Self-Consistent Phonon Formulation of Anharmonic Lattice Dynamics

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(Received 24 July 1969)

The self-consistent phonon theory of anharmonic lattice dynamics is derived via a stationary functional formulation. The crystal dynamics is approximated by a set of damped oscillators, and these are used to construct a trial action, analytically continued into the complex time-temperature plane. Using the action, a free-energy functional is required to be stationary with respect to the trial oscillators. The resulting phonon modes are undamped at the first order of approximation, whereas to second order the phonon spectral function is determined self-consistently. Expressions are obtained in first order for various thermodynamic derivatives, such as pressure, elastic constants, specific heats, and thermal expansion.

I. INTRODUCTION

THE traditional Born–von Kármán theory of lattice dynamics,[1] proposed more than a half-century ago, has been one of the most firmly rooted concepts in the physics of solids. It assumes that the vibrations of atomic nuclei about their mean positions in the crystal are of small amplitude relative to the internuclear separations, and that the ratio of these quantities is a legitimate small expansion parameter in a perturbation treatment. This fundamental assumption seems so reasonable that it was all the more surprising to have it invalidated by recent computations[2,3] in the case of the rare-gas crystals. These computations show that the Born-von Kármán expansion is at least of impracticably slow convergence near the melting temperature of these crystals,[2] and that for helium the convergence is completely nonexistent at any temperature.[3]

It has also been found that a renormalized perturbation expansion,[4–9] which has come to be known as the self-consistent phonon theory, provides[10–12] a much more adequate treatment of lattice dynamics in the rare gases over the complete temperature range of the solid phase. A renormalized theory of this type was first written down by Hooton,[13] following a much earlier mention by Born[14] and Hooton's subsequent development[15] of a rudimentary form. Not until much more recently, however, has the theory been given[4–9] in a variety of more general and elegant forms based on the modern techniques of many-body theory. We choose not to review each of these developments in detail here,[16] but wish only to state that in our opinion no one of these authors has derived the most general and complete set of results that is achievable nor has used as simple and self-contained a formalism as possible.

In this paper we attempt to collect the results of the previous authors on the self-consistent phonon theory; to correct some minor errors; to extend the results to more general situations in several directions; to correlate these results by deriving them all from a single formalism; and to select a formalism for their statement which we feel is clearer and more compact than others, while no less powerful. The functional variation technique which we employ, while not entirely novel, at least has not been used previously in the study of lattice dynamics for which we feel it is ideally suited.

II. FORMAL DEVELOPMENT

The self-consistent phonon approach to lattice dynamics is based on the collective picture of the fundamental dynamical variables. The view is adopted that the elementary excitations of the crystal, at least for low excitation energy, are collective vibrational waves, or phonons. The phonons are introduced directly as the appropriate basis set of coordinates, and do not have to be constructed as the modes of response of the crystal to a small disturbance from equilibrium.[17] Thus a model phonon dynamics is constructed, with adjustable parameters which are optimized such that the low-lying excitation spectrum of the model system approximates as closely as possible the corresponding spectrum of the true system.

[1] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, England, 1954).
[2] M. L. Klein, G. Horton, and J. L. Feldman, Phys. Rev. (to be published).
[3] F. W. de Wette and B. R. A. Nijboer, Phys. Letters **18**, 19 (1965).
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[11] V. V. Goldman, G. K. Horton, and M. L. Klein, Phys. Rev. Letters **21**, 1527 (1968); Phys. Letters **28A**, 341 (1968).
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[14] M. Born, in *Festschrift zur Feier des Zweihundertjährigen Bestehens der Akademie der Wissenschaften der Universität Gottingen I. Mathematisch-Physikalische Klasse* (Springer-Verlag, Berlin, 1951).
[15] D. J. Hooton, Phil. Mag. **46**, 422 (1955); **46**, 433 (1955); Z. Physik **142**, 42 (1955).
[16] See N. R. Werthamer, Am. J. Phys. **37**, 763 (1969).
[17] W. Brenig, Z. Physik **171**, 60 (1963); D. R. Fredkin and N. R. Werthamer, Phys. Rev. **138**, A1527 (1965); G. Meissner, Z. Physik **205**, 249 (1967); N. S. Gillis and N. R. Werthamer, Phys. Rev. **167**, 607 (1968).

If the model phonons are assumed to be undamped, their dynamics may be specified by a model Hamiltonian, with the model potential energy being a quadratic form in the atomic displacements. To account for damping, however, the model phonons should be chosen to have a finite lifetime, and so their dynamics must be determined rather by a model action. To allow conveniently for a statistical ensemble of systems in thermal equilibrium at inverse temperature β, the time variable should be analytically continued into the time-temperature plane in the usual way.[18] It is also especially useful to consider the crystal to be under the influence of externally applied time-dependent forces. Thus the model action operator for the crystal is chosen as

$$\mathcal{S}=\sum_i \int_0^{-i\beta} dt[\tfrac{1}{2}M_i|\dot{\mathbf{u}}_i(t)|^2-\mathbf{F}_i(t)\cdot\mathbf{u}_i(t)] +\tfrac{1}{2}\sum_{i\neq j}\int_0^{-i\beta}dt_1\int_0^{-i\beta}dt_2 \times\tfrac{1}{2}[\mathbf{u}_{ij}(t_1)\cdot\mathbf{\Phi}_{ij}(t_1-t_2)\cdot\mathbf{u}_{ij}(t_2)]. \quad (1)$$

In this expression M_i is the mass of the ith atom and $\mathbf{u}_i$ denotes its displacement, the deviation of its instantaneous position $\mathbf{r}_i$ from its mean position $\mathbf{R}_i$, so that $\mathbf{u}_i(t)=\mathbf{r}_i(t)-\mathbf{R}_i$. The ith atom is acted on by an external force $\mathbf{F}_i(t)$. The notation $\mathbf{u}_{ij}\equiv\mathbf{u}_i-\mathbf{u}_j$ is used for a displacement difference, and T is the ordering symbol for the displacement operators which do not commute at different times. The t integration is along the imaginary time-temperature axis. The phonons described by the action $\mathcal{S}$ will be damped because of the retarded (i.e., frequency-dependent) spring constants $\mathbf{\Phi}_{ij}(t_1-t_2)$ which otherwise remain as freely adjustable parameters.

The true free energy,

$$\mathcal{F}=-\beta^{-1}\ln\mathrm{Tr}[\exp(-\beta\mathcal{H})], \quad (2)$$

can be reexpressed by adding and subtracting the model action,

$$\mathcal{F}=-\beta^{-1}\ln\mathrm{Tr}\{\exp[-i\mathcal{S}-(\beta\mathcal{H}-i\mathcal{S})]\} =-\beta^{-1}\ln\mathrm{Tr}[\exp(-i\mathcal{S})] -\beta^{-1}\ln\left\langle T\left[\exp\left(-i\int_0^{-i\beta}dt\,\tilde{V}(t)\right)\right]\right\rangle, \quad (3)$$

where

$$\tilde{V}(t)\equiv\exp(\mathcal{S}t/\beta)(\mathcal{H}-i\beta^{-1}\mathcal{S})\exp(-\mathcal{S}t/\beta), \quad (4)$$

and where the angular brackets imply thermal average over the model distribution,

$$\langle\mathcal{O}\rangle\equiv\mathrm{Tr}[\mathcal{O}\exp(-i\mathcal{S})]/\mathrm{Tr}[\exp(-i\mathcal{S})]. \quad (5)$$

[18] A. A. Abrikosov, L. P. Gor'kov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963); L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (W. A. Benjamin, Inc., New York, 1962).

If the model system is to approximate closely the true low-lying energy spectrum, then $\mathcal{H}-i\beta^{-1}\mathcal{S}$ must be small in some average sense. Hence it should be a good approximation to expand $\mathcal{F}$ in cumulants (also frequently called semi-invariants) of $\tilde{V}$, and to truncate the series after the first term or two. The cumulant expansion in an operator x is defined via a parameter α as

$$\ln\langle e^{\alpha x}\rangle=\sum_{n=1}^{\infty}(n!)^{-1}\alpha^n M_n(x), \quad (6)$$

so that

$$M_1(x)=\langle x\rangle, \quad M_2(x)=\langle x^2\rangle-\langle x\rangle^2,$$

and

$$M_n(x)=\lim_{\alpha\to 0}d^n(\ln\langle e^{\alpha x}\rangle)/d\alpha^n. \quad (7)$$

Thus the cumulant expansion of $\mathcal{F}$ is

$$\mathcal{F}=-\beta^{-1}\ln\mathrm{Tr}[\exp(-i\mathcal{S})]-\beta^{-1}\sum_{n=1}^{\infty}(n!)^{-1} \times M_n\left(-i\int_0^{-i\beta}dt\,\tilde{V}(t)\right). \quad (8)$$

The evaluation of even the leading cumulant would appear to be quite complicated, especially because of the noncommuting nature of the displacement operators $\mathbf{u}_i(t)$ at differing time temperatures t and the necessity for the t-ordering operator. Nevertheless, Feynman has shown that since $\mathcal{S}$ is a quadratic form in the $\mathbf{u}_i(t)$, the results obtained by treating the t orderings in a careful way will always be the same as if the operators were regarded as c numbers and their commutation properties ignored. A similar conclusion has been arrived at by Edwards[19] using a different argument. Thus a purely classical algebraic procedure is fully justified.

