iron is surrounded by fluoride ligands, this contribution is expected to be especially small, since in the first part of this section, the covalency of the fluorine produced a gradient comparable to that arising directly from the distorted ligand field. The latter gradient is expected to be smaller than the gradient due to the valence electron by a factor of about $b^{-3}/\langle r^{-3}\rangle$, where b is the iron-fluorine distance (about 4 a.u.) and $\langle r^{-3}\rangle$ of the electron is about 5.1 a.u. according to Ingalls.[26] This is a factor of about 3×10^{-3}. Thus, the covalent contribution is expected to amount to only about 0.3% of the total quadrupole splitting in FeF_2.

The formalism of the theory directly follows that outlined for K_3FeF_6 above. When this is applied, and a value for $\alpha_{d\pi}$ of 0.05 a.u. is assumed,[27] the covalent contribution is about 0.25%.

ACKNOWLEDGMENT

The authors wish to acknowledge the assistance of G. de Pasquali with the synthesis of the ferric compounds.

[26] R. L. Ingalls, Ph.D. Thesis, Carnegie Institute of Technology, 1962 (unpublished).

[27] Hubbard *et al.* give values of $\alpha_{d\pi}$ equal to 0.03 and 0.07 for $KMnF_3$ and $KNiF_3$, respectively.

PHYSICAL REVIEW B VOLUME 1, NUMBER 4 15 FEBRUARY 1970

Crystallization and Instabilities in Highly Anharmonic Crystals*

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(Received 17 June 1969)

A unified treatment of crystalline order and instabilities in highly anharmonic crystals at all temperatures is presented. This treatment is based on the study of singularities in the atomic-displacement correlation function or its Fourier transform (structure factor). As a result, it is rigorously shown that in the thermodynamic limit the mean-square fluctuations of the equilibrium position of a lattice particle are infinite in one and two dimensions at nonzero temperatures and in one dimension at *zero temperature*. This result, which is proved for an interacting many-body system without assuming the harmonic approximation, is obtained by using an exact Dyson equation for the displacement-response function. At finite temperatures, the demonstration of similar instabilities in a variety of condensed many-body systems of one and two dimensions is usually based on inequalities originally due to Bogoliubov. Since an analogous inequality can readily be extracted from the Dyson equation of the present approach, our method allows the extension of these results in anharmonic crystals to zero temperature. Finally, it is shown that additional dynamical information in this Dyson equality can be used to derive the relationship between elastic anomalies and sound absorption in the vicinity of critical points from the anomalous increase of the second derivative of the displacement-autocorrelation function.

I. INTRODUCTION

In a number of physical systems, the traditional approach to lattice dynamics, that of expanding the interatomic potential in powers of atomic displacements, is entirely inadequate. Conspicuous examples are the so-called quantum crystals, such as the crystalline forms of the isotopes of helium, where the zero-point motions are large, or the paraelectrics of the $SrTiO_3$ family, where the polarizations are large. In particular, when applied to solid helium, the harmonic approximation yields a negative dynamical matrix and, therefore, imaginary phonon frequencies.[1] On the other hand, x-ray measurements show that these systems *do* form crystals with well-defined structures. For these reasons, a *microscopic* theory of such highly anharmonic crystals must specify a criterion for crystalline ordering which does not start from the harmonic approximation. Of a variety of choices available for selection as such a criterion, two are of particular interest. They are related to two different theoretical treatments—the single-particle and the collective picture—which have emerged for allowing the displacive motions of the particles in such systems to be large.[2]

In the single-particle picture, it has been shown[3] that long-range order in the crystalline phase may be attributed to a translational symmetry breaking statistical operator. This gives rise to nonvanishing Fourier components ρ_κ of the one-particle density for nonzero reciprocal lattice vectors $\boldsymbol{\kappa}$. The umklapp phonons, which are revealed as Bragg peaks in the scattering of x-rays, can then be obtained as the symmetry restoring collective

* Work supported by U. S. Atomic Energy Commission under Contract No. AT(30-1)-3699, Technical Report No. NYO-3699-39, and the Deutsche Forschungsgemeinschaft. A short account of this work was reported by G. Meissner, Bull. Am. Phys. Soc. **14**, 367 (1969).

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[1] F. W. de Wette and B. R. A. Nijboer, Phys. Letters **18**, 19 (1965).

[2] N. R. Werthamer, Am. J. Phys. **37**, 763 (1969). This paper gives a detailed review of the two different approaches to the theory of highly anharmonic crystals.

[3] G. Meissner, Z. Physik **205**, 249 (1967).

modes without reference to the harmonic approximation. Vanishing Fourier components ρ_κ of the one-particle density at all nonzero reciprocal lattice vectors $\boldsymbol{\kappa}$, therefore, exclude conventional crystalline long-range order. Using the method of Bogoliubov inequalities,[4] applied previously to a variety of condensed many-body systems,[5,6] it has recently been proved[7] that $\rho_\kappa=0$ for all $\boldsymbol{\kappa}\neq 0$ in one and two dimensions and at $T\neq 0$°K in the thermodynamic limit for classical particles interacting through a Lennard-Jones pair potential.

In this paper, the approach of the displacement-correlation function (the so-called collective picture) is used in a unified treatment to place arguments on crystalline order and instabilities in highly anharmonic crystals on a rigorous basis. The treatment is based on the study of singularities in the atomic-displacement–correlation function or its Fourier transform (structure factor) obtained from rigorous asymptotic solutions of an exact Dyson equation for the complex displacement susceptibility. The approach and the results are of interest for several reasons. First, at finite temperatures, our approach reproduces the results on the absence of crystalline order in one- and two-dimensional quantum-mechanical systems obtained classically in Ref. 7, which used inequalities involving the one-particle density. In contrast to the technique of inequalities, the results on crystalline order in anharmonic crystals obtained from singularities of the displacement-correlation function in the present approach can be extended to zero temperature. Second, the singular behavior of the displacement-autocorrelation function of highly anharmonic crystals—as summarized in Table I—is worth recording, since the collective picture can more readily be adapted to numerical computation. In two dimensions it follows, for example, that the displacement-autocorrelation function depends logarithmically on the particle number at $T\neq 0$°K but is strictly bounded at $T=0$°K. This is of practical importance for molecular dynamical calculations of anharmonic effects, where one- and two-dimensional systems are frequently used. Third, our approach derives in a unified way the relationship between elastic anomalies and sound absorption in the vicinity of critical points from the anomalous increase of the second derivative of the same displacement-correlation function.

The results on crystallization at $T\neq 0$°K indicate a close relation between the two criteria for crystalline ordering. This follows from the fact that in both concepts the instabilities are caused by the long-wavelength behavior of the system. In this limit, the continuity equation relates the Fourier component of the one-particle density linearly to that of the longitudinal atomic displacement. Since the concept of the atomic displacement allows the incorporation of nonlongitudinal contributions, which are projected out in the one-particle density concept, it could also be applied to the study of directional long-range order.

