On the coarse-grained density and compressibility of a non-ideal crystal

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The isothermal compressibility of a general crystal is derived and discussed within (classical) density functional theory. Starting from the microscopic particle density, we carefully coarse grain to obtain the thermodynamic compressibility and the long wavelength limits of the correlation functions of elasticity theory. We explicitly show that the isothermal compressibility is not the wavenumber to zero limit of the (total) density correlation function. The latter also cannot be obtained from the static structure factor measured in a scattering experiment.

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I. INTRODUCTION

In crystals, where translational invariance is spontaneously broken, strain enters as additional thermodynamic variable in the free energy. It describes the distortion of the solid and thus the trace of the strain tensor is connected to the change in density. In ideal crystals, where all atoms can be unambiguously assigned to lattice sites and all lattice sites are occupied, both are actually equivalent. In real crystals, point defects like interstitials and vacancies are present and density fluctuations also change by defect diffusion. The particle number in a unit cell of the crystal can change by deformation of the cell (captured in the strain) or by motion of point defects through the cell. The presence of defects opens the question how density and strain fluctuations are defined in real crystals. Here, no one-to-one mapping of atoms to lattice positions is possible. Therefore, the displacement vector field, whose symmetrized (in linear approximation) gradient gives the strain, cannot be obtained from the individual displacements of the atoms from their lattice positions. Only recently microscopic definitions of strain and density fluctuations in real crystals were derived from the statistical mechanical description of real crystals, overcoming this difficulty. The latter work followed an earlier suggestion by Szamel and Ernst. An intriguing finding of the microscopic approach concerns the coarse-grained density field \(\delta n(r, t)\) which enters into the free energy or, consecutively, the theory of crystal elasticity. Even for arbitrarily large wavelengths, particle density fluctuations with wavenumbers close to all (finite) reciprocal lattice vectors contribute to the coarse-grained density field. This arises because at the macroscopic level strain fluctuations and defect density independently cause changes in the total particle density, and strain fluctuations require contributions from wavenumbers around finite reciprocal lattice vectors in order to be determined in Fourier space. In this contribution, we discuss this at first surprising finding within the framework of density functional theory.

Based on the microscopic definition of the coarse grained variables of elasticity theory, we can address another intriguing question, originally raised by Stillinger and M. Fuchs. Whether the structure factor in the limit of wavevector to zero is analytic and approaches the compressibility? We find that due to the long-ranged displacement correlations, the small wavevector limit in the correlation function of the coarse-grained density field actually is non-analytic and depends on the direction relative to the crystal lattice. We derive these results from density functional theory and can thus put them on a firm microscopic basis. Thus, we generalize results obtained within the harmonic crystal approximation. Correcting the equations (A8) in the appendix of Ref. we also derive relations between fluctuation functions and thermodynamic derivatives. Based on these results the elastic constants of crystals with point defects could be measured by microscopy techniques in colloidal crystals or by simulation.

The paper is organized as follows: in Sect. II we recall definitions and results from Ref. and derive expressions for the fluctuations of displacement and density fields in terms of microscopic quantities. To facilitate application of the expressions, in Sect. III we invert these relations considering two sets of independent fluctuations, coarse-grained density and displacement field or displacement field and defect density. In Sect. IV and the Appendices we show that the small wavevector limit of the coarse-grained density fluctuation function does not agree with the isothermal compressibility \(\kappa\). In Sect. V the reason for the disagreement and (static) scattering experiments are discussed. We conclude that these experiments do not allow to measure the compressibility in a crystal, in contrast to the familiar situation in liquids and gases.
II. COARSE-GRAINED FIELDS AND THEIR CORRELATION FUNCTIONS

In crystals, according to the Goldstone theorem, the spontaneous breaking of translational symmetry induces long-ranged correlations. Specifically, the displacement vector field \( \mathbf{u}(r, t) \) possesses correlations which decay like the inverse distance. While the familiar expression \( \mathbf{u}(r, t) = \sum_i \mathbf{u}_i(t) \delta(r - R^i) \), with the displacement \( \mathbf{u}_i(t) = r_i(t) - R^i \) of particle \( i \) from its lattice site \( R^i \), can be used in ideal crystals, in real crystals, in which defects are present, this expression is invalid. In order to find the microscopic definition of \( \mathbf{u}(r, t) \) and of the other fields of elasticity theory, the following approach was followed.

A. Microscopic starting point in density functional theory

The microscopic approach to find the displacement field in a real crystal starts from the particle density field \( \rho(r, t) \) (considering, for simplicity, a one-component crystal of point particles interacting with a spherically symmetric pair-potential)

\[
\rho(r, t) = \sum_{i=1}^{N} \delta(r - r^i(t))
\]

where \( N \) is the number of particles in the volume \( V \). Spatial Fourier transformation gives fluctuations close to vectors \( \mathbf{g} \) of the reciprocal lattice

\[
\delta \rho_{\mathbf{g}}(\mathbf{q}, t) = \rho(\mathbf{g} + \mathbf{q}, t) - n_\mathbf{g} V \delta_\mathbf{q} \mathbf{0},
\]

where

\[
\rho(\mathbf{k}, t) = \int d^d r e^{-i\mathbf{k} \cdot \mathbf{r}} \rho(\mathbf{r}, t) = \sum_{i=1}^{N} e^{-i\mathbf{k} \cdot \mathbf{r}^i(t)},
\]

and

\[
n_\mathbf{g} = \frac{1}{V} \langle \rho(\mathbf{g}) \rangle = \frac{1}{V} \sum_{i=1}^{N} \langle e^{-i\mathbf{g} \cdot \mathbf{r}^i} \rangle.
\]

Here, the general wave vector \( \mathbf{k} \) was divided up into reciprocal lattice vector \( \mathbf{g} \) and wave vector \( \mathbf{q} \), which lies within the first Brillouin zone; \( \langle \rangle \) brackets indicate canonical averaging at fixed temperature \( T \). The \( n_\mathbf{g} \) are the Bragg-peak amplitudes (Debye-Waller factors) which serve as order parameters for the spontaneous breaking of homogeneity (translational invariance).

Classical density functional theory (DFT)\(^\text{15,17}\) can then be employed in order to derive the correlation functions of the microscopic density fluctuations in Eq. \(^\text{2}\). The fundamental Ornstein-Zernike relation provides a connection to the inverse density-density correlation matrix \( J_{\mathbf{g} \mathbf{g}'}(\mathbf{q}) \)

\[
V k_B T \delta \rho_{\mathbf{g} \mathbf{g}'} = \sum_{\mathbf{g}''} \langle \delta \rho^*_\mathbf{g} (\mathbf{q}) \delta \rho_{\mathbf{g}''}(\mathbf{q}) \rangle J_{\mathbf{g}'' \mathbf{g}'}(\mathbf{q}) .
\]

The (infinite-dimensional) Hermitian matrix \( J_{\mathbf{g} \mathbf{g}'} \) is the double Fourier-transform of the direct correlation function \( c(r_1, r_2) \).

\[
J_{\mathbf{g} \mathbf{g}'}(\mathbf{q}) = \frac{k_B T}{V} \int d^d r_1 \int d^d r_2 e^{i\mathbf{g} \cdot \mathbf{r}_1} e^{-i\mathbf{g} \cdot \mathbf{r}_2} e^{i\mathbf{q} \cdot \mathbf{r}_1 2} \left( \frac{\delta(\mathbf{r}_1 2)}{n(r_1 2)} - c(r_1 2, r_2 1) \right).
\]

The direct correlation function is one of the central quantities of DFT\(^\text{15,17}\) and is obtained as second functional derivative of the excess free energy \( F_{\text{ex}} \) with respect to the average density profile, \( k_B T c(r_1, r_2) = \frac{\delta F_{\text{ex}}}{\delta n(r_1, r_2)} \). Given an (approximate) expression for the free energy, \( J_{\mathbf{g} \mathbf{g}'} \) can thus be taken as known. It constitutes the only input for the ensuing theory.

