Phonons and Elasticity in Disordered binary Crystals

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#### Nomenclature
1. Introduction and Problem statement

“... Where are the atoms?” — Per Bak in [Bak86]

This question — originally coined in the context of icosahedral (quasi)crystals — highlights the importance of structure characterization in contemporary crystallography. A clear microscopic picture of the atomic arrangements in a crystal is not only key to understanding its equilibrium properties. But it also serves as a reference state to characterize deviations from equilibrium — such as deformations. In this sense, it is the starting point of every atomistic approach to elasticity theory on which this thesis will focus. First of all, it will be useful to obtain a better understanding of the non-equilibrium aspect of elastic deformations and the challenges encountered in the presence of point defects. We do this by working along the four schematic binary\(^1\) crystal samples shown in figure 1.1:

Figure 1.1(a) depicts the particle positions \(r^{(is)} \in \mathbb{R}^{d=2}\) in the classical ground state at temperature \(T = 0\), with \(i\) being the particle index and \(s\) the species index. In the ground state, the particles form a perfect periodic lattice, which can be described by vectors \(R^{(is)}\) pointing at the \(b^{th}\) atom in the \(i^{th}\) unit-cell. The set \(\{R^{(is)}\}\) forms the equilibrium/reference configuration of the crystal. In a configuration as shown in figure 1.1(b), the particles randomly deviate from their equilibrium positions. As long as these deviations stay small compared to the lattice constant \(a\), each particle can still be assigned to an equilibrium position. In that case, a set of displacement vectors \(\{u^{(is)}\}\) with \(u^{(is)} := r^{(is)} - R^{(is)}\) can be uniquely defined. The non-equilibrium state is characterized by the set \(\{u^{(is)}\}\) and so is its potential energy \(\Phi = \Phi (\{r^{(is)}\}) \sim \Phi (\{u^{(is)}\})\). The Taylor expansion of \(\Phi\) about the equilibrium configuration reads [BH88]

\[
\Phi \left( \{r^{(is)}\} \right) = \Phi \left( \{R^{(is)}\} \right) + \sum_{i,j=1}^{N} \sum_{s,s' = 1}^{B} \frac{\partial^2 \Phi}{\partial u^{(is)}_i \partial u^{(js')}_{j}} \left( \{R^{(is)}\} \right) u^{(is)}_i u^{(js')}_{j} + \mathcal{O} \left( u^3 \right) \quad (1.1)
\]

where the linear contribution to \(\Phi\) vanishes by the equilibrium assumption for the \(\{R^{(is)}\}\) and the cubic corrections \(\mathcal{O} \left( u^3 \right)\) can be neglected in the limit of small

\(^1\)The term "binary" explicitly refers to the case of \(B = 2\) particle species in the crystal but is meant in a broader sense: Much of the following discussions holds also for the general case \(B \geq 2\). Where \(B = 2\) is assumed, this is mostly for ease of discussion and can in principle be generalized to an arbitrary number of species.
Chapter 1 Introduction and Problem statement

Figure 1.1.: Schematic samples of a binary 2-dimensional crystal in various states of order (a) shows the classical zero-temperature ground state with the basis and the lattice constant $a$ highlighted. It serves as a reference for defining particle displacements $u^{(i_s)}$, marked by green arrows in (b). (c) illustrates point defects for the single large species. (d) shows intersite defects between large and small species.

$\{\|u^{(i_s)}\| \ll a\}$. Note that we use Einstein notation for Greek and only for Greek indices.