In Sec. II, we specify our criterion for crystalline ordering within the approach of the collective picture. The definition of the basic functions in our approach to the study of instabilities in highly anharmonic crystals will be given in Sec. III. In Sec. IV, we outline a derivation of the Dyson equation for the displacement-response function which was previously introduced in an analysis of phonon excitations in quantum crystals at all wave vectors.[8] An inequality analogous to Bogoliubov's inequalities is extracted from this Dyson equation in Sec. V. Asymptotic solutions of this equation are then used to extend the results obtained from Bogoliubov's inequalities to zero temperature. The similarity between these instabilities in anharmonic crystals and interacting Bose systems is noted. In Table I, the singularities of the displacement-autocorrelation function in anharmonic crystals are summarized. Finally, it is shown in Sec. VI that the Dyson equation can be used to derive the relationship between elastic anomalies and sound absorption in the vicinity of critical points from the anomalous increase of the second derivative of the displacement-autocorrelation function. In this context, the rigorous relation between the long-wavelength limit of the phonon self-energy and the isothermal elastic constants derived in Ref. 12 is used. For completeness, we give a derivation of this result which emphasizes the general validity of similar relations between second derivatives of the free-energy functional with respect to an intensive parameter and the free-enthalpy functional with respect to the conjugate field.

II. SPECIFICATION OF CRYSTALLINE ORDERING

In this section, we specify a criterion for crystalline ordering and formulate a necessary condition for instabilities of highly anharmonic crystals using the collective picture without starting from the harmonic approximation. In order to be specific, we consider a many-body system of N atoms of mass M with a Hamiltonian

$$H=\sum_{\alpha=1}^{N}\frac{\mathbf{p}^2(\alpha)}{2M}+V(\mathbf{x}_1,\ldots,\mathbf{x}_N). \tag{1a}$$

In the case of solid helium, one usually considers pair interactions alone,

$$V(\mathbf{x}_1,\ldots,\mathbf{x}_N)=\tfrac{1}{2}\sum_{\alpha\neq\alpha'}v(\mathbf{x}(\alpha)-\mathbf{x}(\alpha')), \tag{1b}$$

[4] N. N. Bogoliubov, Phys. Abh. SU 6, 1 (1962); 6, 113 (1962); 6, 229 (1962); H. Wagner, Z. Physik 195, 273 (1966).
[5] P. C. Hohenberg, Phys. Rev. 158, 383 (1967).
[6] N. D. Mermin and H. Wagner, Phys. Rev. Letters 17, 1133 (1966).
[7] N. D. Mermin, Phys. Rev. 176, 250 (1968).
[8] G. Meissner, Phys. Rev. Letters 21, 435 (1968); Phys. Letters 27A, 261 (1968).

though our method does not require this restriction. For simplicity, however, we shall restrict the discussion to monatomic solids with a Bravais lattice. To allow for the possibility of sizable fluctuations of the atoms around their lattice sites, we assume the *equilibrium positions* of the atoms—rather than the atoms themselves—to be arranged in a regular array. Thus, we describe crystallization at a given temperature $T(\beta=1/k_BT)$ under a possible external force $\mathbf{E}(\alpha)$, coupled to the position operator $\mathbf{x}(\alpha)$, by identifying the mean-equilibrium position of the αth atom $\langle\mathbf{x}(\alpha)\rangle$ with the lattice site $\mathbf{R}(\alpha)$. That is,

$$\mathbf{R}(\alpha)\equiv\langle\mathbf{x}(\alpha)\rangle=\mathrm{Tr}[e^{-\beta(H-\mathbf{E}\cdot\mathbf{x})}\mathbf{x}(\alpha)]/\mathrm{Tr}e^{-\beta(H-\mathbf{E}\cdot\mathbf{x})}. \quad (2)$$

The increment

$$\mathbf{E}\cdot\mathbf{x}\equiv\sum_{\alpha,l}E_l(\alpha)x_l(\alpha),\quad l=1,2,3;\alpha=1,2,\ldots,N \quad (3)$$

to the basic many-body Hamiltonian H, is useful in discussing a crystal under external stress or hydrostatic pressure. This is vital when treating helium, since liquid helium does not solidify under its own vapor pressure.

Though the fluctuations of the displacement operator of the αth atom with its lth component

$$u_l(\mathbf{R}(\alpha))=x_l(\alpha)-R_l(\alpha) \quad (4)$$

are presumably large in such highly anharmonic crystals, they should, nevertheless, be less than the lattice spacing. Only then is it guaranteed that the atoms are localized in a volume $\sim a^3$ (a=lattice constant) about the lattice site, and that on the average there is no more than one such particle localized in this volume. The appearance of infinite mean-square fluctuations $\langle\mathbf{u}^2(\alpha)\rangle$, thus, entails an exclusion of a latticelike array of atoms and, therefore, the absence of conventional crystalline order in this approach. Therefore, the condition of bounded mean-square fluctuations is necessary for the stability of such a lattice. The dependence of bounded $\langle\mathbf{u}^2(\alpha)\rangle$ on dimensionality and temperature of the system can be obtained from the Fourier transform $D_{ll}(\mathbf{q})$ of the equal-time displacement-correlation function

$$D_{ll'}(\alpha-\alpha')=\langle u_l(\mathbf{R}(\alpha))u_{l'}(\mathbf{R}(\alpha'))\rangle=N^{-1}\sum_{\mathbf{q}}e^{i\mathbf{q}\cdot[\mathbf{R}(\alpha)-\mathbf{R}(\alpha')]}D_{ll'}(\mathbf{q}), \quad (5)$$

because $\langle\mathbf{u}^2\rangle$ is given by the trace over $D_{ll'}(\alpha-\alpha')$ for $\alpha=\alpha'$:

$$\langle\mathbf{u}^2(\alpha)\rangle=N^{-1}\sum_{\mathbf{q},l}D_{ll}(\mathbf{q}). \quad (6a)$$

The right-hand side of (6a) can also be written as an integral over the volume element $d^sq=q^{s-1}dqd\Omega$ with the dimensionality s and the corresponding angle element $d\Omega$:

$$\langle\mathbf{u}^2\rangle=\frac{v_0}{(2\pi)^s}\int_{\mathrm{BZ}}d^sq\sum_l D_{ll}(\mathbf{q}), \quad (6b)$$

where v_0 is the volume per unit cell. Due to the integration over the first Brillouin zone in (6b), the behavior of $D_{ll}(\mathbf{q})$ in the limit of small $\mathbf{q}$ is crucial for bounded $\langle\mathbf{u}^2\rangle$. Instabilities arising from a divergent displacement-autocorrelation function $\langle\mathbf{u}^2\rangle$ can, therefore, be obtained from studying singularities of $D_{ll}(\mathbf{q})$ in the limit of small $\mathbf{q}$. Technically, we may obtain the behavior of $D_{ll}(\mathbf{q})$ by using an exact Dyson equation for the dynamical displacement-correlation function. For these reasons, we first need certain basic dynamical quantities and their relation to the Fourier transform of the autocorrelation function $D_{ll}(\mathbf{q})$.