In Ref. \(^\text{2}\), the dissipationless Zwanzig-Mori equations for (microscopic) density and momentum density fluctuations are given in terms of \( J_{\mathbf{g} \mathbf{g}'} \). They are solved by the following ansatz for the microscopic density fluctuations

\[
\delta \rho_{\mathbf{g}}(\mathbf{q}, t) = -i n_\mathbf{g} \delta \alpha \mathbf{u}_\alpha(\mathbf{q}, t) - n_\mathbf{g} \frac{\delta n(\mathbf{q}, t)}{n_0},
\]

with Greek indices denoting spatial directions; repeated indices are summed over (Einstein summation convention). Equation \(^\text{7}\) expresses that for wave vectors \( \mathbf{q} \) within the first Brillouin zone, the four macroscopic fields \( \delta n(\mathbf{q}, t) \) and \( \delta \mathbf{u}(\mathbf{q}, t) \) determine the hydrodynamic contributions of the microscopic density field. Because equilibrium correlation functions of the microscopic density fluctuations on the left hand side of Eq. \(^\text{7}\) can be calculated within DFT, this ansatz allows us to calculate correlation functions of the macroscopic fields. Moreover, explicit expressions for the coarse grained density and displacement fields follow using the two summations

\[
\frac{n_0}{N_0} \sum_{\mathbf{g}} n_\mathbf{g}^*,
\]

\[
N_0 \sum_{\mathbf{g}} n_\mathbf{g}^* \mathbf{g}_0 \mathbf{g}_β \, ,
\]

and the relation \( \sum_{\mathbf{g}} |n_\mathbf{g}|^2 = 0 \). For completeness, we list here the results for the macroscopic densities. The coarse grained density is

\[
\delta n(\mathbf{q}, t) = \frac{n_0}{N_0} \sum_{\mathbf{g}} n_\mathbf{g}^* \delta \rho_{\mathbf{g}}(\mathbf{q}, t),
\]

where the average particle number density \( n_0 = N/V \) and a normalization constant \( N_0 = \sum_{\mathbf{g}} |n_\mathbf{g}|^2 \) appear. The displacement field is

\[
u_\alpha(\mathbf{q}, t) = i N_0^{-\frac{1}{2}} \sum_{\mathbf{g}} n_\mathbf{g}^* \mathbf{g}_β \delta \rho_{\mathbf{g}}(\mathbf{q}, t),
\]

with a normalization matrix \( N_αβ = \sum_\mathbf{g} |n_\mathbf{g}|^2 g_α g_β \). Note that in equilibrium \( \langle \mathbf{u} \rangle = 0 \), allowing us to replace \( \mathbf{u} \) with \( \delta \mathbf{u} \) for notational uniformity.
Equations (9) and (10) express the macroscopic fields in terms of microscopic particle density (11). It is intriguing that contributions from all finite lattice vectors $\mathbf{g} \neq 0$ are present in the coarse-grained density. Even in the limit of vanishing wave vector, $q \to 0$, it is not sufficient to measure particle density fluctuations close to the center of the first Brillouin zone, in order to determine the thermodynamic density field in crystals. Fluctuations from the regions around all lattice vectors contribute and describe how macroscopically strain fluctuations and defect density independently cause changes in the total particle density.

B. Correlation functions

It is now conceptually straightforward albeit somewhat tedious to derive the correlation functions of the macroscopic fields in terms of expressions containing the direct correlation function. Using Eq. (7), one gets

$$
\langle \delta \rho_{\alpha}^*(\mathbf{q}) \delta \rho_{\alpha'}^*(\mathbf{q}) \rangle = n_{\alpha}^* n_{\alpha'}^* g_{\alpha} g_{\alpha'} \langle \delta u_{\alpha}^*(\mathbf{q}) \delta u_{\alpha}^*(\mathbf{q}) \rangle + \frac{\langle \delta n(\mathbf{q}) \delta n(\mathbf{q}) \rangle}{n_0^2} + i g_{\alpha} \langle \delta u_{\alpha}^*(\mathbf{q}) \delta n(\mathbf{q}) \rangle - i \langle \delta n(\mathbf{q}) \delta u_{\alpha}^*(\mathbf{q}) \rangle g_{\alpha}^* \, ,
$$

Inserting this into Eq. (8) and with the help of the two summations (3), one obtains the following set of equations

$$
V_{k_B} T \delta_{ij} = \left( \frac{\langle \delta n_{\alpha}^* \delta n_{\beta} \rangle}{n_0^2} - \frac{\langle \delta n_{\alpha} \delta n_{\beta} \rangle}{n_0} \right) \left( \frac{\nu^*(\mathbf{q})}{\mu_{\alpha}^*(\mathbf{q})} \right) \left( \frac{\mu_{\alpha}^*(\mathbf{q})}{\lambda_{\alpha\beta}^*(\mathbf{q})} \right) \, ,
$$

The single matrix elements are

$$
\langle \delta n_{\alpha}^* \delta n_{\beta} \rangle = V_{k_B} T \left( \frac{1}{\nu} + \mu_{\alpha}^* \frac{\lambda_{\alpha\beta}}{\nu} \right) \left( 1 + \frac{\mu_{\alpha}^*}{\nu} \right)^{-1} \mu_{\beta} \mu_{\beta} \, ,
$$

$$
\langle \delta u_{\alpha}^* \delta u_{\beta} \rangle = V_{k_B} T \left( \lambda_{\alpha\beta} \nu - \mu_{\alpha} \mu_{\beta}^{-1} \nu \right)^{-1} \mu_{\beta} \mu_{\beta} \, ,
$$

$$
\langle \delta u_{\alpha}^* \delta u_{\beta} \rangle = V_{k_B} T \left( \lambda_{\alpha\beta} \nu - \mu_{\alpha} \mu_{\beta}^{-1} \nu \right)^{-1} \mu_{\beta} \mu_{\beta} \, ,
$$

$$
\langle \delta u_{\alpha}^* \delta u_{\beta} \rangle = V_{k_B} T \left( \lambda_{\alpha\beta} \nu - \mu_{\alpha} \mu_{\beta}^{-1} \nu \right)^{-1} \mu_{\beta} \mu_{\beta} \, ,
$$

The $q$-dependent constants of elasticity $\nu(\mathbf{q}), \mu_{\alpha}(\mathbf{q}),$ and $\lambda_{\alpha\beta}(\mathbf{q})$ are defined in terms of integrals containing the crystal direct correlation function.

$$
\nu(\mathbf{q}) = \frac{k_B T}{V} \int d^d r_1 \int d^d r_2 n(r_1) n(r_2) e^{-iq r_{12}} \times \left( \frac{\delta(r_{12})}{n(r_1)} - c(r_{12}, r_{2}) \right) \approx \nu + O(q^2),
$$

$$
\mu_{\alpha}(\mathbf{q}) = \frac{k_B T}{V} \int d^d r_1 \int d^d r_2 c(r_{12}, r_2) \left( 1 - e^{-iq r_{12}} \right) \times n(r_1) \nabla_{\alpha} n(r_2) \approx i \mu_{\alpha} \gamma_{\alpha\beta} + O(q^2),
$$

$$
\lambda_{\alpha\beta}(\mathbf{q}) = \frac{k_B T}{V} \int d^d r_1 \int d^d r_2 c(r_{12}, r_2) \left( 1 - e^{-iq r_{12}} \right) \times \left( \nabla_{\alpha} n(r_1) \right) \left( \nabla_{\beta} n(r_2) \right) \approx \lambda_{\alpha\beta} \delta q_{\alpha} q_{\beta} + O(q^2).
$$