The first step is to introduce space- and time-temperature Fourier transforms. We assume that the set of mean atomic positions $\mathbf{R}_i$ form a regular crystalline array, with n atoms per unit cell labeled by an index σ. The centers of the N unit cells in the crystal are connected by lattice vectors $\boldsymbol{\tau}$ and the position of the σth atom relative to the center of its cell is denoted by $\mathbf{R}_\sigma$. Then $\mathbf{u}_i(t)$ can be represented as

$$\mathbf{u}_i(t)=N^{-1}\textstyle\sum_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}_i}\mathbf{u}^\sigma(\mathbf{k}t). \quad (9)$$

The time-temperature transform provides the further representation

$$\mathbf{u}^\sigma(\mathbf{k}t)=i\beta^{-1}\textstyle\sum_\nu e^{-iz_\nu t}\mathbf{u}^\sigma(\mathbf{k}z), \quad (10)$$

where $z=\pi i\nu/\beta$ and ν is an even integer, provided that t lies in the region of the complex plane $-\beta\leq\mathrm{Im}\,t<0$.

[19] S. F. Edwards, in *Analysis in Function Space*, edited by W. T. Martin and I. Segal (Massachusetts Institute of Technology Press, Cambridge, Mass., 1964).

A similar representation holds for $\Phi_{ij}(t-t')$,

$$\Phi_{ij}(t-t')=N^{-1}\sum_{\mathbf{k}} i\beta^{-1}\sum_{\nu} e^{i\mathbf{k}\cdot\mathbf{R}_{ij}-iz(t-t')}\Phi^{\sigma\sigma'}(\mathbf{k}z), \quad (11)$$

where $\mathbf{R}_{ij}\equiv\mathbf{R}_i-\mathbf{R}_j$. Then $\mathcal{S}$ diagonalizes into

$$\mathcal{S}=i\beta^{-1}\sum_{\nu} N^{-1}\sum_{\mathbf{k}}\sum_{\sigma,\sigma'}\{\tfrac{1}{2}\delta\mathbf{u}^{\sigma}(\mathbf{k}z)^{\dagger}\cdot[\mathbf{D}^{\sigma\sigma'}(\mathbf{k}z)]^{-1}\cdot\delta\mathbf{u}^{\sigma'}(\mathbf{k}z) -\tfrac{1}{2}\mathbf{F}^{\sigma}(\mathbf{k}z)^{\dagger}\cdot\mathbf{D}^{\sigma\sigma'}(\mathbf{k}z)\cdot\mathbf{F}^{\sigma'}(\mathbf{k}z)\}. \quad (12)$$

We define the notation

$$\delta\mathbf{u}^{\sigma}(\mathbf{k}z)\equiv\mathbf{u}^{\sigma}(\mathbf{k}z)-\sum_{\sigma'}\mathbf{D}^{\sigma\sigma'}(\mathbf{k}z)\cdot\mathbf{F}^{\sigma'}(\mathbf{k}z) \quad (13)$$

and

$$\mathbf{D}^{\sigma\sigma'}(\mathbf{k}z) \equiv(M_{\sigma}z^{2}\mathbf{1}\delta_{\sigma,\sigma'}+\delta_{\sigma,\sigma'}\sum_{\sigma''}\Phi^{\sigma\sigma''}(0,z)-\Phi^{\sigma\sigma'}(\mathbf{k}z))^{-1}, \quad (14)$$

where the inverse is taken within the $3n$-dimensional vector space formed by the direct product of three-dimensional Cartesian space with n-dimensional σ space. The operators $\delta\mathbf{u}^{\sigma}(\mathbf{k}z)$ become the independent dynamical variables in the model system.

This diagonalization of $\mathcal{S}$ allows a prototype correlation function to be evaluated explicitly. For an arbitrary vector $\mathbf{Q}^{\sigma}$,

$$\langle\exp\{i\sum_{\sigma}\mathbf{Q}^{\sigma}\cdot[\mathbf{u}^{\sigma}(\mathbf{k}t)-\mathbf{u}^{\sigma}(\mathbf{k}t')]\}\rangle=\mathrm{Tr}\left\{\exp\left[i\sum_{\sigma}\mathbf{Q}^{\sigma}\cdot\frac{1}{i}\left(\frac{\delta}{\delta\mathbf{F}^{\sigma}(\mathbf{k}t)}-\frac{\delta}{\delta\mathbf{F}^{\sigma}(\mathbf{k}t')}\right)\right]\exp(-i\mathcal{S})\right\}\Big/\mathrm{Tr}\exp(-i\mathcal{S})$$
$$=\exp[i\beta^{-1}\sum_{\nu}\sum_{\sigma,\sigma'}i\mathbf{Q}^{\sigma}\cdot\mathbf{D}^{\sigma\sigma'}(\mathbf{k}z)\cdot\mathbf{F}^{\sigma'}(\mathbf{k}z)(e^{-izt}-e^{izt'})]\exp[-\beta^{-1}\sum_{\nu}\sum_{\sigma,\sigma'}\mathbf{Q}^{\sigma}\cdot\mathbf{D}^{\sigma\sigma'}(\mathbf{k}z)\cdot\mathbf{Q}^{\sigma'}(1-e^{-iz(t-t')})]. \quad (15)$$

Since this is true for arbitrary $\mathbf{Q}^{\sigma}$, both sides of the equation may be expanded in powers of $\mathbf{Q}^{\sigma}$ and the coefficients equated term by term. The result to first order is that

$$\langle\mathbf{u}^{\sigma}(\mathbf{k}t)\rangle=i\beta^{-1}\sum_{\nu}e^{-izt}\sum_{\sigma'}\mathbf{D}^{\sigma\sigma'}(\mathbf{k}z)\cdot\mathbf{F}^{\sigma'}(\mathbf{k}z), \quad (16)$$

so that from definition (13),

$$\delta\mathbf{u}^{\sigma}(\mathbf{k}z)=\mathbf{u}^{\sigma}(\mathbf{k}z)-\langle\mathbf{u}^{\sigma}(\mathbf{k}z)\rangle, \quad (17)$$

and $\delta\mathbf{u}^{\sigma}(\mathbf{k}z)$ can be identified with the displacement from the mean position, in the presence of the applied force $\mathbf{F}^{\sigma}(\mathbf{k}z)$. Furthermore, to second order in $\mathbf{Q}^{\sigma}$,

$$\langle\delta\mathbf{u}^{\sigma}(\mathbf{k}t)\delta\mathbf{u}^{\sigma'}(\mathbf{k}t')\rangle=\beta^{-1}\sum_{\nu}e^{-iz(t-t')}\mathbf{D}^{\sigma\sigma'}(\mathbf{k}z), \quad (18)$$

so that $\mathbf{D}^{\sigma\sigma'}(\mathbf{k}z)$ is identified as the phonon propagator (i.e., displacement autocorrelation function). Finally, Eq. (15) can be rewritten in the form

$$\langle\exp\{i\sum_{\sigma}\mathbf{Q}^{\sigma}\cdot[\delta\mathbf{u}^{\sigma}(\mathbf{k}t)-\delta\mathbf{u}^{\sigma}(\mathbf{k}t')]\}\rangle =\exp[-\beta^{-1}\sum_{\nu}(1-e^{-iz(t-t')}) \times\sum_{\sigma,\sigma'}\mathbf{Q}^{\sigma}\cdot\mathbf{D}^{\sigma\sigma'}(\mathbf{k}z)\cdot\mathbf{Q}^{\sigma'}], \quad (19)$$

where it can be recognized as a slightly generalized form of the familiar Gaussian averaging theorem.[20] At this point the applied force $\mathbf{F}^{\sigma}(\mathbf{k}z)$ has fulfilled its usefulness (at least until consideration is given to transport properties as the response to an externally applied disturbance) and is set equal to zero.

A. First-Order Approximation to $\mathcal{F}$

With these important theorems established, the leading cumulants can be evaluated explicitly. The first one is

$$-\beta^{-1}M_{1}\left(-i\int_{0}^{-i\beta}dt\,\tilde{V}(t)\right) =\tfrac{1}{2}\sum_{i\neq j}\left\langle v_{ij}(\mathbf{R}_{ij}+\mathbf{u}_{ij})-i\beta^{-1}\int_{0}^{-i\beta}dt_{1}\int_{0}^{-i\beta}dt_{2} \times\tfrac{1}{2}T[\mathbf{u}_{ij}(t_{1})\cdot\Phi_{ij}(t_{1}-t_{2})\cdot\mathbf{u}_{ij}(t_{2})]\right\rangle, \quad (20)$$

where it is assumed that atoms i and j interact via a potential $v_{ij}(\mathbf{r}_i-\mathbf{r}_j)$. But using Taylor's theorem and Eq. (19), we have

$$\langle v_{ij}(\mathbf{R}_{ij}+\mathbf{u}_{ij})\rangle=\langle\exp(\mathbf{u}_{ij}\cdot\nabla)\rangle v_{ij}(\mathbf{R}_{ij}) =\exp(\tfrac{1}{2}\mathbf{D}_{ij}:\nabla\nabla)v_{ij}(\mathbf{R}_{ij}), \quad (21)$$

where the gradients operate on the explicit $\mathbf{R}_{ij}$ dependence of v, and where

$$\mathbf{D}_{ij}\equiv\langle\mathbf{u}_{ij}\mathbf{u}_{ij}\rangle =N^{-1}\sum_{\mathbf{k}}\sum_{\sigma_1,\sigma_2}i\beta^{-1}\sum_{\nu}(\delta_{\sigma_1,\sigma}-e^{-i\mathbf{k}\cdot\mathbf{R}_{ij}}\delta_{\sigma_1,\sigma'}) \times(\delta_{\sigma_2,\sigma}-e^{i\mathbf{k}\cdot\mathbf{R}_{ij}}\delta_{\sigma_2,\sigma'})\mathbf{D}^{\sigma_1\sigma_2}(\mathbf{k}z). \quad (22)$$

[20] See, e.g., A. A. Maradudin, E. W. Montroll, and G. H. Weiss, *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic Press Inc., New York, 1963), Chap. VII, Sec. 2.