III. DYNAMICAL DISPLACEMENT CORRELATIONS

In this section, we recall a few definitions[9] which are useful for our approach to studying instabilities in highly anharmonic crystals.

We first rewrite the Fourier transform of the equal-time displacement-correlation function:

$$D_{ll'}(\mathbf{q})=\tfrac{1}{2}\langle\{u_l(\mathbf{q},t),\,u_{l'}(-\mathbf{q},\,t)\}\rangle. \quad (7)$$

In this equation $\{\cdots\}$ denotes the anticommutator of the Fourier transforms of displacement operators in the Heisenberg picture, using the lattice periodicity

$$u_l(\mathbf{R}(\alpha),t)=N^{-1/2}\sum_{\mathbf{q}}e^{-i\mathbf{q}\cdot\mathbf{R}(\alpha)}u_l(\mathbf{q},t). \quad (8)$$

The spectral function $\tau_{ll'}(\mathbf{q},\omega)$ is given in terms of the commutator of displacement operators

$$\langle[u_l(\mathbf{q},t),u_{l'}(-\mathbf{q},\,t')]\rangle=\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}e^{-i\omega(t-t')}\tau_{ll'}(\mathbf{q},\omega). \quad (9)$$

These two functions, therefore, satisfy the fluctuation-dissipation theorem

$$D_{ll'}(\mathbf{q})=\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\tau_{ll'}(\mathbf{q},\omega)\coth\tfrac{1}{2}\beta\omega. \quad (10)$$

Frequency moments $\langle\omega_{ll'}{}^n\rangle_\tau$ of $\tau_{ll'}$ are obtained if we differentiate (9) and take the $t\to t'^+$ limit

$$\left\langle\left[\frac{\partial^n}{\partial t^n}u_l(\mathbf{q},t),u_{l'}(-\mathbf{q},\,t')\right]\right\rangle_{t=t'^+}=\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}(-i\omega)^n\tau_{ll'}(\mathbf{q},\omega)\equiv(-i)^n\langle\omega_{ll'}{}^n(\mathbf{q})\rangle_\tau. \quad (11)$$

The spectral representation for the dynamical displacement-response function or the complex susceptibility is given by

$$\chi_{ll'}(\mathbf{q},z)=\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\frac{\tau_{ll'}(\mathbf{q},\omega)}{z-\omega}. \quad (12)$$

[9] P. C. Martin, in *Statistical Mechanics of Equilibrium and Nonequilibrium*, edited by J. Meixner (North-Holland Publishing Company, Amsterdam, The Netherlands, 1965), Sec. 3.

It is useful to recall at this point that $\chi_{l_1l_{1'}}(\mathbf{q},z)$ may be obtained[10] from the analytic continuation of the Fourier transform of the two-point displacement-correlation function

$$\chi_{l_1l_{1'}}(\mathbf{q},z_\nu)=\int_0^{-i\beta}d\tau_1 e^{-iz_\nu(\tau_1-\tau_{1'})}\times\sum_{\alpha_1\alpha_{1'}}e^{-i\mathbf{q}\cdot[\mathbf{R}(\alpha_1)-\mathbf{R}(\alpha_{1'})]}\chi_{l_1l_{1'}}(1,1'). \quad (13)$$

In this equation, τ_1 and $\tau_{1'}$ are purely imaginary numbers running between 0 and $-i\beta$, $z_\nu=2\pi i\nu/\beta$, with $\nu=0, \pm1, \pm2, \ldots$, and $1\equiv(\alpha_1,\tau_1)$. A formal yet convenient method of generating correlation functions of the type $\chi_{l_1l_{1'}}(1,1')$ is the functional-derivative technique.[11] Adopting the "interaction picture" for the possibly time-dependent external force $\mathbf{E}(\alpha,\tau)$, these functions may be obtained from the generalized free-enthalpy functional

$$G[\mathbf{E},T]=-\frac{1}{\beta}\ln\mathrm{Tr}\left[e^{-\beta H}\hat{T}\times\exp\left(-i\int_0^{-i\beta}d\tau\sum_{\alpha,l}E_l(\alpha,\tau)x_l(\alpha,\tau)\right)\right], \quad (14)$$

where $\hat{T}$ is the time-ordering symbol acting on the imaginary times $0\leq\tau\leq-i\beta$. We require the one-point function which corresponds to the time-dependent mean-particle position

$$\langle\mathbf{x}(1)\rangle=-i\beta[\delta/\delta\mathbf{E}(1)]G, \quad (15)$$

and the two-point function which determines displacements from the mean position due to variations in the external force $\mathbf{E}(2)$,

$$\begin{aligned}\delta\langle\mathbf{x}(1)\rangle&=-i\beta[\delta^2/\delta\mathbf{E}(1)\delta\mathbf{E}(2)]G\cdot\delta\mathbf{E}(2)\\&=-\chi(1,2)\cdot\delta\mathbf{E}(2).\end{aligned} \quad (16)$$

Here, a summation-integration convention over repeated indices and a tensor notation for spatial subscripts have been adopted. Therefore, χ is a three-by-three matrix in the case of Bravais lattices. The static displacement susceptibility follows from (12), (13), and (16) as

$$\begin{aligned}\chi(\mathbf{q},z=0)&=-\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\frac{\boldsymbol{\tau}(\mathbf{q},\omega)}{\omega}=-\langle\omega^{-1}(\mathbf{q})\rangle_\tau\\&=i\int_0^{-i\beta}d\tau\langle\hat{T}\mathbf{u}(\mathbf{q},\tau)\mathbf{u}(-\mathbf{q},0)\rangle.\end{aligned} \quad (17)$$

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

[11] This method is of physical importance in relating thermodynamic derivatives to the long-wavelength static limit of dynamical quantities.