Equilibrium expansions in displacement $u$ like eq. (1.1) are fundamental to two different but equivalent approaches to elasticity theory. Firstly, the tensor of elastic constants $K$ can be obtained as the second strain derivatives of the (Helmholtz) free energy $F$ [Wal98, chapter 1]. This is the conventional definition of elastic constants$^2$ and will henceforth be referred to as the static/thermodynamic approach. In the classical low-temperature limit $K$ follows from the potential expansion (1.1) because $F = \Phi$. First proposed by C. Feldman et al. [Fel64], the static “potential expansion” approach was generalized to nonprimitive lattices by D. C. Wallace [Wal98, chapter 2]. Secondly, by considering the displacements $u^{(i_s)}$ as time-dependent variables$^3$, the dynamic approach can be constructed [BH88; LW70] that will later be considered in the form of hydrodynamics. By a plane-wave ansatz for the displacements $u^{(i_s)}$ and periodic boundary conditions, the Hamiltonian equations of motion (e.o.m.) can be brought to the form of an eigenvalue problem

$$\omega^2 u^{(a)}(q) = \sum_{b=1}^{B} D^{(ab)}(q) \cdot u^{(b)}(q). \quad (1.2)$$

The “dynamical (block) matrix” $D$ yields $d \times B$ eigenvalues $\omega_0^2(q)$ for each allowed wave vector $q$, which group into branches, the “(phonon) dispersion relations”. Due

$^2$Practical advantages of the second approach are pointed out in [Wal98, section 3.12].

$^3$In a real crystal, the particle positions are identified with those of the atomic nuclei by the Born–Oppenheimer approximation. The electronic degrees of freedom then are accounted for by the form of the potential energy $\Phi$. 

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to the Goldstone theorem, \( d \) of these phonon\(^4 \) branches obey \( \lim_{\mathbf{q} \to 0} \omega_{\sigma} (\mathbf{q}) = c_{\sigma} (\mathbf{q}) q \) from which the speeds of sound \( c_{\sigma} (\mathbf{q}) \) and the elastic constants can be read. This is also known as the “method of long waves” [Wal98, section 3.12]. Besides the “acoustic” phonon modes, eq. (1.2) yields \((B - 1) \times d\), “optical”\(^5 \) modes with generically positive eigenfrequencies \( \omega_{\sigma} (\mathbf{q} = 0) > 0 \).

If the crystal from figure 1.1(a) is slowly heated to finite temperatures \( T > 0 \), both static and dynamic potential expansion method can still be used approximatively as long as thermal lattice vibrations stay small compared to the lattice constant \( a \). Alternatively, [Kan95] introduced an expansion of the free energy \( \mathcal{F} \) in the spirit of eq. (1.1), viz for ideal crystals.

But what about defects? As the thermal vibrations further increase in amplitude, a considerable number of atoms will diffuse to other unit cells. Consequently, the information on their original equilibrium site is lost and the small displacements \( \mathbf{u}^{(b)} \) essential to the expansion (1.1) may no longer be well-defined. The practicality of the potential expansion method deteriorates with an increasing amount of “point defects” in the equilibrium state. Two manifestations of that problem are schematically illustrated in figures 1.1(c) and (d). The point defects in figure 1.1(c) consist in “holes/vacancies” and “interstitials”, corresponding to empty or multiply occupied unit cells. A unique one-to-one mapping like in figure 1.1(b) is, if at all, only possible for small \( \| \mathbf{u}^{(b)} \| \ll a \). In figure 1.1(d) both the equilibrium positions \( \mathbf{R}^{(b)} \) and the stoichiometry from figure 1.1(a) are preserved but the basis positions are randomized by so-called “antisite defects”. This leads to ambiguities in the reference configuration and thus in the definition of the \( \mathbf{u}^{(b)} \). To summarize, expansions in potential energy \( \Phi \) or free energy \( \mathcal{F} \) cannot be based on single particle displacements \( \mathbf{u}^{(b)} \) in systems where point defects occur at high concentrations.

This thesis presents a generalization of the e.o.m. (1.2) valid in crystals at all temperatures below the melting point and including arbitrary amounts of (point) defects. To that end, a counterpart \( \mathbf{A} \) to the dynamical matrix \( \mathbf{D} \) from eq. (1.2) is derived. The approach is based entirely on the methods of classical statistical mechanics — notably crystal hydrodynamics within the Zwanzig–Mori formalism — and classical density functional theory (DFT). It was originally proposed by M. Ernst et G. Szamel [SE93] for one-component crystals and improved in that regime by M. Fuchs and C. Walz [Wal09; WF10]. The present work follows these foundations in restricting itself to the isothermal e.o.m. within the canonical ensemble. New aspects like antisite defects and optical phonons emerge by means of the multiple-species description. The finding of optical phonons, however, differs from the previous results in not being a hydrodynamic mode.