The small wavevector limit and the index-symmetries $\mu_{\alpha\beta} = \mu_{\beta\alpha}$ and $\lambda_{\alpha\beta\gamma} = \lambda_{\beta\gamma\alpha} = \lambda_{\gamma\alpha\beta}$ are discussed in detail in Ref. [2]. Their connection to thermodynamic derivatives will be recalled in Eq. (27). The obtained set of equations is best given in proper matrix notation

$$
V_{k_B} T \delta_{ij} = \left( \frac{\langle \delta n_{\alpha}^* \delta n_{\beta} \rangle}{n_0^2} - \frac{\langle \delta n_{\alpha} \delta n_{\beta} \rangle}{n_0} \right) \left( \frac{\nu^*(\mathbf{q})}{\mu_{\alpha}^*(\mathbf{q})} \right) \left( \frac{\mu_{\alpha}^*(\mathbf{q})}{\lambda_{\alpha\beta}^*(\mathbf{q})} \right) \, ,
$$

with Latin indices $i = 0, \alpha$. Obviously, the matrix of correlation functions of the macroscopic variables are given by the inverse of the matrix of the constants of elasticity

$$
\left( \frac{\langle \delta n_{\alpha}^* \delta n_{\beta} \rangle}{n_0^2} - \frac{\langle \delta n_{\alpha} \delta n_{\beta} \rangle}{n_0} \right) = V_{k_B} T \left( \frac{\nu^*(\mathbf{q})}{\mu_{\alpha}^*(\mathbf{q})} \right) \left( \frac{\mu_{\alpha}^*(\mathbf{q})}{\lambda_{\alpha\beta}^*(\mathbf{q})} \right)^{-1} \, ,
$$

The second line of each expression is a non-trivial alternative, which is here given for completeness.

We thus reached our first aim of expressing the correlation functions of the macroscopic variables, total density and displacement vector field, in terms of integrals containing the functional derivative of the free energy with respect to density, i.e. the direct correlation function. Let us note in passing that translation and rotational symmetries yields the expected $q$-divergences or dependencies of the correlations in the limit $q \to 0$, especially $\langle \delta u_{\alpha}^* \delta u_{\beta} \rangle \propto 1/q^2$ follows from $\lambda_{\alpha\beta}(\mathbf{q}) \propto q^2$. 


III. INVERSE RELATIONS

While equations (10) predict the fluctuations of the macroscopic coarse-grained density and displacement field based on the constants of elasticity obtained from the direct correlation function and thus the free energy, experimentally, the inverse relations are of interest: expressing the constants of elasticity of the crystal in terms of measurable correlation functions. Two different sets can be used in experiment. Either displacement field and coarse-grained density fluctuations can be recorded, or displacement field and defect density. For reference, we provide the inverse relations for both cases in this section.

A. Including coarse-grained density

The matrix equation (14) can be inverted in order to find the elastic functions \( \nu(q) \), \( \mu_\alpha(q) \), and \( \lambda_{\alpha\beta}(q) \) in terms of measurable fluctuation functions. Straightforwardly one finds:

\[
\frac{\nu(q)}{k_B T} = \left( \frac{\delta n^* \delta n}{n_0^2} \right)^{-1} + \left( \frac{\delta n^* \delta n}{n_0^2} \right)^{-1} \frac{\delta n^* \delta n}{n_0} \left( \frac{\delta u^*_{\alpha} \delta u_{\beta}}{n_0} \right) - \left( \frac{\delta n^* \delta n}{n_0^2} \right)^{-1} \left( \frac{\delta n^* \delta n}{n_0} \right)^{-1} \left( \frac{\delta n^* \delta n}{n_0^2} \right)^{-1} \left( \frac{\delta n^* \delta n}{n_0} \right)^{-1} (17a)
\]

\[
\frac{\lambda_{\alpha\beta}(q)}{k_B T} = \left( \frac{\delta u^*_{\alpha} \delta u_{\beta}}{n_0} \right) - \left( \frac{\delta n^* \delta n}{n_0} \right)^{-1} \left( \frac{\delta n^* \delta n}{n_0} \right)^{-1} R^{-1},
\]

\[
\frac{\mu_\alpha(q)}{k_B T} = \left( \frac{\delta u^*_{\alpha} \delta u_{\beta}}{n_0} \right)^{-1} + \left( \frac{\delta n^* \delta n}{n_0} \right)^{-1} \left( \frac{\delta n^* \delta n}{n_0} \right)^{-1} \left( \frac{\delta n^* \delta n}{n_0} \right)^{-1} \left( \frac{\delta n^* \delta n}{n_0} \right)^{-1} (17c)
\]

These relations enable one to determine the functions \( \lambda_{\alpha\beta}(q) \), \( \mu_\alpha(q) \), and \( \nu(q) \) from measurements of fluctuation functions.

B. Including defect density

Although the relation between the constants of elasticity and the fluctuations of the coarse-grained fields is complete, it is worthwhile to consider a second set of variables. So far the displacement field \( u_\alpha \) appeared in two different ways. It contributes to the coarse-grained density, but it also appears as broken symmetry variable. In this section we introduce the point defect density \( c \) in lieu of the coarse-grained density, and keep the displacement field.

The correlation functions of the coarse-grained density and displacement field are easily transformed into correlations between the fluctuations of displacement field and the point defect density using the definition

\[
\delta c(q, t) = -\delta n(q, t) - i\omega_0 q_0 \delta u_\alpha(q, t).
\]

The set of variables \( \{\delta c(q), \delta u_\alpha(q)\} \) may be more appropriate to describe an experiment when few defects are present and \( \delta c(q, t) \) can be measured easily. Thus (14) is transformed into

\[
V k_B T \delta_{ij} = \left( \frac{\delta c^* \delta c}{n_0^2} \right) \left( \frac{\delta u^*_{\alpha} \delta u_{\alpha}}{n_0^2} \right) \left( \frac{\nu^*(q)}{n_0 V_\alpha(q)} \right) \left( \frac{\mu^*_{\alpha}(q)}{n_0 V_\alpha(q)} \right) \Lambda_{\alpha\beta}(q) \right)_{ij}.
\]

The combination of the constants of elasticity appearing here is directly connected to the hydrodynamic equation of the momentum density expressed in terms of point defect density and displacement field as hydrodynamic variables. There the time derivative of the momentum density couples to the displacement field via (the negative of)

\[
\Lambda_{\alpha\beta}(q) = \lambda_{\alpha\beta}(q) - i\eta_\alpha \mu_\beta(q) + i\mu_\alpha(q) \eta_\beta + q_\alpha \nu(q) q_\beta .
\]

The coupling to the point defect density is given by (the negative of)

\[
V_\alpha(q) = \frac{1}{n_0} \left( \mu^*_{\alpha}(q) - i\eta_\alpha \nu(q) \right).
\]
IV. ISOTHERMAL COMPRESSIBILITY OF CRYSTALS

In this section the compressibility is derived from a thermodynamic consideration, details are given in the Appendices. The situation described is one in which no pre-stress is applied to the crystal in equilibrium.