IV. DYSON EQUATION FOR DISPLACEMENT-RESPONSE FUNCTION

The Dyson equation for the complex displacement susceptibility $\chi(\mathbf{q},z)$ will be used explicitly for studying instabilities in highly anharmonic crystals, and, in this section, we outline its derivation using definitions of the preceding one. We obtain this Dyson equation by deriving an exact spectral representation for the inverse of the complex displacement susceptibility $\chi^{-1}(\mathbf{q},z)$. For these reasons, we examine the high-frequency behavior $|z|>\omega$ of $\chi(\mathbf{q},z)$ given in Eq. (12),

$$\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\frac{\boldsymbol{\tau}(\mathbf{q},\omega)}{z-\omega}=\frac{1}{z^2}\int\frac{d\omega}{2\pi}\omega\boldsymbol{\tau}+\frac{1}{z^4}\int\frac{d\omega}{2\pi}\omega^3\boldsymbol{\tau}+\cdots.$$

The frequency moments of even powers vanish, since $\boldsymbol{\tau}(\mathbf{q},\omega)$ is odd in ω. Therefore, in the notation of Eq. (11), we may write

$$\chi(\mathbf{q},z)=\frac{\langle\omega\rangle_\tau}{z^2}\cdot\left[1+\frac{1}{z^2}\langle\omega\rangle_\tau^{-1}\cdot\langle\omega^3(\mathbf{q})\rangle_\tau+\mathbf{O}\left(\frac{1}{z^4}\right)\right], \quad (18)$$

where $\mathbf{O}$ means "a dyadic of the order of." The inversion of (18) in the limit of large z then leads to

$$\begin{aligned}\chi^{-1}(\mathbf{q},z)=z^2\{1-(1/z^2)\langle\omega\rangle_\tau^{-1}\cdot\langle\omega^3(\mathbf{q})\rangle_\tau\\-\mathbf{O}(1/z^4)\}\cdot\langle\omega\rangle_\tau^{-1}.\end{aligned} \quad (19)$$

Since the remainder in (19) tends to zero as z^{-2} for large z, it can be expressed for all z by a dispersion integral. We then obtain the spectral representation

$$\begin{aligned}\chi^{-1}(\mathbf{q},z)=z^2\langle\omega\rangle_\tau^{-1}-\langle\omega\rangle_\tau^{-1}\cdot\langle\omega^3(\mathbf{q})\rangle_\tau\cdot\langle\omega\rangle_\tau^{-1}\\-\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\frac{\omega\boldsymbol{\Gamma}(\mathbf{q},\omega)}{z^2-\omega^2}.\end{aligned} \quad (20)$$

For the static inverse susceptibility, we obtain from (20)

$$\begin{aligned}\chi^{-1}(\mathbf{q},0)=-\langle\omega\rangle_\tau^{-1}\cdot\langle\omega^3(\mathbf{q})\rangle_\tau\cdot\langle\omega\rangle_\tau^{-1}\\+\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\frac{\boldsymbol{\Gamma}(\mathbf{q},\omega)}{\omega}.\end{aligned} \quad (21)$$

The spectral width function $\boldsymbol{\Gamma}(\mathbf{q},\omega)$ has the same symmetry properties as the spectral function $\boldsymbol{\tau}(\mathbf{q},\omega)$, and, therefore,

$$\int_{-\infty}^{+\infty}d\omega\frac{\Gamma_{ll'}(\mathbf{q},\omega)}{2\pi\omega}\geq0. \quad (22)$$

By subtracting (21) from (20), we may express the inverse of the displacement-response function in the form of the dispersion relation

$$\begin{aligned}\chi^{-1}(\mathbf{q},z)=z^2\langle\omega\rangle_\tau^{-1}+\chi^{-1}(\mathbf{q},0)\\-z^2\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\frac{\boldsymbol{\Gamma}(\mathbf{q},\omega)}{\omega(z^2-\omega^2)}.\end{aligned} \quad (23)$$

TABLE I. Singularities of the displacement-autocorrelation function $\langle \mathbf{u}^2 \rangle$ in anharmonic crystals as a function of temperature (T) and dimensionality (s).

Dimensionality (s)	$\langle \mathbf{u}^2\rangle (T\neq 0°\mathrm{K})$ $q_{\min}=0$	$q_{\min}\propto N^{-1/s}$	$\langle \mathbf{u}^2\rangle (T=0°\mathrm{K})$ $q_{\min}=0$	$q_{\min}\propto N^{-1/s}$
1	$T/q\to\infty$	TN (unstable)	$\ln q\to\infty$	$\ln N$
2	$T\ln q\to\infty$	$T\ln N$	q (finite)	$N^{-1/2}$
3	Tq (finite)	$TN^{-1/3}$	q^2 (finite)	$N^{-2/3}$

Using formula (23), the Dyson equation may finally be written in the form

$$\left\{ z^2\langle \omega\rangle_\tau^{-1} + \chi^{-1}(\mathbf{q},0) - z^2\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\frac{\mathbf{\Gamma}(\mathbf{q},\omega)}{\omega(z^2-\omega^2)}\right\}\cdot\chi(\mathbf{q},z)=\mathbf{1}, \quad (24)$$

where $\mathbf{1}$ is the three-by-three unit matrix. Equations (23) and (24) may be used to define phonons as elementary excitations in solids. According to Eq. (16), these elementary excitations may be studied by considering the response of the crystal to an external force $\mathbf{E}(1)$ coupled to the position operator $\mathbf{x}(1)$. Poles of χ or zeros of the real part of its inverse

$$\mathrm{Re}\chi^{-1}[\mathbf{q},\omega_s(\mathbf{q})]\equiv 0, \quad (25)$$

therefore, determine the relation between frequency $\omega_s(\mathbf{q})$ and wave vector $\mathbf{q}$ of these phonon excitations, where s denotes the polarization branches. This definition is quite general and does not refer to the harmonic approximation. The imaginary part of χ^{-1} is given precisely by the spectral-width function $\mathbf{\Gamma}$. Therefore, $\Gamma_s[\mathbf{q},\omega_s(\mathbf{q})]$ is responsible for lifetime and renormalization effects of the particular phonon mode of frequency $\omega_s(\mathbf{q})$. The attenuation of sound $A_s(\mathbf{q})$, in amplitude per cm, due to such a damped phonon mode may then be written

$$\frac{\Gamma_s[\mathbf{q},\omega_s(\mathbf{q})]}{2M\omega_s(\mathbf{q})}=A_s(\mathbf{q})\frac{\partial\omega_s(\mathbf{q})}{\partial|\mathbf{q}|}. \quad (26)$$

Another aspect of the Dyson Eq. (24) will be discussed in Sec. V.

V. BOGOLIUBOV INEQUALITIES AND SINGULARITIES IN DISPLACEMENT-AUTOCORRELATION FUNCTION

In this section, we derive, from the Dyson Eq. (24), an inequality analogous to Bogoliubov's inequalities. We then discuss the way in which the asymptotic forms of the Dyson equation—for $z=0$ in the limit of small $\mathbf{q}$—may be used to extend the results on the singularities in the displacement-autocorrelation function obtained from the Bogoliubov inequalities.