Hence, substituting back into Eq. (20) yields

$$-\beta^{-1}M_1\left(-i\int_0^{-i\beta}dt\ \tilde{V}(t)\right)=\tfrac{1}{2}\sum_{i\neq j}\exp(\tfrac{1}{2}\mathbf{D}_{ij}:\nabla\nabla)v_{ij}(\mathbf{R}_{ij})$$
$$-\tfrac{1}{2}N^{-1}\sum_{\mathbf{k}}\sum_{\sigma,\sigma'}\beta^{-1}\sum_{\nu}\mathbf{D}^{\sigma\sigma'}(\mathbf{k}z):\mathbf{\Phi}^{\sigma\sigma'}(\mathbf{k}z). \quad (23)$$

By truncating the cumulant expansion, keeping only M_1 and discarding all higher cumulants, a minimum principle[21] is established on the free energy,

$$\mathfrak{F}\leq\mathfrak{F}_1\equiv-\beta^{-1}\ln\mathrm{Tr}[\exp(-i\mathcal{S})]$$
$$+\tfrac{1}{2}\sum_{i\neq j}\exp(\tfrac{1}{2}\mathbf{D}_{ij}:\nabla\nabla)v_{ij}(\mathbf{R}_{ij})$$
$$-\tfrac{1}{2}\sum_{\mathbf{k}}\sum_{\sigma,\sigma'}\beta^{-1}\sum_{\nu}\mathbf{D}^{\sigma\sigma'}(\mathbf{k}z):\mathbf{\Phi}^{\sigma\sigma'}(\mathbf{k}z). \quad (24)$$

Thus far no specification has been made of the model force constants $\mathbf{\Phi}_{ij}$. The best choice at this first order of approximation is those which minimize $\mathfrak{F}_1$. Then the stationary condition

$$\delta\mathfrak{F}_1/\delta\mathbf{\Phi}^{\sigma\sigma'}(\mathbf{k}z)=0 \quad (25)$$

leads by straightforward differentiation and application of Eq. (18) to

$$\mathbf{\Phi}^{\sigma\sigma'}(\mathbf{k}z)=\sum_{\tau}\sum_{\sigma''}[\delta_{\sigma,\sigma'}-\delta_{\sigma'',\sigma'}\exp(-i\mathbf{k}\cdot\boldsymbol{\tau}_{\sigma\sigma'})]$$
$$\times\exp[\tfrac{1}{2}\mathbf{D}^{\sigma\sigma''}(\boldsymbol{\tau}_{\sigma\sigma''}):\nabla\nabla]\nabla\nabla v_{\sigma\sigma''}(\boldsymbol{\tau}_{\sigma\sigma''}). \quad (26)$$

We use the notation $\boldsymbol{\tau}_{\sigma\sigma'}\equiv\boldsymbol{\tau}+\mathbf{R}_\sigma-\mathbf{R}_{\sigma'}$, and if we make the correspondence $\mathbf{R}_{ij}\leftrightarrow\boldsymbol{\tau}_{\sigma\sigma'}$, then similarly $\mathbf{D}_{ij}\leftrightarrow\mathbf{D}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})$ and $v_{ij}(\mathbf{R}_{ij})\leftrightarrow v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})$.

One prominent feature of this result is that the right-hand side of (26) is independent of z. This means that to this approximation, which we may term the first-order self-consistent phonon approximation, the best choice of force constants is not retarded and the associated phonons are not damped. It is also significant that the expression differs from that of the quasiharmonic approximation only in the presence of the factor $\exp(\frac{1}{2}\mathbf{D}:\nabla\nabla)$, which tends to unity in the limit of vanishingly small rms displacements. Expanding $\exp(\frac{1}{2}\mathbf{D}:\nabla\nabla)$ in powers of $\mathbf{D}$ shows that only even derivatives of v, in the usual sense of the anharmonic perturbation theory, enter at this first-order approximation. The differential factor can be turned into a more manageable integral expression by Fourier transformation:

$$\exp(\tfrac{1}{2}\mathbf{D}:\nabla\nabla)\nabla\nabla v(\boldsymbol{\tau})=(2\pi)^{-3}\int d^3q\ \exp(-\tfrac{1}{2}\mathbf{D}:\mathbf{qq})$$
$$\times\int d^3u\ \exp(i\mathbf{q}\cdot\mathbf{u})\nabla\nabla v(\boldsymbol{\tau}+\mathbf{u})$$
$$=\int d^3u\ \rho_2(\mathbf{u})\nabla\nabla v(\boldsymbol{\tau}+\mathbf{u}), \quad (27)$$

where

$$\rho_2(\mathbf{u})\equiv\exp(-\tfrac{1}{2}\mathbf{u}\cdot\mathbf{D}^{-1}\cdot\mathbf{u})\Big/\int d^3u$$
$$\times\exp(-\tfrac{1}{2}\mathbf{u}\cdot\mathbf{D}^{-1}\cdot\mathbf{u}). \quad (28)$$

The final form can be interpreted by recognizing that $\rho_2(\mathbf{u})$ is just the diagonal part of the two-particle density matrix for a system of noninteracting phonons with autocorrelation $\mathbf{D}$. Thus the only difference between expression (26) and the force constants in the quasiharmonic approximation is that here the force constants for instantaneous two-particle separation $\boldsymbol{\tau}+\mathbf{u}$ are averaged over the thermal equilibrium distribution of relative displacements $\mathbf{u}$.

To complete the analysis of this first-order approximation, an explicit expression for $\mathbf{D}$ can be exhibited. The first step is to diagonalize the force-constant tensor to obtain phonon eigenfrequencies $\omega_{\mathbf{k}\lambda}$ and orthogonal polarization eigenvectors $\mathbf{e}_{\mathbf{k}\lambda}{}^\sigma$ with branch index λ:

$$\sum_{\sigma'}(M_\sigma M_{\sigma'})^{-1/2}\mathbf{\Phi}^{\sigma\sigma'}(\mathbf{k})\cdot\mathbf{e}_{\mathbf{k}\lambda}{}^{\sigma'}=\omega_{\mathbf{k}\lambda}{}^2\mathbf{e}_{\mathbf{k}\lambda}{}^\sigma. \quad (29)$$

Then the first term in the free-energy expression (24) becomes

$$-\beta^{-1}\ln\mathrm{Tr}[\exp(-i\mathcal{S})]=\beta^{-1}\sum_{\nu}\sum_{\mathbf{k}}\sum_{\sigma,\sigma'}\tfrac{1}{2}\int\delta\mathbf{\Phi}^{\sigma\sigma'}(\mathbf{k}z)$$
$$:[(M_\sigma M_{\sigma'})^{1/2}z^2\mathbf{1}\delta_{\sigma,\sigma'}+\mathbf{\Phi}^{\sigma\sigma'}(\mathbf{k}z)]^{-1}$$
$$=\sum_{\mathbf{k}\lambda}\tfrac{1}{2}\int\delta\omega_{\mathbf{k}\lambda}{}^2(2\omega_{\mathbf{k}\lambda})^{-1}\coth\tfrac{1}{2}\beta\omega_{\mathbf{k}\lambda}$$
$$=\beta^{-1}\sum_{\mathbf{k}\lambda}\ln(2\sinh\tfrac{1}{2}\beta\omega_{\mathbf{k}\lambda}), \quad (30)$$

and so the stationary condition on $\mathfrak{F}_1$, Eq. (25), yields

$$\mathbf{D}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})=N^{-1}\sum_{\mathbf{k}\lambda}(2\omega_{\mathbf{k}\lambda})^{-1}\coth\tfrac{1}{2}\beta\omega_{\mathbf{k}\lambda}$$
$$\times\mathbf{E}_{\mathbf{k}\lambda}{}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})^*\mathbf{E}_{\mathbf{k}\lambda}{}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}), \quad (31)$$

where a compact notation is

$$\mathbf{E}_{\mathbf{k}\lambda}{}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})\equiv M_\sigma{}^{-1/2}\mathbf{e}_{\mathbf{k}\lambda}{}^\sigma-M_{\sigma'}{}^{-1/2}\mathbf{e}_{\mathbf{k}\lambda}{}^{\sigma'}$$
$$\times\exp(-i\mathbf{k}\cdot\boldsymbol{\tau}_{\sigma\sigma'}). \quad (32)$$

Expression (31) shows why the word self-consistent has been used to describe this theoretical approach. The phonon frequencies are the eigenvalues of a dynamical matrix which depends on $\mathbf{D}$, and $\mathbf{D}$ itself depends on the phonon frequencies. The combination of Eqs. (26) and (31), together with definitions (27)–(29) and (32), represent an implicit nonlinear equation for the phonons such that their frequencies depend on their own thermal population.

