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Decay of pair correlations in three-dimensional crystals

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The long-range behavior of spatial correlations in three-dimensional crystals is analyzed in the context of a Landau model. A scaling argument is used to show that the two-particle density distribution $\rho_2(\vec{r}_1,\vec{r}_2)$ decays to its asymptotic value $\rho_1(\vec{r}_1)\rho_1(\vec{r}_2)$ as $1/r_{12}$ when the distance r_{12} between the positions $\vec{r}_1$ and $\vec{r}_2$ in the crystal becomes large. An elastic analogy is developed whereby this asymptotic behavior may also be interpreted in terms of displacement fields induced by the action of point forces. The slow $1/r_{12}$ decay of the density correlations is seen to be entirely consistent with expressions for the elastic moduli and the thermal diffuse scattering intensity.

I. INTRODUCTION

Although the literature on x-ray and neutron scattering from crystals is quite extensive, there are suprisingly few results dealing with the decay of molecular correlations in real space. For instance, one would like to know how the two-particle density distribution $\rho_2(\vec{r}_1, \vec{r}_2)$ decays to its asymptotic value $\rho_1(\vec{r}_1)\rho_1(\vec{r}_2)$ as the distance between the positions $\vec{r}_1$ and $\vec{r}_2$ in the crystal becomes large, and how this decay is reflected in expressions for the elastic constants. Experimentally one knows that lattice vibrations manifest themselves in the thermal diffuse scattering of x rays from near-perfect crystals,[1] and it would be useful to develop a clear understanding of how this thermal motion is related to the spatial correlation of atomic positions.

In his 1954 paper on the pair correlation function in space and time, $G(\vec{r}, t)$, Van Hove[2] gives what is apparently the only definite statement in the literature regarding the decay of $\rho_2(\vec{r}_1, \vec{r}_2)$. For the three-dimensional harmonic model, Van Hove states, without proof, that for fixed t, $\vec{r}\rightarrow\infty$, $G(\vec{r}, t)$ approaches its asymptotic value, the convergence being in $|\vec{r}|^{-1}$. This result implies, at least for the harmonic model, that $\rho_2(\vec{r}_1, \vec{r}_2) - \rho_1(\vec{r}_1)\rho_1(\vec{r}_2)$ decays to zero at large distances as the reciprocal of the distance r_{12} between the positions $\vec{r}_1$ and $\vec{r}_2$ in the crystal.

Aside from the Van Hove statement, there are two independent lines of reasoning which place restrictions on the decay of $\rho_2(\vec{r}_1, \vec{r}_2)$. Both arguments lead to the same result, namely that $\rho_2(\vec{r}_1, \vec{r}_2) - \rho_1(\vec{r}_1)\rho_1(\vec{r}_2)$ must decay to zero as r_{12}^{-3} or slower if the equilibrium state of the system is to possess the directional properties of a single crystal. The first argument, due to Stillinger,[3] derives from the extension of the compressibility equation for fluids to the case of anisotropic elastic solids. One can readily show that the response of the system to long-wavelength external body forces (which must necessarily depend on the direction of these forces for an anisotropic body) will be independent of direction if $\rho_2(\vec{r}_1, \vec{r}_2) - \rho_1(\vec{r}_1)\rho_1(\vec{r}_2)$ decays to zero faster than r_{12}^{-3}. But this would contradict the original assumption, namely that the state of the body is crystalline. The second argument, presented recently by Gruber and Martin,[4] is based on the BBGKY equations. These authors show that if one imposes an $\mathcal{L}^1$-clustering condition on the molecular distribution functions, then the single-particle density distribution $\rho_1(\vec{r})$ must be constant. This assumed clustering, which at the level of the two-point function implies that $\rho_2(\vec{r}_1, \vec{r}_2) - \rho_1(\vec{r}_1)\rho_1(\vec{r}_2)$ goes to zero faster than r_{12}^{-3}, is therefore incapable of yielding equilibrium states with the symmetry appropriate to a crystal. One can only conclude from this that if the body is crystalline, then the molecular distribution functions do not satisfy $\mathcal{L}^1$ clustering.

In this paper the decay of $\rho_2(\vec{r}_1, \vec{r}_2) - \rho_1(\vec{r}_1)\rho_1(\vec{r}_2)$ is analyzed for three-dimensional crystals in the context of a Landau model, which has been used to argue that translational long-range order does not exist in one and two dimensions[5] and, more recently, as the basis for a model of two-dimensional solids.[6] Inasmuch as the Landau theory is essentially exact in its treatment of long-wavelength fluctuations and since these will be seen to give rise to the dominant correlations at large distances, the results obtained should hold for any system which on a macroscopic level obeys linear elasticity theory. A brief synopsis of the relevant parts of the Landau theory is given in the next section and, in Sec. III, scaling arguments are used to deduce the asymptotic form of the density correlations. In Sec. IV, a macroscopic elastic analogy is developed whereby the density correlations are interpreted in terms of macroscopic displacement fields induced by the action of point forces. In Sec. V, the effects of the slow rate of decay of the density correlations on expressions for the elastic constants and thermal diffuse scattering intensity are analyzed.

II. BASIC APPROACH

The notation introduced in this section is essentially that of Lifshitz and Pitaevskii[5] and, for simplicity, only Bravais lattices are considered. The primitive translation vectors of the direct lattice are denoted by $\vec{a}_i$ ($i=1,2,3$) and those of the associated reciprocal lattice by $\vec{b}_i$.