In order to extract an analogue of Bogoliubov's inequality, we start from the static limit ($z=0$) of Eq. (24) using (21) for $\chi^{-1}(\mathbf{q},0)$ and (17) for $\chi(\mathbf{q},0)$:

$$\left\{\langle\omega\rangle_\tau^{-1}\cdot\langle\omega^3(\mathbf{q})\rangle_\tau\cdot\langle\omega\rangle_\tau^{-1} - \int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\frac{\mathbf{\Gamma}(\mathbf{q},\omega)}{\omega}\right\}\cdot\langle\omega^{-1}(\mathbf{q})\rangle_\tau=\mathbf{1}. \quad (27)$$

Due to (22), we obtain from (27) the inequality

$$\langle\omega\rangle_\tau^{-1}\cdot\langle\omega^3(\mathbf{q})\rangle_\tau\cdot\langle\omega\rangle_\tau^{-1}\cdot\langle\omega^{-1}(\mathbf{q})\rangle_\tau\geq\mathbf{1}. \quad (28a)$$

This is the generalized Bogoliubov inequality. It may be verified by writing the ω moments in (28a) explicitly,

$$\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\omega^3\tau_{AA^\dagger}(\mathbf{q},\omega)\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\frac{\tau_{AA^\dagger}(\mathbf{q},\omega)}{\omega} \geq\left|\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\omega\tau_{AA^\dagger}(\mathbf{q},\omega)\right|^2, \quad (28b)$$

where $A\equiv u_l(\mathbf{q},t)$. Introducing the further abbreviation $C\equiv\dot{u}_{l'}(\mathbf{q},t')$ and the relations

$$\omega^2\tau_{AA^\dagger}(\mathbf{q},\omega)=\tau_{CC^\dagger}(\mathbf{q},\omega)=\omega\tau_{CA^\dagger}(\mathbf{q},\omega),$$

Eq. (28b) may be recast in the form

$$\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\omega\tau_{CC^\dagger}(\mathbf{q},\omega)\cdot\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\frac{\tau_{AA^\dagger}(\mathbf{q},\omega)}{\omega} \geq\left|\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\tau_{CA^\dagger}(\mathbf{q},\omega)\right|^2. \quad (28c)$$

This leads to the frequently used version of Bogoliubov's inequality[5,6]

$$\langle[[C,H],C^\dagger]\rangle\tfrac{1}{2}\langle\{A,A^\dagger\}\rangle\geqq k_BT|\langle[C,A^\dagger]\rangle|^2. \quad (29)$$

The commutators $\langle[[C,H],C^\dagger]\rangle$ and $\langle[C,A^\dagger]\rangle$ in (29) and the related ω moments $\langle\omega^3(\mathbf{q})\rangle_\tau$ and $\langle\omega(\mathbf{q})\rangle_\tau$ in (28b) may be evaluated explicitly for the Hamiltonian H in (1a) with a pair interaction (1b)

$$M\langle\omega\rangle_\tau=M\langle[C,A^\dagger]\rangle=\mathbf{1} \quad (30)$$

and

$$M\langle\omega^3(\mathbf{q})\rangle_\tau=M\langle[[C,H],C^\dagger]\rangle =(MN)^{-1}\sum_{\alpha\neq\alpha'}[1-e^{-i\mathbf{q}\cdot\mathbf{R}(\alpha\alpha')}] \times\langle\nabla\nabla v(\mathbf{x}(\alpha\alpha'))\rangle. \quad (31)$$

The notation $\mathbf{x}(\alpha\alpha')\equiv\mathbf{x}(\alpha)-\mathbf{x}(\alpha')$ and $\mathbf{R}(\alpha\alpha')\equiv\langle\mathbf{x}(\alpha\alpha')\rangle$ has been introduced for convenience. The anticommutator

$$\tfrac{1}{2}\langle\{A,A^\dagger\}\rangle\equiv D_{ll}(\mathbf{q}). \quad (32)$$

From Eq. (29), therefore, we obtain the long-wavelength behavior of the Fourier transform of the displacement-autocorrelation function

$$\lim_{q\to 0} D_{ll'}(\mathbf{q}) \geq \frac{k_BT}{M^2q^2}\frac{1}{\{(2MN)^{-1}\sum_{\alpha\neq\alpha'} R_l(\alpha\alpha')R_{l'}(\alpha\alpha')\langle\nabla_l\nabla_{l'}v[\mathbf{x}(\alpha\alpha')]\rangle q_lq_{l'}/q^2\}}. \tag{33}$$

The coefficient of q^2 in the denominator on the right-hand side of (33) is bounded in the thermodynamic limit, provided that for $r\to\infty$ (e.g., in two dimensions)

$$\nabla^2 v(r) \sim 1/r^{4+|\epsilon|}, \tag{34}$$

as discussed in detail in Ref. 7. From the identity

$$\langle\nabla_l\nabla_{l'}v[\mathbf{x}(\alpha\alpha')]\rangle \equiv \int d^3r\nabla_l\nabla_{l'}v(\mathbf{r})\langle\delta[\mathbf{r}-\mathbf{x}(\alpha\alpha')]\rangle,$$

we see that the singular behavior at $r=0$, e.g., of a Lennard-Jones two-particle interaction

$$v(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6], \tag{35}$$

is compensated, since

$$g(\mathbf{r})=(MN)^{-1}\sum_{\alpha\neq\alpha'}\langle\delta[\mathbf{r}-\mathbf{x}(\alpha\alpha')]\rangle \tag{36a}$$

represents the pair-distribution function of the crystal. The inequality (33), therefore, respresents the basic result that

$$\lim_{q\to 0} D_{ll}(\mathbf{q}) \geq \text{const}\times(T/q^2). \tag{36b}$$

The behavior of this limit at zero temperature may be obtained from asymptotic solutions of the full Dyson equation in the limit of small q and z. To obtain this solution, we first expand $\boldsymbol{\chi}^{-1}(\mathbf{q},0)$ in (23) for small $\mathbf{q}$ so that we may write the expansion of (21)

$$\chi_{ik}^{-1}(\mathbf{q},0)=-Z_{ikjl}q_jq_l+O_{ik}(q^4). \tag{37}$$

This expansion is possible in the absence of long-range interaction, where $\boldsymbol{\chi}^{-1}(\mathbf{q},0)$ is a regular function of $\mathbf{q}$ for $\mathbf{q}\to 0$. The coefficients are given by

$$Z_{ikjl}=M\frac{\partial^2}{\partial q_j\partial q_l}\left\{M\langle\omega_{ik}{}^3(\mathbf{q})\rangle_\tau - \int_{-\infty}^{+\infty}\frac{d\omega}{\pi}\Gamma_{ik}(\mathbf{q},\omega)/(2M\omega)\right\},\quad \mathbf{q}=0. \tag{38}$$