B. Thermodynamic Derivatives at First Order

1. Pressure

Before going on to consider the next term in the cumulant expansion of $\mathfrak{F}$, it is worth enlarging upon the

[21] Since $\ln\langle e^x\rangle\geq\langle x\rangle$ for positive definite weighting factor. This is the basis for the Peierls variational principle.

results thus far to obtain formulas for some of the thermodynamic derivatives such as the pressure, elastic constants, specific heat, etc. The analysis thus far has determined the phonon modes of vibration for a fixed choice of crystal structure and lattice spacings. But of course these latter are also specified by the requirement that they minimize the free energy. The size and shape of the unit cell can be measured by a tensor $\mathbf{a}$ such that each lattice vector $\boldsymbol{\tau}$ is given by $\boldsymbol{\tau}=\mathbf{a}\cdot\mathbf{n}$, where $\mathbf{n}$ is a set of three integers numbering the unit cells. Thus the volume of the unit cell equals $\det\mathbf{a}$. For cubic crystals, $\mathbf{a}=a\mathbf{1}$, where a is then just the lattice constant. We allow for the possibility (usually a theoretical luxury, but vital when treating solid helium) of an externally applied hydrostatic pressure p, in the presence of which the appropriate thermodynamic potential is the Gibbs free energy,

$$\begin{aligned}\mathcal{G}&=pV+\mathcal{F}\\ &\leq\mathcal{G}_1\equiv pV+\mathcal{F}\\ &=pV+\sum_{\mathbf{k}\lambda}\left[\beta^{-1}\ln(2\sinh\tfrac{1}{2}\beta\omega_{\mathbf{k}\lambda})-\tfrac{1}{4}\omega_{\mathbf{k}\lambda}\coth\tfrac{1}{2}\beta\omega_{\mathbf{k}\lambda}\right]\\ &\quad+\tfrac{1}{2}N\sum_{\boldsymbol{\tau}}\sum_{\sigma,\sigma'}\langle v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle,\end{aligned}\tag{33}$$

where V is the volume of the crystal. Then the condition that $\mathcal{G}$ be stationary with respect to any change in the unit cell becomes

$$\mathbf{a}\cdot(\partial\mathcal{G}/\partial\mathbf{a})=0,\tag{34}$$

which implies

$$p\mathbf{1}=-\tfrac{1}{2}(N/V)\sum_{\boldsymbol{\tau}}\boldsymbol{\tau}\sum_{\sigma,\sigma'}\langle\nabla v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle.\tag{35}$$

This equation can be used either to calculate the lattice constants for fixed pressure or to calculate the pressure for a particular choice of lattice constants.

As it must, the right-hand side of Eq. (35) can be shown to be just the thermal equilibrium average of the microscopic stress tensor operator, but the demonstration requires the additional condition that $\mathcal{G}$ is also stationary with respect to the internal positions $\mathbf{R}_\sigma$ of the atoms within the unit cell, subject to the constraint that $\sum_\sigma\mathbf{R}_\sigma=0$. The condition

$$\partial(\mathcal{G}-\boldsymbol{\Lambda}\cdot\sum_{\sigma'}\mathbf{R}_{\sigma'})/\partial\mathbf{R}_\sigma=0,\tag{36}$$

using a Lagrange parameter $\boldsymbol{\Lambda}$ for the constraint, yields

$$N\sum_{\boldsymbol{\tau}}\sum_{\sigma'\neq\sigma}\langle\nabla v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle-\boldsymbol{\Lambda}=0.\tag{37}$$

The only physically reasonable solution is that there is no net force on any atom,

$$\sum_{\boldsymbol{\tau}}\sum_{\sigma'}\langle\nabla v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle=0,\tag{38a}$$

which implies that

$$\boldsymbol{\Lambda}=-N\textstyle\sum_{\boldsymbol{\tau}}\sum_{\sigma}\langle\nabla v_{\sigma\sigma}(\boldsymbol{\tau}+\mathbf{u})\rangle.\tag{38b}$$

Also, multiplying Eq. (37) by $\mathbf{R}_\sigma$ and summing on σ gives the important condition

$$\tfrac{1}{2}N\sum_{\boldsymbol{\tau}}\sum_{\sigma,\sigma'}\mathbf{R}_{\sigma\sigma'}\langle\nabla v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle=0.\tag{39}$$

Adding this null expression to Eq. (35) shows that the stress tensor can equally well be written

$$p\mathbf{1}=-\tfrac{1}{2}(N/V)\sum_{\boldsymbol{\tau}}\sum_{\sigma,\sigma'}\boldsymbol{\tau}_{\sigma\sigma'}\langle\nabla v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle,\tag{35'}$$

which is just the form obtained microscopically.

2. *Isothermal Elastic Constants*

Although there is no ambiguity in calculating the stress tensor either macroscopically or microscopically, the evaluation of the elastic constants does present a dilemma. The macroscopic elastic constants are defined, in general,[22,23] as the fourth-rank tensor

$$\mathbf{C}=V^{-1}(\mathbf{a}\cdot\partial/\partial\mathbf{a})(\mathbf{a}\cdot\partial/\partial\mathbf{a})\mathcal{G}-p\mathbf{I},\tag{40}$$

with the notation

$$(\mathbf{I})_{\alpha\beta\gamma\delta}=\delta_{\alpha,\beta}\delta_{\gamma,\delta}-\delta_{\alpha,\delta}\delta_{\beta,\gamma}.\tag{41}$$

Carrying out the second differentiation, beginning with Eq. (35) for the stress tensor, leads to the (isothermal) elastic constants

$$\begin{aligned}\mathbf{C}=\tfrac{1}{2}(N/V)\sum_{\boldsymbol{\tau}}\sum_{\sigma,\sigma'}\big[&\langle(\boldsymbol{\tau}\nabla)(\boldsymbol{\tau}\nabla)v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle\\ &+\langle(\boldsymbol{\tau}\nabla)\nabla v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle\cdot(\mathbf{a}\cdot\partial/\partial\mathbf{a})\mathbf{R}_{\sigma\sigma'}\\ &+\tfrac{1}{2}\langle(\boldsymbol{\tau}\nabla)\nabla\nabla v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle:(\mathbf{a}\cdot\partial/\partial\mathbf{a})\mathbf{D}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})\big].\end{aligned}\tag{42}$$

The second line in this expression can be evaluated by differentiating the internal equilibrium condition (38),

$$\begin{aligned}&(\mathbf{a}\cdot\partial/\partial\mathbf{a})\sum_{\boldsymbol{\tau}}\sum_{\sigma'}\langle\nabla v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle\\ &=\sum_{\boldsymbol{\tau}}\sum_{\sigma'}\big[\langle(\boldsymbol{\tau}\nabla)\nabla v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle+\langle\nabla\nabla v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle\\ &\quad\times(\mathbf{a}\cdot\partial/\partial\mathbf{a})\mathbf{R}_{\sigma\sigma'}+\tfrac{1}{2}\langle\nabla\nabla\nabla v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle\\ &\qquad:(\mathbf{a}\cdot\partial/\partial\mathbf{a})\mathbf{D}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})\big]=0.\end{aligned}\tag{43}$$

This latter equation can be solved for $(\mathbf{a}\cdot\partial/\partial\mathbf{a})\mathbf{R}_\sigma$ by using Eqs. (26) and (29) at $\mathbf{k}=0$,

$$\begin{aligned}&(\mathbf{a}\cdot\partial/\partial\mathbf{a})\mathbf{R}_\sigma\\ &=-\sum_{\lambda}{}'\,\omega_{0\lambda}{}^{-2}\sum_{\sigma'}(M_\sigma M_{\sigma'})^{-1/2}\mathbf{e}_{0\lambda}{}^{\sigma}\mathbf{e}_{0\lambda}{}^{\sigma'}\\ &\quad\times\sum_{\boldsymbol{\tau}}\sum_{\sigma''}\big[\langle(\boldsymbol{\tau}\nabla)v_{\sigma'\sigma''}(\boldsymbol{\tau}_{\sigma'\sigma''}+\mathbf{u})\rangle\\ &\quad+\tfrac{1}{2}\langle\nabla\nabla\nabla v_{\sigma'\sigma''}(\boldsymbol{\tau}_{\sigma'\sigma''}+\mathbf{u})\rangle:(\mathbf{a}\cdot\partial/\partial\mathbf{a})\mathbf{D}^{\sigma'\sigma''}(\boldsymbol{\tau}_{\sigma'\sigma''})\big],\end{aligned}\tag{44}$$

[22] G. Leibfried and W. Ludwig, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1961), Vol. 12, pp. 257ff.

[23] T. H. K. Barron and M. L. Klein, Proc. Phys. Soc. (London) 85, 523 (1965).

where the prime on the λ sum omits the three acoustic branches for which $\omega_{0\lambda}{}^2=0$. Substituting into Eq. (42) and rearranging leads to

$$\mathbf{C}=\tfrac{1}{2}(N/V)\sum_{\tau}\sum_{\sigma,\sigma'}\langle(\boldsymbol{\tau}\nabla)(\boldsymbol{\tau}\nabla)v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle - (N/V)\sum_{\lambda}{}'\,\omega_{0\lambda}{}^{-2}\mathbf{U}_\lambda\mathbf{U}_\lambda+\mathbf{C}', \quad (45)$$

where it is convenient to introduce the notation

$$\mathbf{U}_\lambda\equiv\sum_{\tau}\sum_{\sigma,\sigma'}\tfrac{1}{2}\langle(\boldsymbol{\tau}\nabla)\nabla v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle\cdot\mathbf{E}_{0\lambda}{}^{\sigma\sigma'}, \quad (46)$$

and where the $\mathbf{C}'$ term contains the effects of the variation of $\mathbf{D}$,

$$\mathbf{C}'=\tfrac{1}{2}(N/V)\sum_{\tau}\sum_{\sigma,\sigma'}\tfrac{1}{2}(\boldsymbol{\tau}\mathbf{1}-\sum_{\lambda}{}'\,\omega_{0\lambda}{}^{-2}\mathbf{U}_\lambda\mathbf{E}_{0\lambda}{}^{\sigma\sigma'}) \times\langle\nabla\nabla\nabla v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle:(\mathbf{a}\cdot\partial/\partial\mathbf{a})\mathbf{D}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}). \quad (47)$$