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\(^4\)The term “phonon” originates from the interpretation of quantized collective excitations of lattice vibrations as bosonic quasiparticles.

\(^5\)The classification “optical” stems from the coupling of optical phonons to the electromagnetic field in ionic crystals.
It is therefore surprising that in the hydrodynamic limit of small $|q|$ and in absence of inversion symmetry, $\Lambda(q)$ retains couplings of the total momentum density to optic-like modes. Their connection to the phenomenological formulation of crystal hydrodynamics [MPP72; FC76] and the phenomenological elastic constants in particular requires further investigation. Fortunately, another comparison can be drawn from a static method equivalent to the method of long waves for $\Lambda$:

Analogous to the potential expansion (1.1), the free energy $\mathcal{F}$ in a crystal can be expanded as a density functional in terms of linear strain and defect fluctuations [CL10, section 6.4.9]. From the coefficients of that expansion follow a-priori exact DFT expressions for the elastic constants. The approach has been applied in the defect-free case with various approximative density functionals and density parametrizations to both periodic [JM88] and icosahedral [JM87] crystals. Moreover, from a generalization of strain to arbitrary length scales it was possible to obtain dispersion relations [MKR91], including optical phonons [TT95]. The description of the latter has however been restricted to inversion-symmetric crystals. A second focus of this thesis consequently is the derivation of elastic constants from the static DFT approach in binary periodic crystals of arbitrary symmetry and point defect concentrations. The equivalence to the dynamic approach should provide an identical starting point for the calculation of $\mathbf{K}$. From discrepancies in that comparison, the presence of additional contributions to $\mathbf{K}$ in the Zwanzig–Mori formalism will be conjectured that are missed by the original ansatz.

The content of this thesis is structured as follows:

Part I introduces the key concepts and definitions employed in parts II and III. A characterization of crystals and their symmetries from the viewpoint of statistical mechanics is given in chapter 2. Chapter 3 presents the concepts for reversible linear hydrodynamics both within the Zwanzig–Mori approach (sections 3.1 and 3.2) and phenomenologically (section 3.3). The phenomenological part includes the thermodynamic approach to elastic constants, showing how it is linked to the dynamic approach. This part is concluded by a brief introduction to the concept of density functional theory in chapter 4.

The second part II is dedicated to the treatment of phonons and elasticity in disordered binary crystals. The central chapter 5 begins with the derivation of the linear reversible isothermal e.o.m. in the Zwanzig–Mori approach (sections 5.1 and 5.2). This yields the dynamical block matrix $\Lambda(q)$ whose properties are analyzed in section 5.3, paying particular attention to the long-wavelength limit $q \rightarrow 0$. The static DFT approach to elastic constants is treated in chapter 6. For a comparison to the role of optic phonons in chapter 5, a simple model calculation including sublattice displacements is shown. The results from chapter 5 are fleshed out by applications to binary hard sphere (HS) systems both from DFT (section 7.1) and simulation (section 7.2). The last chapter 8 of this part first draws conclusions in section 8.1 from a comparison of the dynamic and static approaches from chapters 5 and 6, respectively. In section 8.2, it turns back to the defect-free classical low-temperature
Introduction and Problem statement

limit. On the example of a honeycomb crystal, it confronts results from [Wal09] and chapter 6 with the corresponding expressions in [Wal98, section 2.7].