At absolute zero the system is assumed crystalline with a periodic microscopic density $n_0(\vec{r})$ given by

$$n_0(\vec{r}) = \sum_{\vec{a}} \delta(\vec{r}-\vec{a}) \tag{2.1}$$

or, as a Fourier series,

$$n_0(\vec{r}) = \frac{1}{v}\sum_{\vec{b}} e^{i\vec{b}\cdot\vec{r}}. \tag{2.2}$$

The sums are to be carried out over all translation vectors of the direct and reciprocal lattices, respectively, and v ($=1/\rho$, ρ being the number density) denotes the volume of a primitive cell in the direct lattice. At finite temperatures T, the atoms of the crystal vibrate about their lattice sites with small displacements $\vec{u}(\vec{r})$ and the microscopic density is given in terms of that at $T=0$ by

$$n(\vec{r}) = n_0(\vec{r}-\vec{u}(\vec{r})). \tag{2.3}$$

The one- and two-particle density distributions are then defined as

$$\rho_1(\vec{r}_1) = \langle n(\vec{r}_1)\rangle, \tag{2.4}$$

$$\rho_2(\vec{r}_1,\vec{r}_2) + \delta(\vec{r}_1-\vec{r}_2)\,\rho_1(\vec{r}_1) = \langle n(\vec{r}_1)n(\vec{r}_2)\rangle, \tag{2.5}$$

which on using (2.2) and (2.3) may be written

$$\rho_1(\vec{r}_1) = \frac{1}{v}\sum_{\vec{b}} e^{i\vec{b}\cdot\vec{r}_1}\langle e^{-i\vec{b}\cdot\vec{u}(\vec{r}_1)}\rangle, \tag{2.6}$$

$$\rho_2(\vec{r}_1,\vec{r}_2) + \delta(\vec{r}_1-\vec{r}_2)\rho_1(\vec{r}_1) = \frac{1}{v^2}\sum_{\vec{b}_1}\sum_{\vec{b}_2} e^{i\vec{b}_1\cdot\vec{r}_1+i\vec{b}_2\cdot\vec{r}_2}\langle e^{-i\vec{b}_1\cdot\vec{u}(\vec{r}_1)-i\vec{b}_2\cdot\vec{u}(\vec{r}_2)}\rangle. \tag{2.7}$$

The angular brackets $\langle\cdots\rangle$ in these expressions denote averaging with respect to the ensemble probability distribution for the displacement fields $\vec{u}(\vec{r})$.

Before stating the Landau theory result for the probability distribution, the mathematical representation of $\vec{u}(\vec{r})$ must first be stipulated. One considers a finite volume V of the crystal spanned by the vectors $\vec{A}_i = N\vec{a}_i$, where N is a large integer, and imposes periodic boundary conditions on $\vec{u}(\vec{r})$. In the present context, these take the form $\vec{u}(\vec{r}+\vec{A}) = \vec{u}(\vec{r})$, where $\vec{A}$ is an arbitrary translation vector in the superlattice generated by $\vec{A}_i$. Under these conditions, $\vec{u}(\vec{r})$ may be expanded in a Fourier series of the form

$$\vec{u}(\vec{r}) = {\sum_{\vec{k}}}' \vec{u}_{\vec{k}}\, e^{i\vec{k}\cdot\vec{r}}, \tag{2.8}$$

where the wave vectors $\vec{k}$ are translation vectors in the lattice reciprocal to the superlattice generated by $\vec{A}_i$. Clearly, one has

$$\int_V d\vec{r}\, e^{i(\vec{k}-\vec{k}')\cdot\vec{r}} = V\delta_{\vec{k},\vec{k}'}, \tag{2.9}$$

so that different Fourier components are orthogonal. The prime affixed to the sum in (2.8) denotes the usual restrictions that the term $\vec{k}=\vec{0}$ is to be excluded from the sum and that one is to sum only over wave vectors which lie within the first Brillouin zone, i.e., whose associated wavelengths are larger than about twice the lattice spacing a.[7] The term $\vec{k}=\vec{0}$ in (2.8) would, of course, correspond to macroscopic motion of the center of mass of the crystal.

The change ΔF in the Helmholtz free energy due to displacements $\vec{u}(\vec{r})$ at constant temperature yields their probability distribution via $\exp(-\Delta F/k_BT)$, where k_B is Boltzmann's constant. At the low temperatures considered, the most probable displacements will be elastic waves and in the Landau theory ΔF is therefore written[5]

$$\Delta F = \tfrac{1}{2}\lambda_{ijlm}\int_V d\vec{r}\, u_{ij}(\vec{r})\,u_{lm}(\vec{r}), \tag{2.10}$$

where

$$u_{ij}(\vec{r}) = \frac{1}{2}\left(\frac{\partial u_i(\vec{r})}{\partial x_j} + \frac{\partial u_j(\vec{r})}{\partial x_i}\right). \tag{2.11}$$

Here λ_{ijlm} is the elastic modulus tensor,[8] $\vec{r}=(x_1,x_2,x_3)$, and summation over repeated indices is implied. The quantity $u_{ij}(\vec{r})$ is just the usual strain tensor of linear elasticity theory. An expression for ΔF in terms of the Fourier coefficients $\vec{u}_{\vec{k}}$ of $\vec{u}(\vec{r})$ is obtained by substituting expression (2.8) into (2.10). On using the orthogonality condition (2.9), one has

$$\Delta F = \tfrac{1}{2}V{\sum_{\vec{k}}}' u_{i\vec{k}}\,u_{l-\vec{k}}\,\phi_{il}(\vec{k}), \tag{2.12}$$

where

$$\phi_{il}(\vec{k}) = \lambda_{ijlm}k_jk_m. \tag{2.13}$$

The real, symmetric[9] tensor ϕ_{il} is thus a quadratic function of the components of $\vec{k}=(k_1,k_2,k_3)$.