A. Connection to elastic coefficients

Starting with the definition of the compressibility of a fluid

\[ \kappa = - \frac{1}{V} \left. \frac{\partial V}{\partial p} \right|_N, \tag{22} \]

the question arises how this has to be generalized to describe the additional degrees of freedom of a periodic crystal. The free energy of a crystal

\[ dF = -pdV + \mu dN + h_{\alpha\beta} du_{\alpha\beta}, \tag{23} \]

includes a term with a stress tensor \( h_{\alpha\beta} \) at constant volume \( V \) and particle number \( N \) times an extensive strain tensor \( U_{\alpha\beta} = V u_{\alpha\beta} \). The work done is \( \delta W = \int h_{\alpha\beta} du_{\alpha\beta} dV \) with the symmetrized linear strain tensor \( u_{\alpha\beta} = \frac{1}{2}(\nabla\alpha u_\beta + \nabla_\beta u_\alpha) \). The compressibility for a periodic crystal is understood as the derivative at constant stress tensor

\[
\kappa = - \frac{1}{V} \left. \frac{\partial V}{\partial p} \right|_{N,h_{\alpha\beta}} = - \frac{1}{n_0^2} \left. \frac{\partial n}{\partial u_{\alpha\beta}} \right|_{u_{\alpha\beta}} = - \left. \frac{1}{n_0^2} \frac{\partial n}{\partial u_{\alpha\beta}} \right|_{u_{\alpha\beta}} \left( \frac{\partial h_{\delta\gamma}}{\partial u_{\alpha\beta}} \right) \left. \frac{\partial h_{\delta\gamma}}{\partial u_{\alpha\beta}} \right|_{u_{\alpha\beta}}^{-1}, \tag{24} \]

using Maxwell and Gibbs-Duhem relations described in Appendix A. There this result is further manipulated to

\[
\kappa = \left( n_0^2 \left. \frac{\partial \mu}{\partial n} \right|_{u_{\alpha\beta}} \right)^{-1} + \frac{1}{n_0^2} \left( \frac{\partial \mu}{\partial u_{\alpha\beta}} \right) \left. \frac{\partial \mu}{\partial u_{\alpha\beta}} \right|_{u_{\alpha\beta}}^{-1} \left. \frac{\partial h_{\delta\gamma}}{\partial u_{\alpha\beta}} \right|_{u_{\alpha\beta}} \left( \frac{\partial h_{\delta\gamma}}{\partial u_{\alpha\beta}} \right) \left. \frac{\partial h_{\delta\gamma}}{\partial u_{\alpha\beta}} \right|_{u_{\alpha\beta}}^{-1}, \tag{25} \]

which is one of our main results. This expression for the isothermal compressibility of a general crystal generalizes results obtained for high symmetry crystals, and, to our surprise, appears novel. Now, the expressions of the elastic constants as thermodynamic derivatives can be entered. They follow from the Gibbs fundamental form of the free energy density \( f = F/V \) given by

\[ df = \mu dn + h_{\alpha\beta} du_{\alpha\beta}, \tag{26} \]

and take the microscopic expressions already introduced in Eq. \( \text{[13]} \):

\[
\frac{\partial^2 f}{\partial n^2} \bigg|_{u_{\alpha\beta}} = \frac{\partial \mu}{\partial n} \bigg|_{u_{\alpha\beta}} = \nu/n_0^2, \tag{27a} \]

\[
\frac{\partial^2 f}{\partial n \partial u_{\alpha\beta}} = \frac{\partial \mu}{\partial n} \bigg|_{u_{\alpha\beta}} = \frac{\partial h_{\alpha\beta}}{\partial n} \bigg|_{u_{\alpha\beta}} = -\mu_{\alpha\beta}/n_0, \tag{27b} \]

\[
\frac{\partial^2 f}{\partial u_{\alpha\beta} \partial u_{\gamma\delta}} = \frac{\partial h_{\alpha\beta}}{\partial u_{\gamma\delta}} \bigg|_{n} = C^0_{\alpha\beta\gamma\delta} = \lambda_{\alpha\beta\gamma\delta} + \lambda_{\beta\gamma\alpha\delta} - \lambda_{\alpha\beta\gamma\delta}. \tag{27c} \]

See Appendix A for an alternative derivation of Eq. \( \text{[27]} \) from the second order variation of the free energy in DFT assuming smoothly varying density profiles. It supplements the derivation in Ref. \( \text{[2]} \) (recalled in Eq. \( \text{[13]} \)), where the equivalence of the hydrodynamic equations was used. The compressibility is thus

\[ \kappa = \nu^{-1} + \nu^{-1} \mu_{\alpha\beta} \left[ C^0_{\alpha\beta\gamma\delta} - \mu_{\alpha\beta} \nu^{-1} \mu_{\gamma\delta} \right]^{-1} \mu_{\gamma\delta} \nu^{-1}. \tag{28} \]

Neglecting the coupling tensor \( \mu_{\alpha\beta} = 0 \) the second term vanishes and the compressibility \( \kappa \) is given by \( \kappa^{-1} = n_0^2 \left. \frac{\partial \mu}{\partial n} \right|_{u_{\alpha\beta}} \), which plays the role of the inverse bulk modulus at constant strain.

B. Including defect density

If one considers the set of independent variables with the defect density \( c \) instead of the coarse-grained density \( n \) with Eq. \( \text{[18]} \) simplifying to \( \partial n = -n_0 du_{\alpha\beta} - dc \) the manipulations leading to Eq. \( \text{[25]} \) have to be adapted. The compressibility is given now in terms of derivatives of the stress tensor at constant defect density \( \sigma_{\alpha\beta} \) and the chemical potential \( \mu \), which are functions of the strain tensor and the defect density \( df = -dc + \sigma_{\alpha\beta} du_{\alpha\beta} \)

\[ \kappa = - \left( n_0^2 \left. \frac{\partial \mu}{\partial c} \right|_{u_{\alpha\beta}} \right)^{-1} \left( \sigma_{\alpha\beta} - \left( n_0 \left. \frac{\partial \mu}{\partial u_{\alpha\beta}} \right|_{c} \right)^{-1} \left. \frac{\partial \mu}{\partial u_{\alpha\beta}} \right|_{c} \right) \times \left( \frac{\partial \sigma_{\alpha\beta}}{\partial u_{\alpha\beta}} \right) \left( \frac{\partial \sigma_{\alpha\beta}}{\partial u_{\alpha\beta}} \right) \left( \frac{\partial \sigma_{\alpha\beta}}{\partial u_{\alpha\beta}} \right) \left. \frac{\partial \sigma_{\alpha\beta}}{\partial u_{\alpha\beta}} \right|_{c}^{-1} \times \left( \frac{\partial \sigma_{\alpha\beta}}{\partial u_{\alpha\beta}} \right) \left( \frac{\partial \sigma_{\alpha\beta}}{\partial u_{\alpha\beta}} \right) \left( \frac{\partial \sigma_{\alpha\beta}}{\partial u_{\alpha\beta}} \right) \left. \frac{\partial \sigma_{\alpha\beta}}{\partial u_{\alpha\beta}} \right|_{c}^{-1}. \tag{29} \]