To construct an equation determining the variation of $\mathbf{D}$, we begin by differentiating Eqs. (31) and (29). Substituting the latter into the former leads to

$$(\mathbf{a}\cdot\partial/\partial\mathbf{a})\mathbf{D}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})=N^{-1}\sum_{\mathbf{k}}\sum_{\lambda,\lambda'}\Delta_{\mathbf{k}\lambda\lambda'} \times\mathbf{E}_{\mathbf{k}\lambda}{}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})\mathbf{E}_{\mathbf{k}\lambda'}{}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})^*\mathbf{g}_{\mathbf{k}\lambda\lambda'}, \quad (48)$$

where it is convenient to introduce the auxiliary quantities,

$$\mathbf{g}_{\mathbf{k}\lambda\lambda'}\equiv\sum_{\sigma,\sigma'}(M_\sigma M_{\sigma'})^{-1/2}\mathbf{e}_{\mathbf{k}\lambda}{}^{\sigma}\mathbf{e}_{\mathbf{k}\lambda'}{}^{\sigma}:(\mathbf{a}\cdot\partial/\partial\mathbf{a})\boldsymbol{\Phi}^{\sigma\sigma'}(\mathbf{k}) \quad (49)$$

and

$$\Delta_{\mathbf{k}\lambda\lambda'}\equiv\frac{1}{\omega_{\mathbf{k}\lambda}{}^2-\omega_{\mathbf{k}\lambda'}{}^2}\left(\frac{\coth\frac{1}{2}\beta\omega_{\mathbf{k}\lambda}}{2\omega_{\mathbf{k}\lambda}}-\frac{\coth\frac{1}{2}\beta\omega_{\mathbf{k}\lambda'}}{2\omega_{\mathbf{k}\lambda'}}\right),\quad\lambda\neq\lambda'$$
$$\equiv\frac{1}{2\omega_{\mathbf{k}\lambda}}\frac{\partial}{\partial\omega_{\mathbf{k}\lambda}}\left(\frac{\coth\frac{1}{2}\beta\omega_{\mathbf{k}\lambda}}{2\omega_{\mathbf{k}\lambda}}\right),\quad\lambda=\lambda'. \quad (50)$$

Finally, differentiating Eq. (26) and substituting into Eq. (49) gives

$$\mathbf{g}_{\mathbf{k}\lambda\lambda'}=\sum_{\tau}\sum_{\sigma,\sigma'}\tfrac{1}{2}\mathbf{E}_{\mathbf{k}\lambda}{}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})\mathbf{E}_{\mathbf{k}\lambda'}{}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})^* :[\langle\nabla\nabla\nabla v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle\cdot(\mathbf{a}/\partial\cdot\partial\mathbf{a})\boldsymbol{\tau}_{\sigma\sigma'} +\tfrac{1}{2}\langle\nabla\nabla\nabla\nabla v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle:(\mathbf{a}\cdot\partial/\partial\mathbf{a})\mathbf{D}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})]. \quad (51)$$

The combination of Eqs. (44), (48), and (51) represent a set of linear inhomogeneous equations for $(\mathbf{a}\cdot\partial/\partial\mathbf{a})\times\mathbf{D}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})$. To present these equations in a simple form, we use the notation κ to denote the set of indices $(\mathbf{k},\lambda,\bar{\lambda})$, and we define the quantities

$$W_{\kappa\lambda''}\equiv\sum_{\tau}\sum_{\sigma,\sigma'}\mathbf{E}_{0\lambda''}{}^{\sigma\sigma'}\cdot\langle\nabla\nabla\nabla v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle :\tfrac{1}{2}\mathbf{E}_{\mathbf{k}\lambda}{}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})\mathbf{E}_{\mathbf{k}\bar{\lambda}}{}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})^*, \quad (52)$$

$$\mathbf{Q}_\kappa\equiv\sum_{\tau}\sum_{\sigma,\sigma'}\boldsymbol{\tau}\langle\nabla\nabla\nabla v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle :\tfrac{1}{2}\mathbf{E}_{\mathbf{k}\lambda}{}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})\mathbf{E}_{\mathbf{k}\bar{\lambda}}{}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})^* \quad (53)$$

and

$$Y_{\kappa,\kappa'}\equiv\sum_{\tau}\sum_{\sigma,\sigma'}\tfrac{1}{2}\mathbf{E}_{\mathbf{k}\lambda}{}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})\mathbf{E}_{\mathbf{k}\bar{\lambda}}{}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})^* :\langle\nabla\nabla\nabla\nabla v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle:\tfrac{1}{2}\mathbf{E}_{\mathbf{k}'\lambda'}{}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})\mathbf{E}_{\mathbf{k}'\bar{\lambda}'}{}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})^* -\tfrac{1}{2}\sum_{\lambda''}{}'\,\omega_{0\lambda''}{}^{-2}W_{\kappa\lambda''}W_{\kappa'\lambda''}. \quad (54)$$

We also introduce the representation

$$(\mathbf{a}\cdot\partial/\partial\mathbf{a})\mathbf{D}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}) =N^{-1}\sum_{\mathbf{k}}\sum_{\lambda,\bar{\lambda}}\mathbf{d}_\kappa\mathbf{E}_{\mathbf{k}\lambda}{}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})\mathbf{E}_{\mathbf{k}\bar{\lambda}}{}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})^*, \quad (55)$$

in terms of a quantity $\mathbf{d}_\kappa$ which can then be shown to satisfy the linear inhomogeneous equation

$$\mathbf{d}_\kappa=\Delta_\kappa(\mathbf{Q}_\kappa+\sum_{\kappa'}Y_{\kappa\kappa'}\mathbf{d}_{\kappa'}). \quad (56)$$

This equation has the formal solution

$$\mathbf{d}_\kappa=\sum_{\kappa'}(1-\Delta Y)_{\kappa\kappa'}{}^{-1}\Delta_{\kappa'}\mathbf{Q}_{\kappa'}. \quad (57)$$

The correction $\mathbf{C}'$ to the elastic constants can then be expressed in terms of $\mathbf{d}_\kappa$, from Eq. (47), as

$$\mathbf{C}'=\tfrac{1}{2}V^{-1}\sum_{\kappa}\mathbf{Q}_\kappa\mathbf{d}_\kappa =\tfrac{1}{2}V^{-1}\sum_{\kappa,\kappa'}\mathbf{Q}_\kappa(1-\Delta Y)_{\kappa\kappa'}{}^{-1}\Delta_{\kappa'}\mathbf{Q}_{\kappa'}. \quad (58)$$

It is an unfortunate fact that Eq. (58) for $\mathbf{C}'$ involves the solution of a complicated equation (which becomes an integral equation in the limit of large crystal volume where the $\mathbf{k}$ vectors form a continuum) rather than being just a straightforward algebraic expression. The kernel Y of the linear equation represents the coupling between phonon modes arising implicitly by their being determined self-consistently, i.e., dependent on their own thermal amplitudes. Since ΔY is schematically of order $\langle u^2\rangle^2\langle\nabla^4 v\rangle/\omega$, involving an average of a higher derivative of the interatomic potential, it is not expected to be large. In fact, numerical computations by Horner,[7] by Koehler,[12] and by Goldman *et al.*[11] indicate that ΔY is of order 0.1 in helium and in neon at temperatures near to melting. Thus it is a fairly crude approximation to neglect ΔY altogether, although it might be sufficient to retain only the diagonal part of ΔY and to approximate

$$\mathbf{C}'\cong\tfrac{1}{2}V^{-1}\textstyle\sum_\kappa\mathbf{Q}_\kappa\Delta_\kappa\mathbf{Q}_\kappa/(1-\Delta_\kappa Y_{\kappa\kappa}). \quad (59)$$

Much computational work remains to be done in studying $Y_{\kappa\kappa'}$ in numerical detail.

The formulas just derived for the elastic constants are not entirely unique because they have not taken

account of the alternative expressions (35) and (35′) for the stress tensor. Equations (45) and (58) are derived from expression (35), whereas different but equivalent formulas could be obtained starting from expression (35′) together with derivatives of the internal equilibrium condition (39). Considerable algebraic manipulation is required to simplify these alternative formulas, but the results are that equivalently

$$\mathbf{C}=\tfrac{1}{2}(N/V)\sum_{\tau}\sum_{\sigma,\sigma'}\langle(\boldsymbol{\tau}_{\sigma\sigma'}\nabla)(\boldsymbol{\tau}_{\sigma\sigma'}\nabla)v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle -(N/V)\sum_{\lambda}{}'\,\omega_{0\lambda}{}^{-2}\mathbf{U}_{\lambda}\mathbf{U}_{\lambda}+\mathbf{C}', \quad (45')$$

$$\mathbf{U}_{\lambda}=\sum_{\tau}\sum_{\sigma,\sigma'}\tfrac{1}{2}\langle(\boldsymbol{\tau}_{\sigma\sigma'}\nabla)\nabla v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle\cdot\mathbf{E}_{0\lambda}{}^{\sigma\sigma'}, \quad (46')$$

$$\mathbf{Q}_{\kappa}=\sum_{\tau}\sum_{\sigma,\sigma'}\langle(\boldsymbol{\tau}_{\sigma\sigma'}\nabla)\nabla\nabla v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle :\tfrac{1}{2}\mathbf{E}_{\mathbf{k}\lambda}{}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})\mathbf{E}_{\mathbf{k}\bar{\lambda}}{}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})^{*} -\sum_{\lambda''}{}'\,\omega_{0\lambda''}{}^{-2}\mathbf{U}_{\lambda''}W_{\kappa\lambda''}, \quad (53')$$

while Eqs. (52), (54), and (58) for $W_{\kappa\lambda''}$, $Y_{\kappa,\kappa'}$ and $\mathbf{C}'$, respectively, are formally unchanged. The net effect of the alternative derivation has been to replace the lattice vector $\boldsymbol{\tau}$ everywhere that it occurs explicitly by the vector $\boldsymbol{\tau}_{\sigma\sigma'}=\boldsymbol{\tau}+\mathbf{R}_{\sigma\sigma'}$.