From the form (2.12) of the free energy, one sees that the probability distribution for the Fourier components $\vec{u}_{\vec{k}}$ of $\vec{u}(\vec{r})$ is Gaussian, and from the general formulas of fluctuation theory,[10] one therefore has the average values

$$\langle u_{i\vec{k}}\, u_{l\vec{k}'}\rangle_V = \frac{k_B T}{V}\, \phi_{il}^{-1}(\vec{k})\, \delta_{\vec{k}',-\vec{k}}\ , \qquad (2.14)$$

$\phi_{il}^{-1}(\vec{k})$ being the matrix inverse of $\phi_{il}(\vec{k})$. Different Fourier components are therefore uncorrelated unless $\vec{k}+\vec{k}'=\vec{0}$. The angular brackets with the subscript V are used to denote averages defined for finite volumes V. The infinite volume limits of such quantities, which are taken by letting the large integer N tend to infinity, are denoted without subscripts.

Equation (2.14) is the most important result in the Landau theory, for by using it one can readily compute the displacement correlation tensor $\langle u_i(\vec{r}_1) u_l(\vec{r}_2)\rangle_V$. Using (2.8) and (2.14), one finds

$$\langle u_i(\vec{r}_1)\, u_l(\vec{r}_2)\rangle_V = \frac{k_B T}{V} \sum_{\vec{k}}{}' \phi_{il}^{-1}(\vec{k}) e^{i\vec{k}\cdot(\vec{r}_1-\vec{r}_2)}\ . \qquad (2.15)$$

Since $\phi_{il}^{-1}(\vec{k}) = \phi_{il}^{-1}(-\vec{k})$, $\langle u_i(\vec{r}_1)\, u_l(\vec{r}_2)\rangle_V$ is an even function of the vector difference $\vec{r}_1-\vec{r}_2$ as well as being invariant under interchange of the indices i and l.[9] It is worth noting that, in contrast to the two-dimensional result, the mean-square displacement $\langle u_i(\vec{r})\, u_i(\vec{r})\rangle$ in three dimensions is finite.[5]

The Gaussian nature of the probability distribution may be used to transform the expressions (2.6) and (2.7) for $\rho_1(\vec{r}_1)$ and $\rho_2(\vec{r}_1, \vec{r}_2)$. Since both $\vec{b}\cdot\vec{u}(\vec{r}_1)$ and $\vec{b}_1\cdot\vec{u}(\vec{r}_1)+\vec{b}_2\cdot\vec{u}(\vec{r}_2)$ are linear functions of normally distributed variables (the Fourier components $\vec{u}_{\vec{k}}$), one has from a well-known general formula[10] that

$$\langle e^{i\vec{b}\cdot\vec{u}(\vec{r}_1)}\rangle = \exp\{-\tfrac{1}{2}\langle[\vec{b}\cdot\vec{u}(\vec{r}_1)]^2\rangle\}, \qquad (2.16)$$

$$\langle e^{i\vec{b}_1\cdot\vec{u}(\vec{r}_1)+i\vec{b}_2\cdot\vec{u}(\vec{r}_2)}\rangle = \exp\{-\tfrac{1}{2}\langle[\vec{b}_1\cdot\vec{u}(\vec{r}_1)+\vec{b}_2\cdot\vec{u}(\vec{r}_2)]^2\rangle\}\ . \qquad (2.17)$$

On using these results in (2.6) and (2.7), it follows that

$$\rho_1(\vec{r}_1) = \sum_{\vec{b}} \rho_{\vec{b}}\, e^{i\vec{b}\cdot\vec{r}_1}, \qquad (2.18)$$

$$\rho_2(\vec{r}_1, \vec{r}_2) + \delta(\vec{r}_1-\vec{r}_2)\rho_1(\vec{r}_1) = \sum_{\vec{b}_1} \rho_{\vec{b}_1} e^{i\vec{b}_1\cdot\vec{r}_1} \sum_{\vec{b}_2} \rho_{\vec{b}_2} e^{i\vec{b}_2\cdot\vec{r}_2} \exp[-b_{1i}b_{2l}\langle u_i(\vec{r}_1)\, u_l(\vec{r}_2)\rangle]\ , \qquad (2.19)$$

where

$$\rho_{\vec{b}} = \frac{1}{v}\, \exp[-\tfrac{1}{2} b_i b_l \langle u_i(\vec{0})\, u_l(\vec{0})\rangle]\ . \qquad (2.20)$$

Hence, to calculate $\rho_1(\vec{r}_1)$ and $\rho_2(\vec{r}_1, \vec{r}_2)$ one need only compute the displacement correlation tensor. This is the subject of Sec. III.

III. DECAY OF DENSITY CORRELATIONS

After having taken the limit $V\to\infty$, the displacements at two widely separated positions in the crystal must be almost statistically independent. Consequently, the correlations $\langle u_i(\vec{r}_1)\, u_l(\vec{r}_2)\rangle$ must tend to zero as r_{12} tends to infinity. On expanding the exponential factor in (2.19) and using (2.18), at large separations one therefore has

$$\rho_2(\vec{r}_1, \vec{r}_2) - \rho_1(\vec{r}_1)\,\rho_1(\vec{r}_2) = \langle u_i(\vec{r}_1)\, u_l(\vec{r}_2)\rangle \frac{\partial\rho_1(\vec{r}_1)}{\partial x_{1i}} \frac{\partial\rho_1(\vec{r}_2)}{\partial x_{2l}} + \tfrac{1}{2}\langle u_i(\vec{r}_1)\, u_l(\vec{r}_2)\rangle\langle u_j(\vec{r}_1)\, u_m(\vec{r}_2)\rangle \frac{\partial^2\rho_1(\vec{r}_1)}{\partial x_{1i}\partial x_{1j}} \frac{\partial^2\rho_1(\vec{r}_2)}{\partial x_{2l}\partial x_{2m}} + \cdots . \qquad (3.1)$$

In general, the first term on the right is not zero, so $\rho_2(\vec{r}_1, \vec{r}_2) - \rho_1(\vec{r}_1)\,\rho_1(\vec{r}_2)$ decays to zero at the same rate as $\langle u_i(\vec{r}_1)\, u_l(\vec{r}_2)\rangle$; as is shown below [see (3.9)], this is as r_{12}^{-1}. When the first term on the right is zero, as it is when either $\vec{r}_1$ or $\vec{r}_2$ corresponds to a lattice site, $\rho_2(\vec{r}_1, \vec{r}_2) - \rho_1(\vec{r}_1)\rho_1(\vec{r}_2)$ decays as r_{12}^{-2} or faster.