The relevant thermodynamic derivatives are now given by (see Eq. \( \text{[15]} \) for the free energy density)

\[ n_0^2 \left. \frac{\partial^2 f}{\partial c^2} \right|_{u_{\alpha\beta}} = -n_0 \left. \frac{\partial \mu}{\partial c} \right|_{u_{\alpha\beta}} = \nu, \tag{30a} \]
\[ n_0 \frac{\partial^2 f}{\partial \nu \partial u_{\alpha\beta}} = -n_0 \frac{\partial \mu}{\partial u_{\alpha\beta}} = n_0 \frac{\partial \sigma_{\alpha\beta}}{\partial \nu} = \nu \delta_{\alpha\beta} + \mu_{\alpha\beta}, \]

\[ \frac{\partial^2 f}{\partial u_{\alpha\beta} \partial u_{\gamma\delta}} \bigg|_{c} = C_{\alpha\beta\gamma\delta}^{c} = C_{\alpha\beta\gamma\delta}^{\nu} + \mu_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\beta} \mu_{\gamma\delta} + \nu \delta_{\alpha\beta} \delta_{\gamma\delta}, \]  
(30b)

An interesting limit is now the vanishing of the coupling between the defect density and the strain field, \( \frac{\partial^2 f}{\partial c \partial u_{\alpha\beta}} = 0 \). This yields two independent contributions to the compressibility

\[ \kappa = \nu^{-1} + (C_{\alpha\beta\gamma\delta}^{c})^{-1} \delta_{\alpha\beta} \delta_{\gamma\delta} \]  
(31)

The first contribution \( \nu^{-1} \) is due to the fluctuations of the defect density, whereas the second one \((C_{\alpha\beta\gamma\delta}^{c})^{-1} \delta_{\alpha\beta} \delta_{\gamma\delta}\) is due to independent fluctuations of the strain tensor, which agrees with the known result for a perfect crystal without external strain.\(^{19}\)

V. CONNECTION - SMALL WAVEVECTOR LIMIT

So far we considered correlation functions and the isothermal compressibility of crystals. In this section we bridge the gap between the density correlation function and the compressibility, and point out the subtle differences between the two expressions. In the second part of this chapter the so-called generalized structure factor is discussed.

In order to understand the connection to the compressibility, the \( q \)-dependence in the limit \( q \to 0 \) of the fluctuation function of the coarse-grained density \(^{16a}\) needs to be discussed in detail

\[ \left\langle \frac{\delta n^* \delta n}{V k_B T n_0} \right\rangle = \nu^{-1}(q) + \nu^{-1}(q) \mu^*_0(q) \]
\[ \times \left( \lambda_{\alpha\gamma\phi} - \mu_{\alpha\gamma}(q) \nu^{-1}(q) \mu^*_\gamma(q) \right)^{-1} \mu_\gamma(q) \nu^{-1}(q) \]
\[ q \geq 0 \]
\[ \nu + \frac{\mu_{\alpha\beta} q_\beta}{\nu} \left[ (\hat{\lambda}_{\alpha\gamma\phi} - \frac{\mu_{\alpha\gamma} \nu^{-\gamma}}{\nu}) q_\phi q_\phi \right]^{-1} \frac{\mu_\gamma q_\gamma}{\nu}. \]  
(32)

Here we used the known small-wavevector expansions of the elastic coefficients, which were defined in Eqs. \(^{13}\). They follow from DFT relations expressing translational and rotational symmetry.\(^{2}\) Noting that only the symmetrized combinations in \( \alpha \leftrightarrow \gamma \) and \( \epsilon \leftrightarrow \phi \) of the term in square brackets are relevant, and with the help of Eqs. \(^{27}\) this expression can be further simplified to

\[ \left\langle \frac{\delta n^* \delta n}{V k_B T n_0} \right\rangle = \frac{\nu}{\nu} + \frac{\mu_{\alpha\beta} q_\beta}{\nu} \left[ (C_{\alpha\gamma\phi} - \frac{\mu_{\alpha\gamma} \nu^{-\gamma}}{\nu}) q_\phi q_\phi \right]^{-1} \frac{\mu_\gamma q_\gamma}{\nu}. \]  
(34)

This expression would agree with the thermodynamic one \(^{25}\), if the factors of \( q_\gamma q_\phi \) canceled \( q_\epsilon q_\phi \). That the limit \( q \to 0 \) is not that simple can be seen even for highly symmetric crystals. For a cubic crystal, the correlation function yields different results in the small \( q \) limit \(^{34}\) depending on the direction of \( q \) relative to the unit cell. And for the hypothetical model of an isotropic crystal, the small \( q \) limit \(^{34}\) is direction independent, but differs from the thermodynamic value from \(^{23}\). The latter simplified case, allows to identify the origin of the discrepancy and will be studied in detail in the next section. Appendix \( \text{B} \) considers the non-analytic nature of the small-\( q \) limit from the point of view of the harmonic free energy derived in Appendix \( \text{A} \).

A. Perfect crystal embedded in a matrix

To study the difference in more detail, it is, as a first simplification, more convenient to look at the simpler problem of a perfect crystal. In this section we also use the more familiar expressions of elasticity theory. The connection to the terms used so far is given in Appendix \( \text{C} \). For a perfect crystal the correlations of the displacement field is given by the (inverse) of the dynamical matrix \( D_{\alpha\beta}(q) \)

\[ \left\langle \delta u^*_\alpha \delta u_\beta \right\rangle = V k_B T D_{\alpha\beta}^{-1}(q). \]  
(35)

The coarse grained density for a perfect crystal is \( \delta n(q, t) = -i n_0 q_\alpha \delta u_{\alpha}(q, t) \) and the dynamical matrix is related with the elastic constants via \( D_{\alpha\gamma}(q) = C_{\alpha\beta\gamma\delta} q_\beta q_\delta \). Thus for the coarse grained density correlation function we get

\[ \left\langle \delta n^* \delta n \right\rangle = q_\alpha D_{\alpha\beta}^{-1}(q) q_\beta = q_\alpha \left( C_{\alpha\beta\phi\epsilon} q_\phi q_\epsilon \right)^{-1} q_\beta \]  
(36)

which shows the same problem in the limit \( q \to 0 \) as it arises in Eq. \(^{34}\), when compared to the thermodynamic compressibility \( \kappa = (C_{\alpha\beta\gamma\delta})^{-1} \delta_{\alpha\beta} \delta_{\gamma\delta} \) (contraction of the inverse of the matrix of elastic constants). For an isotropic crystal the elastic tensor simplifies to the two Lamé coefficients \( C_{\alpha\beta\gamma\delta} = \lambda \delta_{\alpha\beta} \delta_{\gamma\delta} + \mu (\delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma}) \). Thus, the compressibility is \( \kappa^{-1} = \lambda + 2\mu \), whereas the correlation functions yield \( \lambda + 2\mu \) (which corresponds to the longitudinal speed of sound).