The dilemma in definition of the elastic constants which was referred to at the start of this subsection arises upon noting that the elastic constants also have a microscopic definition, in terms of the long-wavelength limit of the phonon dynamical matrix,

$$\lim_{\mathbf{k}\to 0}\rho\omega_{\mathbf{k}\lambda}{}^{2}=\mathbf{k}\hat{e}_{\lambda}:\mathbf{C}:\mathbf{k}\hat{e}_{\lambda}. \quad (60)$$

Here ρ is the mass density and λ indexes the three acoustic modes, which are taken to have long-wavelength orthornormal polarization vectors $\hat{e}_{\lambda}$. If the full Hamiltonian is treated exactly, the macroscopic and microscopic definitions (40) and (60) can be proved rigorously[24] to be equivalent at zero temperature. However, to any finite order of approximation in a systematic perturbation treatment of the dynamics, the two definitions are never equivalent, and, furthermore, the difference between them is a measure of the inaccuracy of the approximation. Thus, in our case the long-wavelength limit of the dynamical matrix (26) leads to elastic constants given by Eq. (45′) but with $\mathbf{C}'=0$. As will be demonstrated in Sec. II C, the quantity $\mathbf{C}'$ is roughly the contribution to the phonon dynamical matrix of the next higher cumulant M_2 in the free-energy expansion. It should also be noted that the expressions exhibited here for the stress tensor and elastic constants (with $\mathbf{C}'=0$) are the same as those obtained[22] in the usual quasiharmonic approximation, except that the interatomic potential is here replaced by its thermal average over dynamic interparticle separations.

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

Note added in proof. Results for the elastic constants similar to those obtained here have also been derived using a different technique by W. Götze and K. H. Michel, Z. Physik **217**, 170 (1968).

3. *Specific Heats and Thermal Strain*

Turning from strain derivatives to temperature derivatives, explicit expressions for the specific heat can also be worked out. From Eq. (33) the entropy is

$$S=\sum_{\mathbf{k}\lambda}[\tfrac{1}{2}\beta\omega_{\mathbf{k}\lambda}\coth\tfrac{1}{2}\beta\omega_{\mathbf{k}\lambda}-\ln(2\sinh\tfrac{1}{2}\beta\omega_{\mathbf{k}\lambda})], \quad (61)$$

as in any noninteracting phonon system. The specific heat, the temperature derivative of the entropy, depends on the external mechanical constraints imposed on the crystal during the temperature change. The situations usually envisioned are constant pressure or constant volume. In the case of noncubic crystals, however, it is also possible to consider[25] the case of constant strain, in which the shape as well as the size of the unit cell is held fixed. Since a "constant volume" specific-heat measurement is usually carried out with the sample filling a closed rigid can, it is the constant strain situation which is more relevant. Denoting this specific heat by c_{a}, it is found from differentiating Eqs. (61) that the macroscopic definition,

$$c_{\mathrm{a}}/V=-(\beta/V)(\partial S/\partial\beta)_{\mathrm{a}}, \quad (62)$$

works out to

$$c_{\mathrm{a}}/V=V^{-1}\sum_{\mathbf{k}\lambda}(\tfrac{1}{2}\beta\omega_{\mathbf{k}\lambda})^{2}\,\mathrm{csch}^{2}(\tfrac{1}{2}\beta\omega_{\mathbf{k}\lambda})+c_{\mathrm{a}}'/V, \quad (63)$$

where

$$c_{\mathrm{a}}'/V=\tfrac{1}{8}\beta^{3}V^{-1}\sum_{\mathbf{k}\lambda}(\partial\omega_{\mathbf{k}\lambda}{}^{2}/\partial\beta)\mathrm{csch}^{2}(\tfrac{1}{2}\beta\omega_{\mathbf{k}\lambda}) \quad (64)$$

is the correction term due to the temperature dependence of the phonon frequencies. Differentiating Eqs. (29), (26), (31), and (38) with respect to β, and performing manipulations similar to those used for the calculation of the elastic constants, leads to the final formula

$$c_{\mathrm{a}}'/V=-\tfrac{1}{8}\beta^{3}V^{-1}\sum_{\kappa}N^{-1}\sum_{\kappa'\kappa''}c_{\kappa}Y_{\kappa\kappa''}(1-\Delta Y)_{\kappa''\kappa'}{}^{-1}c_{\kappa'}, \quad (65)$$

where we introduce the notation

$$c_{\kappa}\equiv\tfrac{1}{2}\delta_{\lambda,\bar{\lambda}}\,\mathrm{csch}^{2}(\tfrac{1}{2}\beta\omega_{\mathbf{k}\lambda}). \quad (66)$$

Exactly the same integral equation is required to be solved for Eq. (65) as in the elastic-constant expression (58).

The specific heat at constant pressure c_p has an additional contribution coming from lattice constant changes with temperature. The difference c_p-c_{a} turns out to conform to the standard thermodynamic requirement

[25] T. H. K. Barron and R. W. Munn, J. Phys. **C1**, 1 (1968).

that

$$(c_p-c_a)/V=\beta^{-1}\mathbf{A}^\dagger:(\mathbf{C}+p\mathbf{I}):\mathbf{A}, \tag{67}$$

where $\mathbf{A}$ is the (second-rank) thermal strain tensor,

$$\mathbf{A}\equiv-\beta^2(\partial\mathbf{a}/\partial\beta)_p\cdot\mathbf{a}^{-1}. \tag{68}$$

The thermal strain tensor is calculated by differentiating the stress tensor, Eq. (35), resulting in the expression

$$\mathbf{A}=-\tfrac{1}{4}\beta^2(\mathbf{C}+p\mathbf{I})^{-1}:V^{-1}\sum_{\kappa,\kappa'}\mathbf{Q}_\kappa(1-\Delta Y)_{\kappa\kappa'}^{-1}c_{\kappa'}. \tag{69}$$

Again the solution of the integral equation enters. The quantity $\mathbf{C}+p\mathbf{I}$ is the (fourth-rank) bulk modulus tensor, whose inverse is to be calculated as if it were a 9×9 second-rank tensor.

The calculation of the specific heat at constant volume c_V is very similar to that of c_p, except that in differentiating the stress tensor Eq. (35), the extra term $(\partial p/\partial\beta)_V$ arises, which is to be determined through the constant-volume constraint, $(\partial\mathbf{a}/\partial\beta):\mathbf{a}^{-1}=0$. This term produces the familiar thermodynamic relation

$$(c_p-c_V)/V=\alpha^2/\beta\chi, \tag{70}$$

where α is the coefficient of thermal expansion and χ is the isothermal compressibility. In terms of the tensors just defined, we have

$$\alpha\equiv V^{-1}(\partial V/\partial T)_p=\mathbf{A}:\mathbf{1}, \tag{71}$$

$$\chi\equiv-V^{-1}(\partial V/\partial p)_T=\mathbf{1}:(\mathbf{C}+p\mathbf{I})^{-1}:\mathbf{1}, \tag{72}$$

and the bulk modulus is

$$\kappa\equiv-V(\partial p/\partial V)_T=\tfrac{1}{9}\mathbf{1}:(\mathbf{C}+p\mathbf{I}):\mathbf{1}. \tag{73}$$

4. *Adiabatic Elastic Constants*

The adiabatic elastic constants differ from the macroscopic definition (40) of the isothermal elastic constants by allowing the temperature to vary with strain subject to the constraint of constant entropy. This calculation requires differentiating Eq. (61) to calculate $(\mathbf{a}\cdot\partial\beta/\partial\mathbf{a})_S$. The result is again that expected from thermodynamic arguments,

$$\mathbf{C}^{ad}-\mathbf{C}^{is}=(\beta c_a/V)^{-1}[(\mathbf{C}^{is}+p\mathbf{I}):\mathbf{A}]^2. \tag{74}$$

C. Second-Order Approximation to $\mathcal{F}$

Having completed our discussion of the first-order self-consistent phonon approximation, we can proceed to consider the second-order term in the cumulant expansion of $\mathcal{F}$. This term gives the leading contribution to the phonon damping rate and also produces a frequency shift connected with the damping through the Kramers-Kronig relations.