A direct argument for the r_{12}^{-1} decay of $\langle u_i(\vec{r}_1)\, u_l(\vec{r}_2)\rangle$ is now given based on its definition (2.15). Letting $\vec{r}=\vec{r}_1-\vec{r}_2$ and using the symmetry properties of $\langle u_i(\vec{r}_1)\, u_l(\vec{r}_2)\rangle_V$, one has

$$\langle u_i(\vec{0}) u_l(\vec{r})\rangle_V = \frac{k_B T}{V} \sum_{\vec{k}}{}' \phi_{il}^{-1}(\vec{k})\, e^{i\vec{k}\cdot\vec{r}}. \qquad (3.2)$$

While obviously depending on the vector $\vec{r}$ and the volume V, this quantity also depends implicitly on the lattice spacing a. For as was discussed in Sec. II, it is precisely this length which provides the criterion for the short-wavelength cutoff of the sum over wave vectors in (3.2). One may therefore write with no loss of generality

$$\langle u_i(\vec{0}) u_l(\vec{r})\rangle_V = \chi_{il}(\vec{r}, V, a)\,, \qquad (3.3)$$

χ_{il} being some function of $\vec{r}$, V, and a.

Consider now $\langle u_i(\vec{0})u_l(\alpha\vec{r})\rangle_V$ with a scaling parameter α; since (2.13) implies that $\phi_{il}^{-1}(\alpha\vec{k}) = \alpha^{-2}\phi_{il}^{-1}(\vec{k})$, (3.2) becomes

$$\langle u_i(\vec{0})u_l(\alpha\vec{r})\rangle_V = \frac{1}{\alpha}\frac{k_B T}{(V/\alpha)^3}\sum_{\vec{k}}{}' \phi_{il}^{-1}(\alpha\vec{k})e^{i\alpha\vec{k}\cdot\vec{r}}. \quad (3.4)$$

But by definition, $V \propto a^3$ and $\vec{k} \propto 1/a$, so the right-hand side of (3.4) is exactly the same as the right-hand side of (3.2) if in the latter a is replaced by a/α. The functions χ_{il} therefore satisfy the scaling relation

$$\chi_{il}(\alpha\vec{r}, V, a) = \alpha^{-1}\chi_{il}(\vec{r}, V/\alpha^3, a/\alpha) \quad (3.5)$$

or, in the $V\to\infty$ limit,

$$\chi_{il}(\alpha\vec{r}, \infty, a) = \alpha^{-1}\chi_{il}(\vec{r}, \infty, a/\alpha). \quad (3.6)$$

Note that if a were zero, χ_{il} would be a homogeneous function[11] of $\vec{r}$ of order -1; i.e.,

$$\chi_{il}(\alpha\vec{r}, \infty, 0) = \alpha^{-1}\chi_{il}(\vec{r}, \infty, 0). \quad (3.7)$$

From these results, the asymptotic form of the displacement correlations may be readily deduced. Multiplying both sides of (3.6) by α and letting $\alpha\to\infty$, one has

$$\lim_{\alpha\to\infty} \alpha\,\chi_{il}(\alpha\vec{r}, \infty, a) = \chi_{il}(\vec{r}, \infty, 0). \quad (3.8)$$

But it follows from (3.7) that $\chi_{il}(\vec{r}, \infty, 0)$ must be of the form $G_{il}(\hat{r})/r$ where $\hat{r} = \vec{r}/r$ and $r = |\vec{r}|$, $G_{il}(\hat{r})$ being a homogeneous function of order zero. From the definition (3.3), the required asymptotic behavior of $\langle u_i(\vec{0})u_l(\vec{r})\rangle$ is therefore

$$\langle u_i(\vec{0})u_l(\vec{r})\rangle = G_{il}(\hat{r})/r + \cdots, \quad r\to\infty. \quad (3.9)$$

On inserting this result into (3.1) and keeping only the first term on the right, for the density correlations one has

$$\rho_2(\vec{r}_1, \vec{r}_2) - \rho_1(\vec{r}_1)\rho_1(\vec{r}_2) = \frac{G_{il}(\hat{r}_{12})}{r_{12}}\frac{\partial\rho_1(\vec{r}_1)}{\partial x_{1i}}\frac{\partial\rho_1(\vec{r}_2)}{\partial x_{2l}} + \cdots. \quad (3.10)$$

It is interesting that the superposition of thermally distributed elastic waves [which is what the ensemble average in (3.9) represents] gives rise to such long-range spatial correlations. Indeed, it is the infinitely long waves which give rise to the term proportional to $1/r$. For as the derivation of (3.9) clearly shows, this term is independent of the short-wavelength cutoff, i.e., the lattice spacing a, and is in fact obtained by letting the cutoff tend to zero.