Using (30) and (31), the first term in (38) may be expressed as

$$M\frac{\partial^2}{\partial q_j\partial q_l}\langle\omega_{ik}{}^3(\mathbf{q})\rangle_\tau\Big|_{\mathbf{q}=0} =(2MN)^{-1}\sum_{\alpha\neq\alpha'}R_j(\alpha\alpha')R_l(\alpha\alpha')\langle\nabla_i\nabla_k v[\mathbf{x}(\alpha\alpha')]\rangle. \tag{39}$$

Rapidly varying terms in $\boldsymbol{\Gamma}(\mathbf{q},\omega)$, responsible for the possible appearance of second sound and the difference between isothermal and adiabatic sound propagation, vanish at zero temperature. With such a spectral width function $\boldsymbol{\Gamma}(\mathbf{q},\omega)$, differentiable in ω, the first nonvanishing term of the remaining contributions to (23) for small $\mathbf{q}$ and z is, therefore, of the order q^2z^2 and, hence, does not contribute to the asymptotic solution of (24). This asymptotic form is, therefore,

$$\tilde{\chi}_{ik}^{-1}(\mathbf{q},z)\equiv\lim_{q\to 0}\chi_{ik}^{-1}(\mathbf{q},z)=z^2M\delta_{ik}-Z_{ikjl}q_jq_l. \tag{40}$$

The matrix $\tilde{\chi}_{ik}^{-1}$ may be diagonalized by introducing orthonormal polarization vectors $e_k{}^s(\mathbf{q})$ with branch indices s:

$$\sum_k \tilde{\chi}_{ik}^{-1}(\mathbf{q},z)e_k{}^s(\mathbf{q})=\{z^2M-\tilde{\omega}_s{}^2(\mathbf{q})\}e_i{}^s(\mathbf{q}). \tag{41a}$$

Equation (41a) may then be recast in the form

$$\tilde{\omega}_s{}^2(\mathbf{q})e_i{}^s(\mathbf{q})=v_0c_{ijkl}q_jq_le_k{}^s(\mathbf{q}), \tag{41b}$$

where

$$c_{ijkl}=v_0^{-1}(Z_{ikjl}+Z_{jkil}-Z_{jikl}). \tag{42}$$

The Dyson Eq. (24) in this static ($z=0$) long-wavelength ($\mathbf{q}\to 0$) limit, therefore, reads

$$v_0c_{ijkl}\lim_{q\to 0}\{q_jq_l\chi_{ki'}(\mathbf{q},0)\}=\delta_{ii'}. \tag{43}$$

The isothermal elastic sonstants[12] c_{ijkl} have been introduced here to summarize certain symmetry relations.[13] The acoustic isothermal sound velocity $v_s(\mathbf{q}/|\mathbf{q}|)$ of branch s in direction $\mathbf{q}/|\mathbf{q}|$ then follows from the asymptotic value of the phonon frequency $\omega_s(\mathbf{q})$:

$$\tilde{\omega}_s(\mathbf{q})\equiv\lim_{q\to 0}\omega_s(\mathbf{q})=v_s(\mathbf{q}/|\mathbf{q}|)q. \tag{44}$$

The spectral function, therefore, has the form

$$\lim_{q\to 0}\tau_{ll'}(\mathbf{q},\omega)=2\pi\sum_s e_l{}^s(\mathbf{q})e_{l'}{}^s(\mathbf{q}) \times\{\delta(\omega-\tilde{\omega}_s(\mathbf{q}))-\delta(\omega+\tilde{\omega}_s(\mathbf{q}))\}/2M\tilde{\omega}_s(\mathbf{q}). \tag{45}$$

Finally, from Eqs. (10) and (45), we obtain the asymptotic behavior at zero temperature:

$$\lim_{q\to 0}D_{ll}(\mathbf{q})=\frac{1}{2Mq}\sum_s\frac{e_l{}^s(\mathbf{q})e_l{}^s(\mathbf{q})}{v_s(\mathbf{q}/|\mathbf{q}|)}\propto\text{const}\times\frac{1}{q}. \tag{46}$$

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

[13] The quantities c_{ijkl} defined in (42) have been shown in Ref. 12 to correspond to the isothermal elastic constants. A derivation of this result and an extension useful for further applications are contained in Sec. VI of this paper.

The q^{-2} singularity of $D_{ll}(\mathbf{q})$ at finite temperatures and the q^{-1} singularity at absolute zero—in (36b) and (46)—are the same as those obtained in the harmonic approximation. The anharmonic effects merely renormalize the elastic constants which determine the coefficients of Tq^{-2} in (36b) and of q^{-1} in (46). Temperature and momentum dependence of these singularities in the Fourier transform of the displacement-autocorrelation function $\lim_{q\to 0} D_{ll}(\mathbf{q})$ agree with those found in the momentum distribution function $n(\mathbf{q})$ of a condensed Bose system. The form of $\lim_{q\to 0} n(\mathbf{q})$ at zero temperature was obtained using perturbation theory,[14] and at finite temperatures the method of Bogoliubov inequalities has been used.[5] The same behavior of this limit was also found using an approximate ground-state wave function.[15]

The displacement-autocorrelation function $\langle \mathbf{u}^2\rangle$ itself follows by inserting the long-wavelength behavior of $D_{ll}(\mathbf{q})$ of (36b) and (46) into (6b). This then leads to the results summarized in Table I. At nonzero temperature,

$$\langle \mathbf{u}^2\rangle \geq \int_{q_{\min}}^{Q} q^{s-3}dq$$

becomes infinite in the thermodynamic limit ($q_{\min}=0$) for one- and two-dimensional systems. For large but finite systems, one obtains the dependence TN, $T\ln N$, and $TN^{-1/3}$ in the dimensions $s=1, 2, 3$, if one introduces a cutoff wavelength $q_{\min}\propto N^{-1/s}$. At zero temperature,

$$\langle \mathbf{u}^2\rangle \propto \int_{q_{\min}}^{Q} q^{s-2}dq\,,$$

the exponent $(s-3)$ in the integration is replaced by $(s-2)$ and $\langle \mathbf{u}^2\rangle$ is now bounded in the thermodynamic limit in two dimensions, whereas in the case of a one-dimensional finite crystal, $\langle \mathbf{u}^2\rangle$ depends logarithmically on the particle number N.