The final part III approaches quasicrystals that originally sparked P. Bak’s question quoted in the beginning (which was reviewed in [GQ08]). It can be considered as separate work from that in part II. Chapter 9 highlights and reviews some of the new aspects and challenges that one faces in trying to generalize the methods of part II to quasicrystals. Only single-species systems are assumed. Unlike the ambiguities that arise from the presence of point defects, the missing of a unique microscopic reference configuration is intrinsic even to an ideal quasicrystal. This is due to the presence of additional Goldstone modes in the form of “phasons”. They correspond to microscopic rearrangements of particles — so-called “phason flips” [Gäh+06] — and lead to a class of energetically equivalent, locally isomorphic equilibrium configurations. The work was started in the hope of circumventing those ambiguities by a reciprocal-space approach, aiming in particular for a description of acoustic phonons. The endeavor drew motivation from inelastic scattering measurements of acoustic-like branches in a quasicrystal [De +07]. However, no conclusive results could be obtained to that end. An argument why in quasicrystals acoustic phonons can only be defined in an approximate sense is consequently included from [JCB07] and ideas for such approximations are sketched. Chapter 10 reformulates the static DFT approach to elasticity of certain two-dimensional quasicrystals from [Lub88] in the context of this work to point out possible applications. Conclusions and an outlook to both parts II and III are given after that.

The three appendices function as supplements to chapter 5: Appendix A presents explicit considerations on the role of the memory matrix for the reversible dynamics in the Zwanzig–Mori approach. An alternative proof of the correct leading order in $q$ of $\Lambda(q)$ is given in appendix B. Appendix C diagonalizes $\Lambda(q)$ approximately and discusses the symmetries of a new coupling tensor.

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6 Certain quasicrystals might be seen as binary systems in a more abstract sense from their connection to R. Penrose’s famous aperiodic tilings of the plane [Pen74] with down to only two elementary tiles incommensurate lengths.
Part I.

Theoretical framework
2. Characterization of crystals

First of all, we set up the statistical mechanics approach and explain how it is related to the experimental observations of crystals. After a classification of crystals from that viewpoint, we turn to the symmetries of periodic crystals and introduce some key concepts for their structural characterization.

2.1. Statistical mechanics approach

For the description of the equilibrium state of a crystal by classical statistical mechanics we need to assume the existence of a crystalline phase at a temperature $T$ where the thermal wavelength $\lambda_T$ is much smaller than the characteristic microscopic length scale, viz the lattice constant $a$,

$$a \gg \lambda_T(T) = \frac{h}{\sqrt{2\pi m k_B T}} \quad \text{where} \quad \frac{h}{k_B} \text{ Planck's constant}, \quad \frac{k_B}{m} \text{ Boltzmann's constant}, \quad \frac{m}{\text{ particle mass}}. \quad (2.1)$$

The microscopic picture of an equilibrium position for each particle is then replaced by an ensemble average $\langle \cdot \rangle$ of functions of the microscopic particle density $\rho(r,t)$. E.g. we introduce the equilibrium density $n$ as

$$n(r) = \langle \rho(r,t) \rangle = \frac{1}{Z} \int d\Gamma \rho(r,t) \rho(\Gamma) \quad (2.2)$$

where $\rho$ and $Z$ are the phase space density respectively partition function of the ensemble chosen. This choice will in practice depend on the experimental setup but is restricted to the canonical ensemble in this thesis. For an $N$-particle system, we thus have

$$Z = \frac{1}{h^{3N} N!} \int d\Gamma e^{-\beta H(\Gamma)}, \quad \rho(\Gamma) = \frac{1}{Z} e^{-\beta H(\Gamma)}$$

with $H$ the Hamiltonian function and $\beta = 1/k_B T$. Generalizations beyond the $(N,V,T)$ ensemble are given in [Mis].

\footnote{For simplification definitions are initially given for a single-species system only. Generalization to crystals of several species is straightforward and will be given separately in paragraph 3.3.1 et seqq.}
Neglecting the non-commutation of momentum and space operators in quantum mechanics, the kinetic part of $H$ can be directly integrated out in eq. (2.2) such that $n$ only depends on the $N$-particle potential $\Phi(\{r_1, r_2, \ldots, r_N\})$. As was pointed out in [Mer68] and shall become transparent from eq. (2.6), $\Phi$ needs to include a device that fixes both center of mass and orientation of the crystal while maintaining the unstrained equilibrium state.