IV. A MACROSCOPIC ELASTIC ANALOGY

An alternative interpretation of the displacement and density correlations in terms of macroscopic elasticity theory is now given. Consider the equations of equilibrium for an elastic body subject to an as yet unchosen body force $\vec{f}$; one has[8]

$$\lambda_{ijlm}\frac{\partial^2 v_l(\vec{r})}{\partial x_j \partial x_m} + f_i(\vec{r}) = 0, \quad (4.1)$$

where the displacement field has been denoted by $\vec{v}$ to distinguish it from $\vec{u}$ considered above. The equations for the Fourier transforms $\vec{v}_{\vec{k}}$ and $\vec{f}_{\vec{k}}$ of $\vec{v}$ and $\vec{f}$ are then, using (2.13),

$$v_{l\vec{k}} = \phi_{il}^{-1}(\vec{k})f_{i\vec{k}}. \quad (4.2)$$

It is the obvious similarity of this equation to (2.14) which is now exploited. After setting $\vec{k}' = -\vec{k}$ and forming $c_i\langle u_{i\vec{k}}u_{l-\vec{k}}\rangle$ in (2.14), one has

$$c_i\langle u_{i\vec{k}}u_{l-\vec{k}}\rangle_V = \frac{k_B T}{V}c_i\,\phi_{il}^{-1}(\vec{k}), \quad (4.3)$$

where $\vec{c}$ is here taken to be an arbitrary constant vector independent of $\vec{k}$. The following choice of the force $\vec{f}$ is now made:

$$f_{i\vec{k}} = \begin{cases} c_i k_B T/V & \text{for } \vec{k} \text{ contributing to the sum in (2.8)} \\ 0 & \text{otherwise,} \end{cases} \quad (4.4)$$

so that by comparing (4.2) with (4.3) one obtains the identity

$$c_i\langle u_{i\vec{k}}u_{l-\vec{k}}\rangle_V = v_{l\vec{k}}. \quad (4.5)$$

On transforming (4.5) from Fourier space to real space and using the symmetry properties of the displacement correlations, it therefore follows that

$$c_i\langle u_i(\vec{0})u_l(\vec{r})\rangle_V = v_l(\vec{r}), \quad (4.6)$$

$\vec{v}$ being the displacement field due to the body force

$$\vec{f}(\vec{r}) = \vec{c}\,\frac{k_B T}{V}\sum_{\vec{k}}{}' e^{i\vec{k}\cdot\vec{r}}. \quad (4.7)$$

This result relates the equilibrium displacement correlations to a definite macroscopic displacement field in an elastic body.

As a first application of the analogy embodied in (4.6) and (4.7), the asymptotic formula (3.9) is rederived and the functions $G_{il}(\hat{r})$ are obtained from a somewhat different point of view. On taking the limit $V\to\infty$, one first has

$$c_i\langle u_i(\vec{0})\,u_l(\vec{r})\rangle = v_l(\vec{r}), \quad (4.8)$$

$\vec{v}$ now being due to the force

$$\vec{f}(\vec{r}) = \vec{c}\,\frac{k_B T}{(2\pi)^3}\int' d\vec{k}\,e^{i\vec{k}\cdot\vec{r}}, \quad (4.9)$$

in which $\lim_{V\to\infty}(1/V)\sum'_{\vec{k}}$ has been replaced by

$(2\pi)^{-3}\int' d\vec{k}$. Since the contribution to the integral from the neighborhood of the origin $\vec{k}=\vec{0}$ may be made arbitrarily small, the restriction $\vec{k}=\vec{0}$ may here be dropped. Scaling arguments are now employed to determine the asymptotic form of $\vec{v}(\vec{r})$ and hence, via (4.8), the asymptotic form of $\langle u_i(\vec{0})u_l(\vec{r})\rangle$. Using (4.9) and introducing the scaling parameter α, one has from (4.1)

$$\lambda_{ijlm}\frac{\partial^2 \alpha v_l(\alpha\vec{r})}{\partial x_j \partial x_m}+c_i k_B T\frac{1}{(2\pi)^3}\int' \alpha^3 d\vec{k}\, e^{i\alpha\vec{k}\cdot\vec{r}}=0\,. \tag{4.10}$$

In the limit $\alpha\to\infty$, the force term becomes a representation of the δ function and, with $\lim_{\alpha\to\infty}\alpha\vec{v}(\alpha\vec{r})=\vec{w}(\vec{r})$, it follows that

$$\lambda_{ijlm}\frac{\partial^2 w_l(\vec{r})}{\partial x_j \partial x_m}+c_i k_B T\delta(\vec{r})=0\,. \tag{4.11}$$

The implications of this result are most apparent when it is combined with (4.8) and (4.9):

$$c_i\langle u_i(\vec{0})\,u_l(\vec{r})\rangle = w_l(\vec{r})+\cdots,\quad \vec{r}\to\infty \tag{4.12}$$

where $\vec{w}(\vec{r})$ is the displacement field due to the point force

$$\vec{f}(\vec{r})=\vec{c}\,k_B T\delta(\vec{r})\,. \tag{4.13}$$

The displacement correlations at large distances are therefore formally equivalent to the elastic displacement field due to a δ-function force.

The mathematical form of $\vec{w}$ may be deduced directly from (4.11): Since $\delta(\vec{r})$ is a homogeneous function of $\vec{r}$ of order -3 and since (4.11) involves only second derivatives of the components of $\vec{w}$, these components must be homogeneous of order -1. The result (4.12) is thus identical in content to (3.9), and one has the correspondence

$$w_l(\vec{r})=c_i\frac{G_{il}(\hat{r})}{r}\,. \tag{4.14}$$

Since the general solution to (4.11) may be expressed in terms of the Green's tensor H_{il} by

$$w_l(\vec{r})=c_i\, k_B T H_{il}(\vec{r})\,, \tag{4.15}$$

it also follows that, aside from the factor of $k_B T$, the displacement correlation tensor is nothing but the Green's tensor for a general anisotropic elastic body.