Including the second-order cumulant, the free-energy functional becomes

$$\mathcal{F}\cong\mathcal{F}_2\equiv\mathcal{F}_1-\tfrac{1}{2}\beta^{-1}M_2\left(-i\int_0^{-i\beta}dt\;\tilde{V}(t)\right)$$

$$=\mathcal{F}_1+\tfrac{1}{2}\beta^{-1}\int_0^{-i\beta}dt_1\int_0^{-i\beta}dt_2$$

$$\times\{\langle T[\tilde{V}(t_1)\tilde{V}(t_2)]\rangle-\langle\tilde{V}\rangle^2\}. \tag{75}$$

Although it is rigorously true that $\mathcal{F}_1\geq\mathcal{F}$, so that a minimization of $\mathcal{F}_1$ is justified as an optimization procedure, there is no longer any general inequality between $\mathcal{F}_2$ and $\mathcal{F}$. Nevertheless, we still select $\mathbf{\Phi}_{ij}(t_1-t_2)$ by requiring that $\mathcal{F}_2$ have stationary variation, through appeal to the condition that $\mathcal{F}_2-\mathcal{F}_1$ in some sense be small. Furthermore, if $\mathcal{F}_2-\mathcal{F}_1$ is a small correction, then it is valid to replace in $\mathcal{F}_2-\mathcal{F}_1$ the factors $\mathbf{\Phi}$ occurring in $\tilde{V}$ by the first-order result, Eq. (26). That is, the approximate expression

$$\tilde{V}(t)\cong\tfrac{1}{2}\sum_{i\neq j}\{e^{\mathbf{u}_{ij}(t)\cdot\nabla}-\tfrac{1}{2}[\mathbf{u}_{ij}(t)\cdot\nabla]^2\langle e^{\mathbf{u}_{ij}\cdot\nabla}\rangle\}v_{ij}(\mathbf{R}_{ij}) \tag{76}$$

is to be substituted into Eq. (75). Rearranging the terms considerably and making liberal use of the Guassian averaging theorem, Eq. (19), leads to the form

$$\mathcal{F}_2-\mathcal{F}_1=\tfrac{1}{4}\sum_{i\neq j}\sum_{l\neq m}\beta^{-1}\int_0^{-i\beta}dt_1\int_0^{-i\beta}dt_2$$

$$\times\tfrac{1}{2}\mathcal{E}_3(\mathbf{D}_{ijlm}(t_1-t_2):\nabla_{ij}\nabla_{lm})$$

$$\times\exp(\tfrac{1}{2}\mathbf{D}_{ij}:\nabla_{ij}\nabla_{ij}+\tfrac{1}{2}\mathbf{D}_{lm}:\nabla_{lm}\nabla_{lm})$$

$$\times v_{ij}(\mathbf{R}_{ij})v_{lm}(\mathbf{R}_{lm}). \tag{77}$$

It proves convenient here to introduce the functions

$$\mathcal{E}_n(x)\equiv e^x-\sum_{s=0}^{n-1}(s!)^{-1}x^s, \tag{78}$$

and to use the notation

$$\mathbf{D}_{ijlm}(t-t')\equiv\langle T[\mathbf{u}_{ij}(t)\mathbf{u}_{lm}(t')]\rangle, \tag{79}$$

which can be expressed in terms of the displacement propagator as

$$\mathbf{D}_{ijlm}(t-t')=i\beta^{-1}\textstyle\sum_\nu e^{-iz(t-t')}N^{-1}\sum_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{R}_{\xi\eta}}$$

$$\times(\delta_{\xi,i}-\delta_{\xi,j})(\delta_{\eta,m}-\delta_{\eta,l})\mathbf{D}^{\sigma_\xi\sigma_\eta}(\mathbf{k}z), \tag{80}$$

a generalization of Eq. (22). Then the condition of stationary variation,

$$\delta\mathcal{F}_2/\delta\mathbf{\Phi}^{\sigma\sigma'}(\mathbf{k}z)=0, \tag{81}$$

leads to the result for $\mathbf{\Phi}$,

$$\mathbf{\Phi}^{\sigma\sigma'}(\mathbf{k}z)=\sum_{\tau}\sum_{\sigma''}[\delta_{\sigma,\sigma'}-\delta_{\sigma'',\sigma'}\exp(-i\mathbf{k}\cdot\boldsymbol{\tau}_{\sigma\sigma'})]\langle\nabla\nabla v_{\sigma\sigma''}(\boldsymbol{\tau}_{\sigma\sigma''}+\mathbf{u})\rangle-i\int_0^{-i\beta}dt\,e^{izt}\sum_{\tau,\tau',\tau''}\sum_{\sigma_1,\sigma_1'}\sum_{\sigma_2,\sigma_2'}\tfrac{1}{2}\exp(-i\mathbf{k}\cdot\boldsymbol{\tau}_{\sigma_1\sigma_2}'')$$
$$\times[\delta_{\sigma,\sigma_1}-\delta_{\sigma,\sigma_1'}\exp(i\mathbf{k}\cdot\boldsymbol{\tau}_{\sigma_1\sigma_1'})][\delta_{\sigma',\sigma_2}-\delta_{\sigma',\sigma_2'}\exp(-i\mathbf{k}\cdot\boldsymbol{\tau}_{\sigma_2\sigma_2'})]$$
$$\times\tfrac{1}{2}\mathcal{S}_2(\beta^{-1}\sum_{\nu}e^{-izt}N^{-1}\sum_{\mathbf{k}'}\sum_{\sigma_3,\sigma_3'}\tfrac{1}{2}\exp(i\mathbf{k}'\cdot\boldsymbol{\tau}_{\sigma_1\sigma_2}'')[\delta_{\sigma_3,\sigma_1}-\delta_{\sigma_3,\sigma_1'}\exp(-i\mathbf{k}'\cdot\boldsymbol{\tau}_{\sigma_1\sigma_1'})]$$
$$\times[\delta_{\sigma_3',\sigma_2}-\delta_{\sigma_3',\sigma_2'}\exp(i\mathbf{k}'\cdot\boldsymbol{\tau}_{\sigma_2\sigma_2'})]\mathbf{D}^{\sigma_3\sigma_3'}(\mathbf{k}',z):\nabla\nabla')\langle\nabla v_{\sigma_1\sigma_1'}(\boldsymbol{\tau}_{\sigma_1\sigma_1'}+\mathbf{u})\rangle\langle\nabla' v_{\sigma_2\sigma_2'}(\boldsymbol{\tau}_{\sigma_2\sigma_2'}+\mathbf{u})\rangle. \quad (82)$$

The expression for $\mathbf{\Phi}$ exhibited in Eq. (82) arises from differentiating, as per Eq. (81), the $\mathbf{D}_{ijlm}$ term in Eq. (77). Strictly speaking, there should be additional contributions to $\mathbf{\Phi}$ arising from differentiating the $\mathbf{D}_{ij}$ and $\mathbf{D}_{lm}$ terms in Eq. (77), but these contributions are expected to be negligible (and, in any event, do not give rise to any phonon damping) and are not included here.

The complex variables z and t can now be analytically continued to the real axis in the usual way.[18] We introduce a spectral representation for the quantity $\mathbf{D}^{\sigma\sigma'}(\mathbf{k}z)$,

$$\mathbf{D}^{\sigma\sigma'}(\mathbf{k}z)=\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\frac{2\omega}{z^2-\omega^2}\mathbf{A}^{\sigma\sigma'}(\mathbf{k}\omega), \quad (83)$$

in terms of a spectral weight function $\mathbf{A}^{\sigma\sigma'}(\mathbf{k}\omega)$. In the first-order approximation the spectral function was a sum of δ functions,

$$\mathbf{A}^{\sigma\sigma'}(\mathbf{k}\omega)\cong\sum_{\lambda}(M_\sigma M_{\sigma'})^{-1/2}\mathbf{e}_{\mathbf{k}\lambda}{}^{\sigma}\mathbf{e}_{\mathbf{k}\lambda}{}^{\sigma'*}(\pi/2\omega_{\mathbf{k}\lambda})$$
$$\times[\delta(\omega-\omega_{\mathbf{k}\lambda})-\delta(\omega+\omega_{\mathbf{k}\lambda})], \quad (84)$$

whereas to second order the δ functions become broadened because of the finite phonon lifetimes. Nonetheless, it is convenient to use the first-order phonon eigenvectors $\mathbf{e}_{\mathbf{k}\lambda}{}^{\sigma}$ as a basis set and to further represent

$$\mathbf{A}^{\sigma\sigma'}(\mathbf{k}\omega)=\sum_{\lambda,\lambda'}(M_\sigma M_{\sigma'})^{-1/2}\mathbf{e}_{\mathbf{k}\lambda}{}^{\sigma}\mathbf{e}_{\mathbf{k}\lambda'}{}^{\sigma'*}A_{\lambda\lambda'}(\mathbf{k}\omega). \quad (85)$$

Then the analytic continuation of $\mathbf{\Phi}^{\sigma\sigma'}(\mathbf{k}z)$ to the real frequency axis becomes, in the polarization index representation,

$$\Phi_{\lambda\lambda'}(\mathbf{k}\omega)\equiv\sum_{\sigma,\sigma'}(M_\sigma M_{\sigma'})^{-1/2}\mathbf{e}_{\mathbf{k}\lambda}{}^{\sigma*}\mathbf{e}_{\mathbf{k}\lambda'}{}^{\sigma'}:\mathbf{\Phi}^{\sigma\sigma'}(\mathbf{k}\omega)$$
$$=\sum_{\tau}\sum_{\sigma,\sigma'}\tfrac{1}{2}\mathbf{E}_{\mathbf{k}\lambda}{}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'})^*\mathbf{E}_{\mathbf{k}\lambda'}{}^{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}):\langle\nabla\nabla v_{\sigma\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle+\int_0^{\infty}dt\,e^{i\omega t}2\,\mathrm{Im}\Big[\sum_{\tau,\tau',\tau''}\sum_{\sigma_1,\sigma_1'}\sum_{\sigma_2,\sigma_2'}$$
$$\times\exp(-i\mathbf{k}\cdot\boldsymbol{\tau}_{\sigma_1\sigma_2}'')\tfrac{1}{2}\mathbf{E}_{\mathbf{k}\lambda}{}^{\sigma_1\sigma_1'}(\boldsymbol{\tau}_{\sigma_1\sigma_1'})^*\mathbf{E}_{\mathbf{k}\lambda'}{}^{\sigma_2\sigma_2'}(\boldsymbol{\tau}_{\sigma_2\sigma_2'}):\tfrac{1}{2}\mathcal{S}_2\Big(N^{-1}\sum_{\mathbf{k}}\sum_{\lambda,\lambda'}\exp(i\mathbf{k}\cdot\boldsymbol{\tau}_{\sigma_1\sigma_2}'')\tfrac{1}{2}\mathbf{E}_{\mathbf{k}\lambda}{}^{\sigma_1\sigma_1'}(\boldsymbol{\tau}_{\sigma_1\sigma_1'})$$
$$\times\mathbf{E}_{\mathbf{k}\lambda'}{}^{\sigma_2\sigma_2'}(\boldsymbol{\tau}_{\sigma_2\sigma_2'})^*(2\pi)^{-1}\int_{-\infty}^{\infty}d\omega\,A_{\lambda\lambda'}(\mathbf{k}\omega)(\cos\omega t\coth\tfrac{1}{2}\beta\omega_{\mathbf{k}\lambda}-i\sin\omega t):\nabla\nabla'\Big)$$
$$\times\langle\nabla v_{\sigma_1\sigma_1'}(\boldsymbol{\tau}_{\sigma_1\sigma_1'}+\mathbf{u})\rangle\langle\nabla' v_{\sigma_2\sigma_2'}(\boldsymbol{\tau}_{\sigma_2\sigma_2'}+\mathbf{u})\rangle\Big]. \quad (86)$$