To show the origin of this difference we consider an isotropic (ideal) solid for which the so-called fundamental solution of elasticity is known. Other symmetries with known solutions are hexagonal\(^{20}\) and pentagonal\(^{21}\). The corresponding problem in two dimensions can be found in \(^{22}\). We consider a three dimensional sphere with volume \( V_B \) embedded in a spherical matrix \( V \) of the same isotropic material. The radius \( R_B \) of the embedded sphere is increased \( R_B \to R_B + \Delta R \) and the surrounding matrix is compressed. To determine the displacement field and the elastic energy of such a deformation one has to solve the equation of elastostatic theory, which is the vanishing of the divergence of the stress tensor, or in
terms of displacement field
\[ \nabla_{\beta} C_{\alpha\beta\gamma\delta} \nabla_{\gamma} u_{\delta} = 0. \] (37)

The solution is a sphere with increased volume \( V_B + \Delta V_B \).
The only non-vanishing displacement field is (homogeneous dilatation)
\[ u_r = \begin{cases} \frac{\Delta r}{\pi_B} & r < R_B \\ \frac{\Delta r}{(\frac{3}{2} \mu)}^2 & r > R_B \end{cases} \] (38)

This yields for the total elastic energy
\[ E = \frac{V_B}{2} (\frac{\Delta V_B}{V_B})^2 [(\lambda + \frac{2}{3} \mu) + \frac{4}{3} \mu \left(1 - \frac{V_B}{V}\right)]. \] (39)

The first part is due to the stretched sphere and the second contribution is from the surrounding matrix. Thus, depending on the ratio \( \frac{V_B}{V} \) the relevant combination of elastic constants changes from \( \lambda + \frac{2}{3} \mu \) for \( \frac{V_B}{V} \to 1 \) to \( \lambda + 2 \mu \) for \( \frac{V_B}{V} \to 0 \). In the limit of vanishing shear modulus \( \mu \) the difference vanishes. Thus, for a fluid it doesn’t matter if one determines the volume fluctuations of a small sphere in surrounding fluid (of the same kind) or if one looks at the global fluctuations of the whole system.

It is worthwhile to note that the same ratio between these two combinations of Lamé coefficients appears in a related context. In Eshelby’s study\(^{22}\) of an inclusion in a matrix of elastic material, the so-called constrained strain \( u_{\alpha\beta}^C \) is given by the stress-free strain \( u_{\alpha\beta}^T \)
\[ u_{\alpha\beta}^C = \frac{\lambda + \frac{2}{3} \mu}{\lambda + 2 \mu} u_{\alpha\beta}^T. \] (40)

An analog problem is a polar fluid in a dielectric medium\(^{15,16,24,25}\). There the susceptibilities show a directional dependence due to the dipolar interaction, and a different combination of dielectric constants is relevant depending on the surrounding medium.

B. Generalized Structure Factor

There is a further aspect which differs in the relation between the compressibility and the correlation of the density fluctuations of a fluid and a crystal. There is a difference if one looks at the elements of the generalized structure factor which contribute to the compressibility, i.e. whether those are different from \( S_{g=0}(q) \to 0 \).

We recall that the generalized structure factor is defined by
\[ S_g(k) = \frac{1}{V} \int d^3r_1 \int d^3r_2 \langle \delta \rho(r_1) \delta \rho(r_2) \rangle e^{-i g \cdot \mathbf{r}} e^{-i k \cdot \Delta \mathbf{r}} \] (41)
\[ = \frac{1}{V} \langle \delta \rho(g/2 + k) \delta \rho(g/2 - k) \rangle, \] (42)

(with \( \mathbf{R} = (r_1 + r_2)/2 \) and \( \Delta \mathbf{r} = r_1 - r_2 \)) and its \( S_0(\mathbf{g} + \mathbf{q}) \) element is measured in a scattering experiment\(^{1,26}\).

In a liquid, where translational invariance dictates that only \( S_0(k) \) is non-vanishing and isotropic, its connection\(^{15,16}\) to the compressibility is well known \( S_0(q \to 0) \to v_0^2 k_B T \kappa \). To convince oneself that such a connection does not hold in a crystal, the definition of the coarse-grained density Eq. \( \|4\) can be used to derive
\[ \langle \delta n^2 \rangle \frac{n^2_0}{n^2_0} = \frac{(2\pi)^d}{N_0^2} \sum_{\mathbf{g}, \mathbf{g}'} S_g \delta^d(\mathbf{g} - \mathbf{g}') \frac{n^2_0}{n_0^2}. \] (43)

where the left hand side becomes \( \kappa \) for \( q \) to zero in the fluid case. Clearly, every element of \( \langle \delta \rho^*(g + q) \delta \rho(g + q) \rangle \) is involved, not just the one with vanishing reciprocal lattice vector \( g = g' = 0 \). Also the correlation of coarse-grained density fluctuations is given by a combination of generalized structure factors \( S_{g-g'}\left(-\mathbf{g} + \mathbf{g}' \right) / 2 - \mathbf{q} \) in the limit \( q \to 0 \) and not just by \( S_{g=0}(q \to 0) \) as for a fluid. Although the possibility that the RHS of the last equation is indeed the compressibility cannot be ruled out, it seems rather unlikely.

VI. CONCLUSIONS AND OUTLOOK

We derived the thermodynamic expression for the isothermal compressibility \( \kappa \) in a general crystal, and discussed its connection to the limit of vanishing wavevector in the density correlation function. The correlation functions were calculated within the framework of density functional theory, with appropriate coarse-graining, in order to allow for a finite density of (point) defects. Explicit expressions for the coefficients in the phenomenological free energy in terms of the direct correlation function of density functional theory were obtained. The correlation function of the coarse-grained density field does not, in general, determine the compressibility. For the case of an ideal isotropic solid, we could identify the origin of the discrepancy from a calculation in macroscopic elasticity theory. It arises from the long-ranged strain fluctuations which decay like \( 1/r^3 \) and thereby cause boundary effects to enter the elastic energy. While in systems with spontaneously broken symmetry, anomalous longitudinal correlations exist in general\(^{23}\) (besides the familiar symmetry restoring fluctuations\(^{24}\)), the present observation appears more related to long-ranged dipolar correlations in polar fluids\(^{25}\). There the dielectric tensor in response to the vacuum electric field depends on the shape of the material and on the boundary conditions. It can be connected to a well defined isotropic dielectric constant only via shape/ boundary-effect dependent
distribution functions. For crystals, it remains to un-
derstand this relation for arbitrary symmetries, and to
derive it from a discussion of the microscopic correlation
functions.

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Appendix A: Free energy

The second order change in free energy \(\Delta F\) due to
a variation in the density distribution \(\delta \rho(r)\) around
the periodic crystalline equilibrium density is\[^{15,17,27}\]

\[
\beta \Delta F = \frac{1}{2} \int \! d^d r_1 d^d r_2 \left( \frac{\delta (r_{12})}{n(r_1)} - c(r_1, r_2) \right) \delta \rho(r_1) \delta \rho(r_2),
\]

(A1)

where \(c(r_1, r_2)\) is the direct correlation function of a peri-
odic crystal. Assuming a smooth density variation, which
is the real space expression of \(T\), i.e. (with the nota-
tional simplification \(\delta u(r) = u(r)\))

\[
\delta \rho(r) = -u(r) \cdot \nabla n(r) + n(r) \frac{\delta n(r)}{n_0},
\]

(A2)

one can evaluate the thermodynamic derivatives appearing
in Eqs. \([27]\). Thus

\[
\delta \rho(r_1) \delta \rho(r_2) = u_{\alpha}(r_1) u_{\beta}(r_2) \nabla_{\alpha n}(r_1) \nabla_{\beta n}(r_2),
\]

which is, in the following, term by term manipulated with
the help of the LMB\[^{30,31}\] equation

\[
\frac{\nabla_{\alpha n}(r)}{n} = \int \! d^d r' c(r, r') \nabla_{\alpha n}(r').
\]

(A4)

The first part is discussed explicitly for a crystal in Masters\[^{30}\] and is equivalent to the discussion of the sur-
face tension in \([31]\). The other parts are transformed
accordingly.