As a second but related example of the macroscopic elastic analogy, consider the local density change induced by fixing a particle. Dividing both sides of (3.1) by $\rho_1(\vec{r}_1)$ and keeping only the first term on the right, one obtains

$$\rho_2(\vec{r}_1,\vec{r}_2)/\rho_1(\vec{r}_1)-\rho_1(\vec{r}_2) = \langle u_i(\vec{r}_1)u_l(\vec{r}_2)\rangle\,\frac{\partial \ln\rho_1(\vec{r}_1)}{\partial x_{1i}}\,\frac{\partial\rho_1(\vec{r}_2)}{\partial x_{2l}}+\cdots\,. \tag{4.16}$$

This expression yields the local density change at a distant point $\vec{r}_2$ induced by fixing a particle at $\vec{r}_1$. Since $\langle u_i(\vec{r}_1)u_l(\vec{r}_2)\rangle = \langle u_i(\vec{0})u_l(\vec{r}_2-\vec{r}_1)\rangle$, on letting $\vec{c}=-\vec{\nabla}_1\ln\rho_1(\vec{r}_1)$ in (4.12) and (4.13), one has

$$-\frac{\partial \ln\rho_1(\vec{r}_1)}{\partial x_{1i}}\langle u_i(\vec{r}_1)u_l(\vec{r}_2)\rangle = w_l(\vec{r}_2-\vec{r}_1)+\cdots\,, \tag{4.17}$$

where $\vec{w}(\vec{r})$ is the displacement field due to the force

$$\vec{f}(\vec{r})=-k_B T\vec{\nabla}_1\ln\rho_1(\vec{r}_1)\,\delta(\vec{r})\,. \tag{4.18}$$

The amplitude of this force, $k_B T\vec{\nabla}_1\ln\rho_1(\vec{r}_1)$, is just the mean statistical force which would act on a particle at the position $\vec{r}_1$; in case $\vec{\nabla}_1\ln\rho_1(\vec{r}_1)=\vec{0}$, as it is when $\vec{r}_1$ corresponds to a lattice site say, then higher-order terms in the expansion (4.16) determine the asymptotic density change. It is noted that in the present context the coordinate $\vec{r}_1$ plays the role of a parameter and for a given value of $\vec{r}_1$, the vector $\vec{c}$ may still be considered a constant vector. Substitution of (4.17) into (4.16) yields the result

$$\rho_2(\vec{r}_1,\vec{r}_2)/\rho_1(\vec{r}_1)-\rho_1(\vec{r}_2) = -\vec{w}(\vec{r}_2-\vec{r}_1)\cdot\vec{\nabla}_2\rho_1(\vec{r}_2)+\cdots\,, \tag{4.19}$$

which to the same order of approximation may be written

$$\rho_2(\vec{r}_1,\vec{r}_2)/\rho_1(\vec{r}_1)=\rho_1(\vec{r}_2-\vec{w}(\vec{r}_2-\vec{r}_1)). \tag{4.20}$$

The effect of fixing a particle is therefore to simply shift the unperturbed density distribution by the amount $\vec{w}(\vec{r}_2-\vec{r}_1)$, without changing its amplitude.

Since the divergence of an elastic displacement field gives the local density change in an elastic body, it may have seemed reasonable, *a priori*, that the local density change $\rho_2(\vec{r}_1,\vec{r}_2)/\rho_1(\vec{r}_1)-\rho_1(\vec{r}_2)$ could be expressed in terms of the divergence of some such field.[3] This is not the case, however, as can be seen from (4.19) written in the form

$$\rho_2(\vec{r}_1,\vec{r}_2)/\rho_1(\vec{r}_1)-\rho_1(\vec{r}_2) = -\vec{\nabla}_2\cdot[\,\rho_1(\vec{r}_2)\,\vec{w}(\vec{r}_2-\vec{r}_1)] +\rho_1(\vec{r}_2)\,\vec{\nabla}_2\cdot\vec{w}(\vec{r}_2-\vec{r}_1)+\cdots\,, \tag{4.21}$$

where the first term on the right, which corresponds to an induced mass flux, is not in general zero. Such terms are always zero in conventional elasticity theory, which deals with a continuum of mass points, but should be expected to appear when elasticity theory is applied to problems involving distribution functions embedded in elastic media.

V. THE $1/r$ DECAY AND THE ELASTIC CONSTANTS

The angular distribution of x rays or neutrons scattered from a system of identical particles is given by the static structure factor $S(\vec{q})$, defined by

$$\rho S(\vec{q}) = \lim_{V\to\infty} \frac{1}{V} \left\langle \left| \sum_i e^{i\vec{q}\cdot\vec{r}_i} \right|^2 \right\rangle_V , \tag{5.1}$$

where $\vec{q}$ is the change in wave vector on scattering and the sum is over all particles i, $\vec{r}_i$ denoting their position vectors. The average is, as in Sec. II, over a canonical ensemble of systems satisfying periodic boundary conditions and the infinite volume limit is to be taken over a sequence of parallelopipeds containing an ever increasing integral number of primitive cells along each edge. Since Bragg scattering results from the underlying periodicity of the lattice rather than from correlations of the atomic positions, a direct measure of these correlations is obtained by subtracting from $S(\vec{q})$ the contribution due to Bragg scattering. Denoting the resulting quantity by $S'(\vec{q})$, one has

$$\rho S'(\vec{q}) = \lim_{V\to\infty} \frac{1}{V} \left(\left\langle \left| \sum_i e^{i\vec{q}\cdot\vec{r}_i} \right|^2 \right\rangle_V - \left| \left\langle \sum_i e^{i\vec{q}\cdot\vec{r}_i} \right\rangle_V \right|^2 \right) \tag{5.2}$$

or, in terms of the molecular distribution functions,

$$\rho S'(\vec{q}) = \rho + \lim_{V\to\infty} \int_V d\vec{r}\, e^{i\vec{q}\cdot\vec{r}} G(\vec{r}), \tag{5.3}$$

where

$$G(\vec{r}) = \frac{1}{v} \int_v d\vec{r}_1 [\rho_2(\vec{r}_1, \vec{r}_1+\vec{r}) - \rho_1(\vec{r}_1)\rho_1(\vec{r}_1+\vec{r})], \tag{5.4}$$

$v = 1/\rho$ being the volume of a primitive cell in the direct lattice. For crystals, $S'(\vec{q})$ gives what is generally referred to as the thermal diffuse scattering.