Furthermore, the relationship between $\mathbf{D}^{\sigma\sigma'}$ and $\mathbf{\Phi}^{\sigma\sigma'}$ is such that $A_{\lambda\lambda'}(\mathbf{k}\omega)$ is determined via an equation of the Dyson type,

$$A_{\lambda\lambda'}(\mathbf{k}\omega)=\mathrm{Im}\{[\omega^2\delta_{\lambda,\lambda'}-\Phi_{\lambda\lambda'}(\mathbf{k}\omega)]^{-1}\}, \quad (87)$$

where matrix inversion is implied. The last pair of equations, (86) and (87), together give a self-consistency condition on the phonons, but here in the second-order approximation the phonons are characterized by the spectral weight function $A_{\lambda\lambda'}(\mathbf{k}\omega)$ rather than by just a set of frequencies and polarization vectors as per Eq. (84). When the self-consistency conditions (86) and (87) are satisfied, the free energy of the crystal becomes

$$\mathcal{F}_2=\sum_{\mathbf{k}\lambda}(2\pi)^{-1}\int_{-\infty}^{\infty}d\omega\,\tfrac{1}{2}\coth\tfrac{1}{2}\beta\omega\tan^{-1}[A_\lambda(\mathbf{k}\omega)/\tilde{A}_\lambda(\mathbf{k}\omega)]+\tfrac{1}{2}N\sum_{\tau}\sum_{\sigma,\sigma'}\langle v_{\sigma,\sigma'}(\boldsymbol{\tau}_{\sigma\sigma'}+\mathbf{u})\rangle$$
$$+\tfrac{1}{4}N\sum_{\tau,\tau',\tau''}\sum_{\sigma_1,\sigma_1'}\sum_{\sigma_2,\sigma_2'}\int_0^{\infty}dt2\,\mathrm{Im}\Big[\tfrac{1}{2}\mathcal{S}_3\Big(N^{-1}\sum_{\mathbf{k}}\sum_{\lambda,\lambda'}\exp(i\mathbf{k}\cdot\boldsymbol{\tau}_{\sigma_1\sigma_2}'')\tfrac{1}{2}\mathbf{E}_{\mathbf{k}\lambda}{}^{\sigma_1\sigma_1'}(\boldsymbol{\tau}_{\sigma_1\sigma_1'})\mathbf{E}_{\mathbf{k}\lambda'}{}^{\sigma_2\sigma_2'}(\boldsymbol{\tau}'_{\sigma_2\sigma_2'})^*$$
$$\times(2\pi)^{-1}\int_{-\infty}^{\infty}d\omega\,A_{\lambda\lambda'}(\mathbf{k}\omega)(\cos\omega t\coth\tfrac{1}{2}\beta\omega-i\sin\omega t):\nabla\nabla'\Big)\langle v_{\sigma_1\sigma_1'}(\boldsymbol{\tau}_{\sigma_1\sigma_1'}+\mathbf{u})\rangle\langle v_{\sigma_2\sigma_2'}(\boldsymbol{\tau}_{\sigma_2\sigma_2'}+\mathbf{u})\rangle\Big]. \quad (88)$$

In the first line of this formula $A_\lambda(\mathbf{k}\omega)$ and $\tilde{A}_\lambda(\mathbf{k}\omega)$ are the imaginary and real parts, respectively, of the λth eigenvalue, for fixed $\mathbf{k}$ and ω, of the $3n\times 3n$ matrix $[\omega^2\delta_{\lambda,\lambda'}-\Phi_{\lambda\lambda'}(\mathbf{k}\omega)]^{-1}$, whose imaginary part is $A_{\lambda\lambda'}(\mathbf{k}\omega)$ by Eq. (87).

This formulation simplifies somewhat if the damping of the phonon modes is sufficiently weak that the spectral function can be represented adequately by a Lorentzian,

$$A_{\lambda\lambda'}(\mathbf{k}\omega)\cong\delta_{\lambda,\lambda'}(\Gamma_{\mathbf{k}\lambda}/\omega_{\mathbf{k}\lambda})\{[(\omega-\omega_{\mathbf{k}\lambda})^2+\Gamma_{\mathbf{k}\lambda}{}^2]^{-1}+[(\omega+\omega_{\mathbf{k}\lambda})^2+\Gamma_{\mathbf{k}\lambda}{}^2]^{-1}\}\,, \tag{89}$$

in terms of a damping parameter $\Gamma_{\mathbf{k}\lambda}$. Then

$$(2\pi)^{-1}\int_{-\infty}^{\infty} d\omega\, A_{\lambda\lambda'}(\mathbf{k}\omega)(\cos\omega t\coth\tfrac{1}{2}\beta\omega-i\sin\omega t)\cong\delta_{\lambda,\lambda'}\omega_{\mathbf{k}\lambda}{}^{-1}\exp(-\Gamma_{\mathbf{k}\lambda}t)(\cos\omega_{\mathbf{k}\lambda}t\coth\tfrac{1}{2}\beta\omega_{\mathbf{k}\lambda}-i\sin\omega_{\mathbf{k}\lambda}t)\,, \tag{90}$$

and the mode frequency and damping factor are determined by

$$\omega_{\mathbf{k}\lambda}=\mathrm{Re}[\Phi_{\lambda\lambda}(\mathbf{k},\omega_{\mathbf{k}\lambda})^{1/2}],$$
$$\Gamma_{\mathbf{k}\lambda}=\mathrm{Im}[\Phi_{\lambda\lambda}(\mathbf{k},\omega_{\mathbf{k}\lambda})^{1/2}]. \tag{91}$$

In this case the single damping factor needs to be calculated, rather than the complete spectral function of ω.

Although these formulas may at first appear forbiddingly complicated, they have several significant features which are quite appealing. In the first place, the presence in Φ of the function $\mathcal{E}_2$ can be interpreted as allowing the phonon-damping rate to incorporate decay processes into any number of other phonons consistent with energy and momentum conservation. The traditional anharmonic perturbation theory prescribes a phonon decay only into two other phonons, a result which can be verified to correspond in the present scheme to replacing $\mathcal{E}_2(x)$ by its small argument limit $\frac{1}{2}x^2$. Evidence which is now available from detailed machine computation of the traditional anharmonic terms indicates[2] that multiple phonon processes apparently make a sizable contribution at higher temperatures, at or above the Debye temperature. It should further be noted that odd numbers of derivatives of the potential now enter at this second order of approximation, whereas only even derivatives contributed in first order.

Also significant is the fact that the spectral function is determined self-consistently: The phonon decay (indicated by the breadth of the spectral peak) takes place into phonons which themselves decay. Such a feature has been indicated[26] to be necessary to produce attenuations of long-wavelength acoustic phonons which correctly conform to the results of a hydrodynamic, rather than collisionless analysis. It can be shown by straightforward algebra that the zero-frequency long-wavelength limit of the phonon dynamical matrix, Eq. (86), leads to a generalization of the isothermal elastic constants, Eq. (45), including the term $\mathbf{C}'$ given by Eq. (58). Thus, as a generalization of Eq. (60),

$$\mathbf{k}\hat{e}_\lambda:\mathbf{C}^{is}:\mathbf{k}\hat{e}_\lambda=\rho\lim_{k\to 0}\lim_{\omega\to 0}\sum_{\sigma,\sigma'}(M_\sigma M_{\sigma'})^{-1/2}\times\mathbf{e}_{\mathbf{k}\lambda}{}^{\sigma *}\mathbf{e}_{\mathbf{k}\lambda}{}^{\sigma'}:\mathbf{\Phi}^{\sigma\sigma'}(\mathbf{k}\omega)\,. \tag{92}$$

In fact, Eqs. (45) and (58) but with $Y_{\kappa\kappa'}\to 0$ are obtained precisely by also making the approximations in Eq. (86) of replacing $\mathcal{E}_2(x)\to\frac{1}{2}x^2$ and, as per Eq. (84),

$$A_{\lambda\lambda'}(\mathbf{k}\omega)\to\delta_{\lambda,\lambda'}(\pi/2\omega_{\mathbf{k}\lambda})[\delta(\omega-\omega_{\mathbf{k}\lambda})-\delta(\omega+\omega_{\mathbf{k}\lambda})],$$

with $\omega_{\mathbf{k}\lambda}$ here being the phonon frequencies to *first* order. These two approximations can also be used in Eq. (86) for all values of $\mathbf{k}$ so as to obtain formulas for phonon frequency shifts and damping factors which are more easily programmable than the fully self-consistent equations. This is the approach which has been followed by Goldman *et al.*[11] and by Koehler[12] in their numerical computations. Although their results indicate a substantially improved agreement with experiment over the first-order phonon spectrum, it will still be of interest to attempt a computation with the fully self-consistent second-order equations (86) and (87).

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