One expands \(u_{\beta}(r_2)\) around \(r_1\), which is valid for a
short range (in \(r_{12}\)) direct correlation function. The
zero order term of \(\Delta F_{(1)}\) vanishes, because of \([A4]\) and
the first order term does not contribute as \(c(r_1, r_2) =
0\) for \(r_1 = r_2\). Since the hydrodynamic variable \(u(r)\) is slowly
varying, one obtains an expression which is quadratic in
\(\nabla u(r)\)

\[
\Delta F_{(1)} = \frac{k_B T}{2} \int \! d^d r_1 d^d r_2 \left( \frac{\delta (r_{12})}{n(r_1)} - c(r_1, r_2) \right) u_{\alpha}(r_1) u_{\beta}(r_2) \nabla_{\alpha n}(r_1) \nabla_{\beta n}(r_2),
\]

(A5)

\[
\Delta F_{(2)} \approx \frac{k_B T}{2} \int \! d^d r_1 d^d r_2 \frac{\delta n(r_1) \delta n(r_2)}{n_0^2}
\]

\[
+ \frac{n(r_1) n(r_2) \delta n(r_1) \delta n(r_2)}{n_0^2} - u_{\alpha}(r_1) \nabla_{\alpha n}(r_1) \frac{n(r_2) \delta n(r_2)}{n_0},
\]

(2)

\[
- \frac{n(r_1) \delta n(r_1)}{n_0} u_{\alpha}(r_2) \nabla_{\alpha n}(r_2),
\]

(3)

\[
\frac{n(r_1) \delta n(r_1)}{n_0} u_{\alpha}(r_2) \nabla_{\alpha n}(r_2),
\]

(4)

The constant of elasticity \(\lambda_{\alpha\beta\gamma\delta}\) is the same one as was
obtained in the framework of hydrodynamic equations of motion\[^{5}\]. For the second term of the free energy, \(\delta n(r_2)\)
is expanded around \(r_1\) and, as hydrodynamic variable,
assumed to be slowly varying

\[
\Delta F_{(2)} = \frac{k_B T}{2} \int \! d^d r_1 d^d r_2 \frac{\delta n(r_1) \delta n(r_2)}{n_0^2}
\]

\[
\times [n(r_1) \delta (r_{12}) - n(r_1) c(r_1, r_2) n(r_2)],
\]

(A8)

\[
= \frac{1}{2} \int \! d^d r \left( \frac{\delta n(r)}{n_0} \right)^2.
\]

(A9)
With
\[
\nu = \frac{k_B T}{V} \int d^4r_1 d^4r_2 \left( n(r_1) \delta(r_{12}) - n(r_1)c(r_{12}, r_2)n(r_2) \right).
\]
(A10)

The third and fourth part yield with the same arguments
\[
\Delta F_{(3,4)} = -\int d^4r \mu_{\alpha \beta} \frac{\delta n(r)}{n_0} \nabla \beta u_\alpha(r),
\]
(11)
\[
\mu_{\alpha \beta} = \frac{k_B T}{V} \int d^4r_1 \int d^4r_2 n(r_1)\nabla \alpha n(r_2)r_{12,\beta}c(r_1, r_2)
\]
(12)

So all of the constants of elasticity \(\nu, \mu_{\alpha \beta}\), and \(\lambda_{\alpha \beta \gamma \delta}\) appear in the expression for the free energy
\[
\Delta F = \frac{1}{2} \int d^4r \nu \left( \frac{\delta n(r)}{n_0} \right)^2 + C_{\alpha \beta \gamma \delta} \nabla \beta u_\alpha(r) \nabla \delta u_\gamma(r)
- \int d^4r \mu_{\alpha \beta} \frac{\delta n(r)}{n_0} \nabla \beta u_\alpha(r)
\]
(A13)

with the Voigt-symmetric elastic constants \(C_{\alpha \beta \gamma \delta} = \lambda_{\gamma \delta} + \lambda_{\beta \alpha \gamma \delta} - \lambda_{\alpha \beta \gamma \delta}\). The replacement in the last step reflects the rotational symmetry as only symmetric combinations of strain enter into the elastic energy and is based upon the rotational analog of the LMBW equation.

\[
r_1 \times \nabla^{(1)} \ln n(r_1) = \int d^4r_2 c(r_1, r_2) \left( r_2 \times \nabla^{(2)} n(r_2) \right).
\]
(A14)

Let us add that the above expression for the free energy also determines the constant \(C_0 = 0\) in Eqs. (89), (90), and (92) of [2], which could not be determined in [2], where the elastic constants were identified via the hydrodynamic equations.

The free energy in terms of the defect density \(\delta c(r)\) and the displacement field \(u(r)\) is
\[
\Delta F = \frac{1}{2} \int d^4r \nu \left( \frac{\delta c(r)}{n_0} \right)^2 + 2 \left( \nu \delta_{\alpha \beta} + \mu_{\alpha \beta} \right) \frac{\delta c(r)}{n_0} \nabla \beta u_\alpha(r)
+ \left( C_{\alpha \beta \gamma \delta} + \nu \delta_{\alpha \beta} \delta_{\gamma \delta} + \mu_{\alpha \beta} \delta_{\gamma \delta} + \delta_{\alpha \beta} \mu_{\gamma \delta} \right) \nabla \beta u_\alpha(r) \nabla \delta u_\gamma(r).
\]
(A15)

### Appendix B: Isothermal compressibility

As a consequence of [23] a Gibbs-Duhem relation can be derived
\[
- Vdp + N d\mu + U_{\alpha \beta} d\mu_{\alpha \beta} = 0,
\]
(B1)
which yields for isothermal change with \(d\mu_{\alpha \beta} = 0\)
\[
N d\mu = V dp.
\]
(B2)

With fixed volume
\[
d\mu = \frac{\partial \mu}{\partial N} \bigg|_{V, \mu_{\alpha \beta}} dN, \quad \text{and} \quad dp = \frac{\partial p}{\partial N} \bigg|_{V, \mu_{\alpha \beta}} dN.
\]
(B3)

This yields
\[
N \frac{\partial \mu}{\partial N} \bigg|_{V, \mu_{\alpha \beta}} = V \frac{\partial p}{\partial N} \bigg|_{V, \mu_{\alpha \beta}} = \frac{\partial p}{\partial \mu} \bigg|_{V, \mu_{\alpha \beta}}
\]
(B4)

This is further manipulated with the Jacobian trick to yield Eq. (24)
\[
\kappa = \frac{1}{n_0^2} \frac{\partial n}{\partial \mu} \bigg|_{\mu_{\gamma \delta}} = \frac{1}{n_0^2} \frac{\partial n}{\partial \mu} \bigg|_{\mu_{\alpha \beta}} \frac{\partial \mu_{\alpha \beta}}{\partial \mu} \bigg|_{\mu_{\gamma \delta}} \bigg|_{\mu_{\alpha \beta}} = \frac{1}{n_0^2} \frac{\partial n}{\partial \mu} \bigg|_{\mu_{\alpha \beta}} \frac{\partial \mu_{\alpha \beta}}{\partial \mu} \bigg|_{\mu_{\gamma \delta}} \bigg|_{\mu_{\alpha \beta}}.
\]
(B5)

The expression in the denominator is understood as the inverse of a fourth rank tensor \(A_{\alpha \beta \gamma \delta}^{-1} A_{\gamma \delta \nu \mu} = \delta_{\alpha \mu} \delta_{\beta \nu}\). (B6)

The first term of the compressibility is basically the only non-vanishing term in the fluid limit
\[
\frac{1}{n_0^2} \frac{\partial n}{\partial \mu} \bigg|_{\mu_{\alpha \beta}} = \left( \frac{\partial \mu}{\partial n} \bigg|_{\mu_{\alpha \beta}} \right)^{-1} = \nu^{-1}.
\]
(B7)