Stillinger[3] has shown that the $|\vec{q}| \to 0$ limit of (5.3) yields the correct generalization of the compressibility equation for fluids to the case of anisotropic elastic solids. One obtains in fact that

$$\lim_{q\to 0} S'(\vec{q}) = \rho k_B T q_i q_j q_l q_m \Lambda_{ijlm}/q^4, \tag{5.5}$$

where $q = |\vec{q}|$ and the relation of Λ_{ijlm} to the elastic modulus tensor λ_{ijlm} is embodied in the conjugate relations

$$\sigma_{ij} = \lambda_{ijlm} u_{lm}, \tag{5.6}$$

$$u_{lm} = \Lambda_{ijlm} \sigma_{ij}, \tag{5.7}$$

σ_{ij} and u_{ij} being the elastic stress and strain tensors, respectively. Since (5.5) yields the response of the system to an infinitely long wavelength external force in the direction of $\vec{q}$, $S'(\vec{q})$ in the limit $q \to 0$ depends, as it must for crystals, on this direction. This fact imposes a rather strong condition on the decay of $G(\vec{r})$. For if $G(\vec{r})$ (in the infinite volume limit) decayed to zero faster than $1/r^3$, the integral would be absolutely convergent and the successive limits $V\to\infty$, $q\to 0$ could be taken immediately, the result being a quantity independent of the direction of $\vec{q}$.[3] Thus, $G(\vec{r})$ can decay to zero no faster than $1/r^3$ for three-dimensional crystals. As stated in the Introduction, an identical result is implied by the recent work of Gruber and Martin[4] on the BBGKY hierarchy. To deduce the actual asymptotic behavior of $G(\vec{r})$ given only that $\lim_{q\to 0} S'(\vec{q})$ exists is, however, an extremely difficult, if not impossible, task. Not only must one carry out the intricate sequence of limits $V\to\infty$, $q\to 0$, but one must bear in mind that for finite volumes $G(\vec{r})$ depends on V and, due to the periodic boundary conditions, does not even decay to zero at large distances.

As has been shown in Sec. III, the density correlations $\rho_2(\vec{r}_1, \vec{r}_2) - \rho_1(\vec{r}_1)\rho_1(\vec{r}_2)$ for the Landau model decay as $1/r_{12}$. Keeping only the first term on the right of (3.1) and substituting it into (5.4) one finds, after several integrations by parts,

$$G(\vec{r}) = \langle u_i(\vec{0}) u_l(\vec{r}) \rangle \frac{\partial^2}{\partial x_i \partial x_l} \times \frac{1}{v} \int_v d\vec{r}_1 \rho_1(\vec{r}_1) \rho_1(\vec{r}_1+\vec{r}) + \cdots . \tag{5.8}$$

In view of (3.9), $G(\vec{r})$ for the Landau model therefore also decays as $1/r$. While it might appear that such a slow rate of decay could lead to divergent elastic constants when one takes the $q\to 0$ limit of (5.3), due to the complicated limits involved this is not necessarily the case. Indeed, for the Landau model, and probably in general, it is definitely not the case. Since (5.2) and (5.3) are formally equivalent, this can be proven simply be showing that the $q\to 0$ limit of (5.2) exists. Setting $\vec{r}_i = \vec{a}_i + \vec{u}(\vec{a}_i)$ in (5.2) and letting $V\to\infty$, one has

$$S'(\vec{q}) = \sum_{\vec{a}} e^{i\vec{q}\cdot\vec{a}} \left(\langle e^{i\vec{q}\cdot[\vec{u}(\vec{a}) - \vec{u}(0)]} \rangle - \langle e^{i\vec{q}\cdot\vec{u}(\vec{a})} \rangle \langle e^{-i\vec{q}\cdot\vec{u}(0)} \rangle \right), \tag{5.9}$$

where the sum over particles i has been replaced by the sum over all lattice translation vectors $\vec{a}$ and the index i has been dropped. After a final transformation using (2.16), $S'(\vec{q})$ becomes

$$S'(\vec{q}) = e^{-\langle[\vec{q}\cdot\vec{u}(\vec{0})]^2\rangle} \times \sum_{\vec{a}} e^{i\vec{q}\cdot\vec{a}} \left(e^{\langle \vec{q}\cdot\vec{u}(\vec{a})\vec{q}\cdot\vec{u}(\vec{0})\rangle} - 1\right), \qquad (5.10)$$

the factor preceding the sum being the usual Debye-Waller factor. Expanding the real exponentials and using the infinite volume limit of (2.15), to leading order for small $\vec{q}$ one now has

$$S'(\vec{q}) = k_B T \sum_{\vec{a}} e^{i\vec{q}\cdot\vec{a}} q_i q_l \frac{1}{(2\pi)^3} \int' d\vec{k}\, \phi_{il}^{-1}(\vec{k}) e^{-i\vec{k}\cdot\vec{a}} = k_B T q_i q_l \int' d\vec{k}\, \phi_{il}^{-1}(\vec{k}) \frac{1}{(2\pi)^3} \sum_{\vec{a}} e^{i(\vec{q}-\vec{k})\cdot\vec{a}}$$

$$= k_B T q_i q_l \int' d\vec{k}\, \phi_{il}^{-1}(\vec{k}) \frac{1}{v} \sum_{\vec{b}} \delta(\vec{q}-\vec{k}-\vec{b}) = \rho k_B T q_i q_l \sum_{\vec{b}} \phi_{il}^{-1}(\vec{q}-\vec{b}) D(\vec{q}-\vec{b}), \qquad (5.11)$$

where $D(\vec{q}-\vec{b})$ vanishes unless $\vec{q}-\vec{b}$ lies within the first Brillouin zone, in which case it is unity. Since the only nonzero contribution to the sum in (5.11) in the $q\to 0$ limit is clearly the term with $\vec{b}=\vec{0}$, one has then

$$\lim_{q\to 0} S'(\vec{q}) = \rho k_B T q_i q_l \phi_{il}^{-1}(\vec{q}). \qquad (5.12)$$

The right-hand side depends, as it should, on the direction of $\vec{q}$, for from (2.13) it follows that $\phi_{il}^{-1}(\vec{q})$ is a homogeneous function of $\vec{q}$ of order -2 and consequently, $q_i q_l \phi_{il}^{-1}(\vec{q})$ is homogeneous of order zero. This result shows that the $1/r$ decay of $G(\vec{r})$ is clearly not at odds with the existence of the elastic constants.