VI. ELASTIC ANOMALIES AND FLUCTUATION INSTABILITIES

In this section, we show that additional dynamical information contained in the Dyson Eq. (24) may be used rigorously to derive the relation between elastic anomalies and sound absorption in the vicinity of critical points from the anomalous increase of the second derivative of the displacement-autocorrelation function. For these reasons, we use another rigorous relationship, namely that the second derivative of the free energy $F[\langle\mathbf{x}\rangle,T]$ with respect to mean positions $\langle\mathbf{x}\rangle$ is equal to the inverse displacement susceptibility χ^{-1}. This result follows from the fact that the free energy $F[\langle\mathbf{x}\rangle,T]$ and the Gibb's potential $G[\mathbf{E},T]$—as defined in Eq. (14)—are related through a Legendre transformation

$$F[\langle\mathbf{x}\rangle,T]=G[\mathbf{E},T]+(1/i\beta)\mathbf{E}(1)\cdot\langle\mathbf{x}(1)\rangle. \quad (47)$$

Therefore, the first-order derivative of the free energy with respect to $\langle\mathbf{x}(1)\rangle$,

$$\beta[\delta/\delta\langle\mathbf{x}(1)\rangle]F=-i\mathbf{E}(1)\,, \quad (48a)$$

is determined by the external force $\mathbf{E}(1)$. Using the equation of motion for $\langle\mathbf{x}(1)\rangle$ obtained from the equation of motion for the operator $\mathbf{x}(1)$,

$$-i\mathbf{E}(1)=M\frac{\partial^2}{\partial\tau_1{}^2}\langle\mathbf{x}(1)\rangle+i\boldsymbol{\kappa}(1)\,, \quad (48b)$$

with $\boldsymbol{\kappa}(1)\equiv\langle\partial V/\partial\mathbf{x}(1)\rangle$, we may eliminate $-i\mathbf{E}(1)$ from (48a) and obtain

$$\beta(\delta/\delta\langle\mathbf{x}(1)\rangle)F=M\frac{\partial^2}{\partial\tau_1{}^2}\langle\mathbf{x}(1)\rangle+i\boldsymbol{\kappa}(1)\,. \quad (48c)$$

Differentiating Eq. (48b) with respect to $\mathbf{E}(1')$ and using the chain rule

$$\delta/\delta\mathbf{E}(1')\equiv(\delta/\delta\langle\mathbf{x}(2)\rangle)\delta\langle\mathbf{x}(2)\rangle/\delta\mathbf{E}(1')\,,$$

we find the equation of motion for $\chi(2,1')$ in the form

$$(-i)\left\{M\frac{\partial^2}{\partial\tau_1{}^2}\delta(1-2)\delta_{ik}+i\frac{\delta\kappa_i(1)}{\delta\langle x_k(2)\rangle}\right\}\chi_{ki'}(2,1')=\delta(1-1')\delta_{ii'}\,, \quad (49a)$$

and from this the inverse of the displacement susceptibility

$$\chi_{ik}{}^{-1}(1,2)=\left\{M\frac{\partial^2}{\partial\tau_1{}^2}\delta(1-2)\delta_{ik}+i\frac{\delta\kappa_i(1)}{\delta\langle x_k(2)\rangle}\right\}(-i)\,. \quad (49b)$$

Differentiating (48c) with respect to $\langle\mathbf{x}(2)\rangle$ reproduces the right-hand side of (49b) and, therefore, leads to the rigorous relationship

$$\beta\frac{\delta^2F}{\delta\langle x_i(1)\rangle\delta\langle x_k(2)\rangle}=\chi_{ik}{}^{-1}(1,2)i\,. \quad (49c)$$

We may multiply (49c) by $\chi_{ki'}(2,1)'$ expressed as the second-order derivative of the Gibbs free energy G with respect to the external source $\mathbf{E}$—see Eq. (16)—in order to recast this relationship in the form[16]

$$\frac{\delta^2F}{\delta\langle x_i(1)\rangle\delta\langle x_k(2)\rangle}\frac{\delta^2G}{\delta E_k(2)\delta E_{i'}(1')}=\beta^{-2}\delta(1-1')\delta_{ii'}\,. \quad (50)$$

[14] J. Gavoret and P. Nozières, Ann. Phys. (N. Y.) 28, 349 (1964).

[15] L. Reatto and G. V. Chester, Phys. Rev. 155, 88 (1967).

[16] Similar relations between the second derivative of the free energy with respect to an intensive parameter (in this case $\langle\mathbf{x}\rangle$) and the second derivative of the free enthalpy with respect to the conjugate field (in this case $\mathbf{E}$) occur in other cases, for example, a condensed Bose system [G. Meissner (unpublished)].

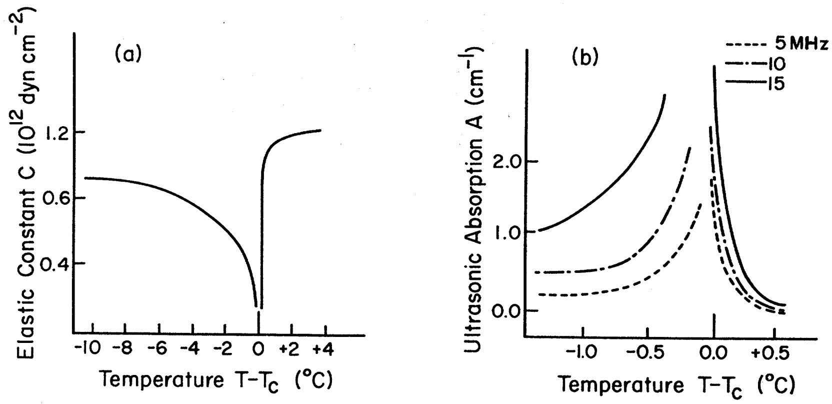

FIG. 1. Schematic representation of the relation between (a) the anomalous decrease in the elasric constants c and (b) the anomalously strong ultrasonic absorption A at different frequencies ω near the critical point T_c in ferroelectrics (see Ref. 17).

From the Fourier space and time transform of (49c) and (50), we readily obtain the elastic or compressibility sum rule in crystals. Since the expectation values of particle positions $\langle \mathbf{x}\rangle$ in a homogeneous deformed ideal crystal are unique functions of the corresponding strains $\mathbf{u}$, we may start from the chain rule

$$\frac{\delta^2 F}{\delta u_{kl}\delta u_{ij}}=\frac{\delta^2 F}{\delta\langle x_{k'}(2)\rangle\delta\langle x_{i'}(1)\rangle}\frac{\delta\langle x_{i'}(1)\rangle}{\delta u_{ij}}\frac{\delta\langle x_{k'}(2)\rangle}{\delta u_{kl}} \tag{51}$$

to obtain this sum rule. In the case of homogeneous deformations in a Bravais lattice, we have, for the strain derivatives of the right-hand side of (51),

$$\delta\langle x_k(1)\rangle/\delta u_{ki}=R_i(\alpha_1)\,, \tag{52}$$

which together with (49c) and (51) yields

$$(2N)^{-1}\left\{\frac{\delta^2 F}{\delta u_{ij}\delta u_{kl}}+\frac{\delta^2 F}{\delta u_{ik}\delta u_{lj}}\right\} =(\beta N)^{-1}\sum_{\alpha_1\alpha_2}\int_0^{-i\beta}d\tau_1\int_0^{-i\beta}d\tau_2 \times\chi_{ik}^{-1}(\alpha_1\alpha_2,\,\tau_1-\tau_2)R_j(\alpha_1)R_l(\alpha_2)\,. \tag{53}$$