### 2.2. Crystallinity in scattering experiments

In experiment, information on the microscopic structure of a bulk crystal is frequently obtained through elastic scattering techniques. An incident plane wave is characterized by a wave vector $k_{\text{incident}}$ giving information on the direction of propagation $\hat{k}_{\text{incident}} := k_{\text{incident}} / k_{\text{incident}}$ and the wavelength $\lambda = 2\pi / k_{\text{incident}} = 2\pi / k_{\text{detected}}$. The interference of waves scattered along $k_{\text{detected}} = k_{\text{incident}} + k$ is measured on a screen in the form of a diffraction pattern like the one shown in figure 2.1. As long as single-scattering events are dominant, that interference is determined by the static structure factor $S_0(q)$. $S_0$ is obtained from a double Fourier transform of the second moment of $f$. It is convenient to split up $f = n + \delta f$ into an equilibrium and a fluctuation part so that we can write

$$S_0(k) = \frac{1}{V} \int d^d r \int d^d r' e^{-i k \cdot (r - r')} \langle \rho(r) \rho(r') \rangle$$

$$= \frac{1}{V} \left| \int d^d r e^{-i k \cdot r} n(r) \right|^2 + \frac{1}{V} \int d^d r \int d^d r' e^{-i k \cdot (r - r')} \langle \delta \rho(r) \delta \rho(r') \rangle$$

(2.3)

$$\equiv n_0^{[2]}(k) + \delta n_0^{[2]}(k).$$

(2.4)

In eq. (2.4) we introduced shorthand notations for the two contributions to $S_0$: $n_0^{[2]}$ is determined by the equilibrium density $n$ whereas $\delta n_0^{[2]}$ arises from density fluctuations $\delta \rho$. The subscript “0” indicates the evaluation of both Fourier transforms at the same wave vector $k$. In translationally invariant systems $\langle \rho(r) \rho(r') \rangle = \langle \rho(0) \rho(r' - r) \rangle$, and every other choice vanishes. Additionally assuming isotropy implies $n_0^{[2]}(k) \propto \delta(k)$. Neither translational invariance nor isotropy are given in crystals, and a generalization of the static structure factor was defined in [WF10].

According to the present definition of the International Union of Crystallography, a material is called a crystal if it shows an essentially discrete diffraction diagram [IUC92]. “Essentially” refers to the omnipresent diffuse background that has to be negligible compared to the sharply localized Bragg peaks. The diffraction pattern shown in figure 2.1 certainly matches that criterion. It is reflected mathematically in eq. (2.4) by the existence of a countably infinite discrete set $G \subset \mathbb{R}^d$ such that $S_0$
2.2 Crystallinity in scattering experiments

Figure 2.1: Electron diffraction pattern of Icosahedrite along a fivefold symmetry axis [Bin+11]

is essentially\(^2\) characterized by \(n_0^{[2]}\) with

\[
n_0^{[2]}(k) = \sum_{g \in G} \left| n_g \right|^2 \delta(k - g)
\]

(2.5)

where a complex weighting factor \(n_g \in \mathbb{C}\) is associated with every \(g \in G\). The identification of a crystal structure then usually consists in retrieving the real space equilibrium density \(n\) which leads to the \(n_0^{[2]}\) observed in wave vector/reciprocal space. The Fourier transform inside the expression

\[
n_0^{[2]}(k) = \frac{1}{V} \left| \int d^d r e^{-ik \cdot r} n(r) \right|^2
\]

takes the desired form (2.5) if and only if \(n\) can be written as

\[
n(r) = \sum_{g \in G} n_g e^{ig \cdot r}.
\]

(2.6)

Consequently, the most general set of crystalline equilibrium densities is given by eq. (2.6) and was termed “almost periodic crystals” by [Lif07] in line with the “almost periodic functions” introduced in [Boh26]. It is characterized by a countable superposition of plane waves with wave vectors \(g\). The above-mentioned requirement of fixed center of mass and orientation of the sample ensures that phase and direction of propagation of these plane waves are well-defined.