It is worth pointing out that the Landau theory and Stillinger expressions for the elastic constants, (5.12) and (5.5), respectively, are actually equal. Since this is not obviously the case, and since the relations (5.6) and (5.7) are not sufficient to prove it, the following argument is given. If stresses σ_{ij}^a are applied to an elastic body, internal stresses σ_{ij} are induced which exactly balance them, that is, $\sigma_{ij}+\sigma_{ij}^a=0$; one also has the equations of equilibrium which in this case are

$$\lambda_{ijlm}\frac{\partial^2 u_l}{\partial x_j \partial x_m} + \frac{\partial \sigma_{ij}^a}{\partial x_j} = 0. \qquad (5.13)$$

With the choice $\sigma_{ij}^a = q_i q_j \sin(\vec{q}\cdot\vec{r})/q^2$ and the substitution $u_l = v_l \cos\vec{q}\cdot\vec{r}$, (5.13) becomes

$$\lambda_{ijlm} q_j q_m v_l = q_i, \qquad (5.14)$$

which on using (2.13) is equivalent to

$$\phi_{il}(\vec{q}) v_l = q_i \qquad (5.15)$$

or

$$v_l = q_i \phi_{il}^{-1}(\vec{q}). \qquad (5.16)$$

Multiplying (5.15) by v_i and (5.16) by q_l and comparing the two results one finds the useful identity

$$\phi_{il}(\vec{q}) v_i v_l = \phi_{il}^{-1}(\vec{q}) q_i q_l. \qquad (5.17)$$

Since $\sigma_{ij} = q_i q_j \sin(\vec{q}\cdot\vec{r})/q^2$, $u_{ij} = -\frac{1}{2}(v_i q_j + v_j q_i) \times \sin\vec{q}\cdot\vec{r}$ [see (2.11)], and $\lambda_{ijlm} = \lambda_{ijml} = \lambda_{jilm}$, on multiplying (5.6) by u_{ij} and (5.7) by σ_{lm}, one also has

$$\sigma_{ij} u_{ij} = \phi_{il}(\vec{q}) v_i v_l \sin^2\vec{q}\cdot\vec{r}, \qquad (5.18)$$

$$\sigma_{lm} u_{lm} = q_i q_j q_l q_m \Lambda_{ijlm} \sin^2(\vec{q}\cdot\vec{r})/q^4. \qquad (5.19)$$

On using (5.17) in (5.18) and comparing with (5.19), one arrives at the desired result, namely

$$\phi_{il}^{-1}(\vec{q}) q_i q_l = q_i q_j q_l q_m \Lambda_{ijlm}/q^4. \qquad (5.20)$$

The elastic constants in Stillinger's approach involve the distribution functions defined in terms of the intermolecular potential, whereas in the Landau approach these distributions depend on the elastic constants as parameters. The result (5.20) shows, however, that if one uses the Landau $G(\vec{r})$ in the Stillinger expression for the elastic constants, one obtains an identity. The Landau theory thus provides a consistent parameterization of $G(\vec{r})$ in terms of the elastic constants.

Finally, consider $S'(\vec{q})$ near a Bragg peak, that is, for $\vec{q}=\vec{b}'+\vec{\delta}$ where $\vec{b}'$ is a nonzero reciprocal-lattice vector and $\vec{\delta}$ is small. The Debye-Waller factor in (5.10) may not here be expanded but the derivation of (5.11) remains otherwise valid. The only nonzero term in the sum in (5.11) now has $\vec{b}=\vec{b}'$, and to leading order in $\vec{\delta}$ one has

$$S'(\vec{b}'+\vec{\delta}) = e^{-\langle[\vec{b}'\cdot\vec{u}(\vec{0})]^2\rangle} b_i' b_l' \phi_{il}^{-1}(\vec{\delta}). \qquad (5.21)$$

This formula provides the basis for elastic constant measurements from the thermal diffuse scattering of x rays; moreover, since $\phi_{il}^{-1}(\vec{\delta}) = |\vec{\delta}|^{-2}\phi_{il}^{-1}(\vec{\delta}/|\vec{\delta}|)$, it also implies that near Bragg peaks $S(\vec{b}'+\vec{\delta})$ diverges as $|\vec{\delta}|^{-2}$. As can be seen from (5.10), this is a direct manifestation of the slow $1/r$ decay of the displacement correlations or, equivalently, of the density correlations.

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[6]D. Nelson, in *Fundamental Problems in Statistical Mechanics*, edited by E. G. D. Cohen (North-Holland, Amsterdam, in press), Vol. 5.
[7]The asymptotic form of the density correlations will be seen to be independent of the choice of the short-wavelength cutoff; this provides *a posteriori* justification for the classical treatment of the fluctuations given in (2.10).
[8]L. D. Landau and E. M. Lifshitz, *Theory of Elasticity*, 2nd ed. (Pergamon, New York, 1970), Sec. 10.
[9]The elastic modulus tensor has the symmetry properties $\lambda_{ijlm}=\lambda_{ijml}=\lambda_{jilm}=\lambda_{lmij}$.
[10]See *Statistical Physics*, Ref. 5, Sec. 111.
[11]A function $f(x)$ is homogeneous of order n if $f(\alpha x)=\alpha^n f(x)$.