For the second term the chemical potential \(\mu\) is expressed as a function of density and strain tensor \(\mu(n, \mu_{\alpha \beta})\)
\[
d\mu = \frac{\partial \mu}{\partial n} \bigg|_{\mu_{\alpha \beta}} dn + \frac{\partial \mu}{\partial \mu_{\alpha \beta}} \bigg|_{n} d\mu_{\alpha \beta} = 0,
\]
(B8)

which yields
\[
\frac{\partial n}{\partial \mu_{\alpha \beta}} \bigg|_{n} = - \left( \frac{\partial \mu}{\partial n} \bigg|_{\mu_{\alpha \beta}} \right)^{-1} \frac{\partial \mu}{\partial \mu_{\alpha \beta}} \bigg|_{n} = n_0 \nu^{-1} \mu_{\alpha \beta}.
\]
(B9)

The last two terms are
\[
\frac{\partial \mu_{\alpha \beta}}{\partial \mu_{\gamma \delta}} \bigg|_{n} = \frac{\partial \mu_{\gamma \delta}}{\partial \mu_{\alpha \beta}} \bigg|_{n} + \frac{\partial \mu_{\alpha \beta}}{\partial \mu_{\gamma \delta}} \bigg|_{n} \frac{\partial n}{\partial \mu_{\alpha \beta}} \bigg|_{n} = C_{\alpha \beta \gamma \delta}^{-1} \mu_{\alpha \beta} \mu_{\gamma \delta},
\]
(B10)
\[
\frac{\partial \mu_{\alpha \beta}}{\partial \mu_{\gamma \delta}} \bigg|_{n} = \frac{\partial \mu_{\gamma \delta}}{\partial \mu_{\alpha \beta}} \bigg|_{n} \left( \frac{\partial \mu_{\alpha \beta}}{\partial \mu_{\gamma \delta}} \bigg|_{n} \right)^{-1} = -n_0 \nu^{-1} \mu_{\gamma \delta}.
\]
(B11)

Thus the compressibility of a periodic crystal in terms of its elastic constants \(\nu, \mu_{\alpha \beta}\), and \(C_{\alpha \beta \gamma \delta}^{-1}\) is indeed Eq. (28)
\[
\kappa = \nu^{-1} + \nu^{-1} \mu_{\alpha \beta} \left( C_{\alpha \beta \gamma \delta}^{-1} - \mu_{\alpha \beta} \nu^{-1} \mu_{\gamma \delta} \right)^{-1} \mu_{\gamma \delta} \nu^{-1}.
\]
(B14)
Appendix C: Elasticity

With the expressions of Sect. III B Eq. (88) reads

$$\langle \delta u_\alpha^* \delta u_\beta \rangle = V k_B T \Lambda_\alpha_\beta^{-1} (q).$$  \hspace{1cm} (C1)

This follows from (19) with $V_\alpha (q) = 0$, or $\nu \delta_\alpha_\beta + \mu_\alpha_\beta = 0$ in the low $q$-limit, for a perfect crystal without point defects and vanishing coupling. The correlations of the coarse-grained density (35) become

$$\langle \delta n^*_n \delta n \rangle = q_\beta \Lambda_\alpha_\beta^{-1} (q) q_\beta = q_\alpha (C_{\alpha\beta\delta} q_\delta q_\alpha)^{-1} q_\beta,$$ \hspace{1cm} (C2)

where we used the small $q$ expansion of the constants of elasticity and took care of the proper symmetric combination as discussed in [2]. The elastic constants $C_{\alpha\beta\gamma\delta}$ of elasticity theory correspond to $C_{\alpha\beta\gamma\delta}^m$ in Eq. (30c), which, with the help of $\nu \delta_\alpha_\beta + \mu_\alpha_\beta = 0$ for a perfect crystal without coupling, could be further simplified (to $C_{\alpha\beta\gamma\delta} = C_{\alpha\beta\gamma\delta}^m - \nu \delta_\alpha_\beta \delta_\gamma_\delta$).

The elastostatic theory is contained in the static limit of the hydrodynamic equations of motion, see Eqs. (87) in [2]. Without point defects the only non-vanishing equation is (87c), which then reads

$$q_\beta C_{\alpha\beta\gamma\delta} q_\delta u_\gamma = 0.$$  \hspace{1cm} (C3)

But this is just the Fourier-transformed equation of elastostatics [87].

Appendix D: Equipartition principle

The harmonic free energy Eq. (A13) from Appendix A can be written in a more compact form with the help of a $4 \times 4$-matrix of elastic coefficients introduced in Eq. (14). Fourier-transformation leads to

$$\Delta F = \frac{1}{2} \int \frac{d^4 q}{(2\pi)^4}$$

$$\left( \frac{\langle \delta n^* (q) \rangle}{n_0}, \frac{\delta u^*_\alpha (q)}{C_{\alpha\beta\gamma\delta}} \right) \nu \mu_\alpha_\beta q_\delta q_\beta C_{\alpha\beta\gamma\delta}^m q_\delta q_\beta$$

The relation (14), which follows from the ansatz (7), thus is identified as statement of the equipartition theorem resulting from this quadratic free energy. It leads to the wavevector-dependent correlation functions of the coarse-grained fields for small $q$.

Interestingly, also the thermodynamic fluctuation functions, which correspond to $q = 0$, can be obtained from the harmonic free energy Eq. (A13), even though they were not the values reached by the limit $q \to 0$ in the $q$-dependent correlation functions. Equation (A13) can be rewritten using the Voigt notation, which shall be given by latin indices $1 \leq i \leq 6$, where $u_i = u_{i\alpha}$ for $(\alpha, \beta) = \{(1, 1); (2, 2); (3, 3); (2, 3); (1, 3); (1, 2)\}$. For spatially constant fluctuations indicated by subscript $q = 0$, one obtains using the thermodynamic derivatives from Eq. (13)

$$\Delta F = \frac{V}{2} \left( \frac{\delta n^*_n}{n_0}, u_i \right) \left( \begin{array}{cc} \nu & -\mu_j \\ -\mu_i & C_{ij}^m \end{array} \right) \left( \frac{\delta n}{n_0} u_j \right)$$ \hspace{1cm} (D2)

Now the $7 \times 7$ matrix of covariances is given by

$$\left( \frac{\langle \delta n^* \delta n \rangle}{n_0^2}, \langle \delta n \delta u_i \rangle \right)_{q=0} = V k_B T \left( \nu \mu_j - \mu_i C_{ij}^m \right)^{-1}$$ \hspace{1cm} (D3)

The correlation of the density fluctuations is thus

$$\langle \frac{\delta n^* \delta n}{n_0^2} \rangle_{q=0} = V k_B T \left( \frac{1}{\nu} + \frac{\mu_i}{\nu} \left[ C_{ij}^m - \frac{\mu_i \mu_j}{\nu} \right]^{-1} \frac{\mu_j}{\nu} \right)$$

$$= V k_B T \left( \frac{1}{\nu} + \frac{\mu_i \mu_j}{\nu} \left[ C_{ij}^m - \frac{\mu_i \mu_j}{\nu} \right]^{-1} \frac{\mu_j}{\nu} \right),$$ \hspace{1cm} (D4)

where in the last line the usual notation is used instead of the Voigt one. This equipartition result agrees with the compressibility in Eq. (28).

Reassuringly, it suffices to discuss the harmonic approximation to the free energy in order to observe the non-analytic structure of the correlation functions in a crystal.

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