Since the right-hand side of (53) is equal to the second derivate of $\lim_{q\to 0}\chi_{ik}^{-1}(\mathbf{q},0)$ with respect to wave vectors $\mathbf{q}$, we obtain, by using (37),

$$(2N)^{-1}\left\{\frac{\delta^2 F}{\delta u_{ij}\delta u_{kl}}+\frac{\delta^2 F}{\delta u_{ik}\delta u_{lj}}\right\}=Z_{ikjl}\,. \tag{54}$$

Equation (54) represents the desired result, that the elastic constants which are defined through combinations of second-order derivatives of the free energy (per particle) with respect to homogeneous deformation $\mathbf{u}$ can be expressed through coefficients Z_{ikjl} of the long-wavelength limit of the inverse of the static displacement susceptibility $\chi_{ik}^{-1}(\mathbf{q},0)$. If we insert the relation—already derived in Ref. 12—

$$\lim_{q\to 0}D_{ik}(\mathbf{q})q_jq_l=k_BT\lim_{q\to 0}\chi_{ik}(\mathbf{q},0)q_jq_l \tag{55}$$

into (43), we obtain

$$v_0c_{ijkl}\lim_{q\to 0}q_jq_lD_{ki'}(\mathbf{q})=k_BT\delta_{ii'}\,. \tag{56}$$

From (56), we see that an anomalous decrease in the elastic constants c_{ijkl} leads to a strong increase in $\lim_{q\to 0}q_jq_lD_{ki'}(\mathbf{q})$ which may not be ruled out in three dimensions. Formula (38) for Z_{ijkl} gives some insight into such elastic anomalies. In a mean-field theory, where $\Gamma_{ik}(\mathbf{q},\omega)$ is neglected, a decrease of the elastic constants in approaching a critical temperature T_c can arise from a temperature dependence of the form

$$(2MN)^{-1}\sum_{\alpha\neq\alpha'}R_j(\alpha\alpha')R_l(\alpha\alpha')\langle\nabla_i\nabla_k v[\mathbf{x}(\alpha\alpha')]\rangle\propto(T-T_c)$$

in the remaining term of (38). Very close to the critical temperature T_c, however, $\Gamma_{ik}(\mathbf{q},\omega)$ may increase strongly and fluctuations may no longer be neglected. The second term in (38) for Z_{ikjl},

$$\frac{\partial^2}{\partial q_j\partial q_l}\int d\omega\frac{\Gamma_{ik}(\mathbf{q},\omega)}{2\pi M\omega}\geq 0\,,$$

due to the symmetry properties of $\boldsymbol{\Gamma}$—Eq. (22)—and the integrand $\Gamma_{ik}(\mathbf{q},\omega)/(2M\omega)$, is proportional to the expression (26) for sound attenuation. The anomalous decrease of elastic constants near critical points may, therefore, occur when the two terms in (38) are of comparable magnitude. This may be related to a strong increase of sound attenuation due to fluctuations. These features are summarized in the fluctuation sum rule

$$(2N)^{-1}\left\{\frac{\delta^2 F}{\delta u_{ij}\delta u_{kl}}+\frac{\delta^2 F}{\delta u_{ik}\delta u_{lj}}\right\} =\lim_{q\to 0}M\frac{\partial^2}{\partial q_j\partial q_l}\left\{M\langle\omega_{ik}^3(\mathbf{q})\rangle_\tau-\int d\omega\frac{\Gamma_{ik}(\mathbf{q},\omega)}{2\pi M\omega}\right\}\,, \tag{57}$$

which readily follows from (54) and (38). Due to the integral in the second term of the right-hand side in (57), sound absorption at all frequencies contributes to the elastic anomaly. Qualitatively, this is in agreement with experiment,[17] as shown schematically in Fig. 1.

Further theoretical details require an extension of the formalism to nonsimple Bravais lattices[18] and an explicit approximate solution of the Dyson Eq. (49). This is not pursued in this paper where we have restricted our attention to rigorous results on instabilities in highly anharmonic crystals which can be obtained in a unified treatment from the structure of the displacement-correlation function. However, the fluctuation sum rule (57) which is a direct implication of the elastic or compressibility sum rule represents an interesting test for the consistency of any such approximation.

VII. CONCLUSIONS

All instabilities discussed in this paper are related to singularities in the long-wavelength limit of the Fourier transform of the displacement-autocorrelation function. The divergences of $\lim_{q\to 0} D_{ll}(\mathbf{q})$ then give rise to unbounded displacement-autocorrelation functions $\langle \mathbf{u}^2 \rangle$. The singularities of Eq. (36b) at finite temperatures and Eq. (46) at absolute zero follow directly from the $\mathbf{q}$ dependence of $D_{ll}(\mathbf{q})$ at small $\mathbf{q}$. The instabilities indicated by unbounded $\langle \mathbf{u}^2 \rangle$, therefore, depend on the dimensionality of the system and, in particular, $\langle \mathbf{u}^2 \rangle$ remains bounded in three dimensions. On the other hand, the anomalous increase of $\lim_{q\to 0} q_j q_l D_{ki'}(\mathbf{q})$ in Eq. (56) due to strongly diminshed elastic constants c_{ijkl} cannot necessarily be ruled out in three dimensions. It is intrinsically related to the dynamical behavior of the system. The role of the interactions in the system becomes particularly clear in that temperature region where sound absorption increases strongly due to fluctuations. The fact that it is the directional-dependent quantity $\lim_{q\to 0} q_j q_l D_{ki'}(\mathbf{q})$ which becomes large in (56) for small elastic constants c_{ijkl} allows this kind to instability to appear for certain modes only.

ACKNOWLEDGMENTS

The author thanks Professor G. V. Chester for stimulating discussions from which he has greatly benefited, and Dr. R. O. Jones for helpful comments on this manuscript.

[17] K. A. Minaeva, A. P. Levanyuk, B. A. Strukov, and V. A. Koptsik, Fiz. Tverd. Tela **9**, 1220 (1967) [English transl.: Soviet Phys.—Solid State **9**, 950 (1967)].

[18] The generalizations necessary to connect the long-wavelength limit of the inverse of the static-displacement response function with the isothermal elastic constants in non-Bravais lattices have been given by W. Götze and K. H. Michel, Z. Physik **217**, 170 (1968).