If there is a finite set \(\{G_1, G_2, \ldots, G_I\} \subset \mathbb{R}^d\) that spans \(G\) by integer linear combinations, i.e.

\[
G = G \left[ \{G_1, G_2, \ldots, G_I\} \right] := \left\{ z_1 G_1 + \ldots + z_I G_I \mid z_1, \ldots, z_I \in \mathbb{Z} \right\}
\]

(2.7)

\(^2\)An introduction into mathematical diffraction theory which would be required for a more rigorous definition of a crystalline diffraction pattern is skipped at this point. It can be found e.g. in the work of Baake and Grimm [Baa99; BG12].
then $n$ belongs to a “quasiperiodic crystal”. In this case, the *smallest* number $D \in \mathbb{N}$ of wave vectors $\mathbf{G}_i$ that is needed to span $\mathbf{G}$ is referred to as the “indexing dimension”. $D$ is the number of integers needed to unambiguously specify the position of a peak in a diffraction pattern, e.g. $D = 6$ in figure 2.1. The best renowned subset of quasiperiodic crystals are “periodic crystals”. Here, the additional requirement of *linearly* independent $\mathbf{G}_i$ holds which implies $D \leq d$ and spatial periodicity. An additional assumption throughout this thesis will be that the number of linearly independent $\mathbf{G}_i$ in a basis of $\mathbf{G}$ matches exactly the physical dimensionality $d$ (“no embeddings”) which for periodic crystals means $D = d$. The term “quasicrystal” introduced in [LS86] is used as an abbreviation for “quasiperiodic crystal” and — depending on convention — may or may not include periodic crystals. For ease of distinction, we will stick to the latter and employ the terminology shown in table 2.1.3 In this terminology which employs no “forbidden-symmetry” criterion4, D. Shechtman’s famous discovery [She+84] consists in a new class of quasicrystals — subsumed as “other” in table 2.1. Up to that point, quasicrystals had only been known and scientifically established in the form of incommensurately-modulated crystals and incommensurate composite crystals [Lif07]. Part III of this thesis will turn to the peculiarities in describing quasicrystals in more detail. The main part II focusses on periodic crystals which we now characterize further by the allowed symmetries of $n$.

\footnote{Note that the most general definition of a crystal given in [Lif07] is not represented in table 2.1 which therefore starts at a subcategory level.}

\footnote{R. Lifshitz argues for the inappropriateness of such restrictions in [Lif03] presenting the two-dimensional fibonacci tiling which cannot be characterized as incommensurately modulated nor as incommensurate composite but still has no forbidden symmetries.}
2.3. Symmetries of periodic crystals

Consider \( D = d = 3 \) w.l.o.g. with \( \mathbf{G}_1, \mathbf{G}_2, \mathbf{G}_3 \) linearly independent.\(^5\) The construction [MS66]

\[
\mathbf{L}_i := \sum_{i,j,k=1}^{3} 2\pi\delta_{ij} \mathbf{G}_j \times \mathbf{G}_k \quad (2.8)
\]

with \( \delta_{ij} \) the rank-3 Levi–Civita symbol defines \( \mathbf{L}_1, \mathbf{L}_2, \mathbf{L}_3 \) such that

\[
\mathbf{L}_i \cdot \mathbf{G}_j = 2\pi\delta_{ij} 
\quad (2.9)
\]

and

\[
n(\mathbf{r}) = n(\mathbf{r} + z_1 \mathbf{L}_1 + z_2 \mathbf{L}_2 + z_3 \mathbf{L}_3) \quad \forall z_1, z_2, z_3 \in \mathbb{Z}.
\quad (2.10)
\]

This is easily verified from the definitions (2.8) and (2.6). In other words, \( n \) is invariant on a lattice (set) \( \mathbb{L} \{\{\mathbf{L}_1, \mathbf{L}_2, \mathbf{L}_3\}\} \subset \mathbb{R}^3 \) spanned by its non-unique basis vectors \( \mathbf{L}_1, \mathbf{L}_2, \mathbf{L}_3 \)

\[
\mathbb{L} \{\{\mathbf{L}_1, \mathbf{L}_2, \mathbf{L}_3\}\} = \{ z_1 \mathbf{L}_1 + z_2 \mathbf{L}_2 + z_3 \mathbf{L}_3 \mid z_1, z_2, z_3 \in \mathbb{Z} \}.
\quad (2.11)
\]

