Sec. III. It would seem possible to achieve this kind of heat flow in He II, with $\tau_d$ given by (3.94). If this was the case, the damping of second sound would have a characteristic dependence on the container's cross-sectional area. Note also that the local drift arising in Poiseuille flow of a phonon gas is formally very similar to the convective heat flow due to the out-of-phase motioni n the two-fluid model. In both cases the resulting temperature distribution has a sharp change near the boundary (which might be thought of as a "thermal" Meissner effect).

In concluding this appendix, we would like to make (B7) more understandable in terms of the standard hydrodynamic equations of the two-fluid model. To begin with, the only dissipative effect we consider is

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[78] V. Ambegaokar and G. Rickayzen, Phys. Rev. **142**, 146 (1965).

the static thermal conductivity $\bar{K}_n$. The conservation law for entropy is now

$$(\partial/\partial t)(\rho s)+\rho s\nabla\cdot\mathbf{v}_n=(1/T)\times\nabla\cdot(\bar{K}_n\nabla T). \qquad \text{(B25)}$$

Performing the usual manipulations (see Ref. 18, page 517 ff.), one is eventually led to

$$(\partial Q/\partial T)+v_{\mathrm{II}}^2 C_V\nabla T=-\bar{K}_n\cdot(\partial/\partial t)\cdot\nabla T. \qquad \text{(B26)}$$

If we neglect the coupling of first and second sound ($C_V\simeq C_P$), then the partial differential equation for the local temperature is

$$\partial^2 T/\partial t^2=v_{\mathrm{II}}^2\nabla^2 T+(\bar{K}_n/C)\cdot(\partial/\partial t)\cdot\nabla^2 T. \qquad \text{(B27)}$$

The generalization of (B27) for a nonlocal thermal conductivity in a single relaxation time approximation is

$$\left(1+\tau\frac{\partial}{\partial t}\right)\times\left(\frac{\partial^2 T}{\partial t^2}-v_{\mathrm{II}}^2\nabla^2 T\right)=\frac{\bar{K}_n}{C}\frac{\partial}{\partial t}\nabla^2 T. \qquad \text{(B28)}$$

In the preceding remarks, we have made use of a linearized version of the two-fluid model and ignored mutual friction and the effects of vorticity. To get some idea of the latter, we might use the modified equation

$$(\partial v_s/\partial t)+\nabla\mu=(-1/\tau_{Vor})(v_s-v_n). \qquad \text{(B29)}$$

In place of (B27), we then find that temperature waves are governed by

$$\left\{\frac{1}{\tau_{Vor}}\left(\frac{\rho}{\rho_n}\right)+\frac{\partial}{\partial t}\right\}\left\{\frac{\partial T}{\partial t}-\frac{\bar{K}_n}{C}\nabla^2 T\right\}=v_{\mathrm{II}}^2\nabla^2 T. \qquad \text{(B30)}$$

We see that there is now a minimum frequency for weakly damped second sound, which occurs for

$$\omega\gg(1/\tau_{Vor})(\rho/\rho_n).$$

In the last year or so, several authors have discussed the excitation spectrum of He II at temperatures within a few millidegrees of $T_\lambda$. In this region, Landau's famous dispersion curve and the two-fluid model predictions based on this spectrum are no longer valid. Ferrell *et al.*[79] have suggested that the long-wavelength entropy waves just below $T_\lambda$ have a dispersion relation $\omega\simeq A(k)k^{3/2}$, where $A(k)$ depends only logarithmically on $k$. What we would like to point out here is that the thermal expansion coefficient diverges[80] as $T\rightarrow T_\lambda$, going as $\log|T-T_\lambda|$. This means that the entropy fluctuations will be more strongly coupled to the density as $T\rightarrow T_\lambda$, with a consequent increase in the scattering cross section.[81] Unfortunately this "critical opalescence" is small, as can be seen from the fact that for $T_\lambda-T\simeq 10^{-4}$°K, we still only have $[C_P/C_V-1]\simeq 0.02$.

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[79] R. E. Ferrell, N. Menyhard, H. Schmidt, F. Schwabl, and D. Szepfalusy, Phys. Rev. Letters **18**, 891 (1967).

[80] C. E. Chase, E. Maxwell, and W. E. Millett, Physica **27**, 1129 (1961); M. H. Edwards, Can. J. Phys. **36**, 884 (1958).

[81] B. I. Halperin and P. C. Hohenberg, Phys. Rev. Letters **19**, 700 (1967).