\( \mathbb{L} \) is called a “Bravais lattice”. In the same way, eq. (2.7) defines a reciprocal (space) lattice \( \mathbb{G} \{\{\mathbf{G}_1, \mathbf{G}_2, \mathbf{G}_3\}\} \) which is spanned by a basis \( \{\mathbf{G}_1, \mathbf{G}_2, \mathbf{G}_3\} \subset \mathbb{G} \). \( \mathbb{L} \) and \( \mathbb{G} \) are mutually dual lattices, i.e. their bases form pairs that satisfy the condition (2.9). Hence the real space Bravais lattice \( \mathbb{L} \) as a starting point of the description is equivalent to the reciprocal lattice \( \mathbb{G} \). The latter is then introduced by discussing the condition of constructive scattering interference which is identical to eq. (2.9) and ultimately leads to Bragg’s law and its diffraction (Bragg) peaks. Equation (2.10) is the counterpart to the (artificial) construction rule of a microscopically periodic crystal lattice. While holding for the average particle density \( n \), lattice-periodicity will not be obeyed by the microscopic particle density \( \rho(\cdot, t) \) at any given time \( t \).

It is obvious from their definitions (2.11) respectively (2.7) that \( \mathbb{L} \) and \( \mathbb{G} \) form abelian groups with respect to vectorial addition of their elements\(^6\). This so-called “translation group” of a Bravais lattice is made visible in defining a building block which contains exactly one lattice point and fills space completely without overlap. The definition of such a primitive “unit-cell” is not unique. It is however preferably made such that it reflects the full symmetry of the given lattice. This can be achieved by constructing the Wigner-Seitz cell [WS33] like e.g. for the square lattice in figure 2.2(a). It is in turn quadratic and can be mapped onto itself by a set \( \mathbb{P}_L \) of symmetry operations, having in common that they leave the central lattice point \( \mathbf{L}_0 (= 0 \) w.l.o.g.) invariant. These point transforms can be described as

\(^5\)The formulation of similar statements for \( D = 2 \) and \( D = 1 \) linearly independent \( \mathbf{G}_i \) in \( d (\geq D) \) dimensions is straightforward. Linear independence of the \( \mathbf{G}_i \) is assumed throughout this section on periodic crystals.

\(^6\)We will denote this group identically to the lattice, i.e. \( \mathbb{L} \) and \( \mathbb{G} \) respectively.
Chapter 2 Characterization of crystals

Figure 2.2.: 2d periodic crystal with subsequently reduced symmetry and the Wigner-Seitz cells (solid light blue). (a) has the full holohedral symmetry. Additionally shown are the bisectant lines for the Wigner-Seitz cell. (b) has a geometrically similar Wigner-Seitz cell with point symmetry reduced to that of a rectangle. It also possesses a glide plane (solid green with arrows for the translation) and gives an example for a non-symmorphic space group. Both (b) and (c) belong to the rectangular crystal system although (c) does not have the full rectangular point symmetry. (c) shows the conventional unit cell (gray stripes) which differs from the Wigner-Seitz cell for this non-primitive, centered, lattice.

- Inversions: \( r \mapsto -r \)
- Reflections \( r \mapsto r - 2(\hat{s} \cdot r)\hat{s} \) with \( \hat{s} \) a mirror plane normal
- Rotations \( r \mapsto R \cdot r \) with \( R \in \text{SO}(3) \) a proper\(^7\) rotation matrix

and concatenations thereof, all representable by matrices. By the periodicity requirement (2.10) the rotations \( R \in P_L \) are restricted to 2, 3, 4 and 6-fold axes [Böh02] which limits the total number of point symmetries allowed in periodic crystals\(^8\). \( P_L \) in turn forms one of a, \( D \)-dependent, number (cf. table 2.2) of different “holohedral point groups”. The subscript “\( L \)” indicates that so far the point-symmetries of a Bravais lattice \( L \) are considered. The lattice-periodic equilibrium density \( n \) can still lower the symmetry, and the defining property for the elements \( P \) of the actual “crystallographic point group” \( P \) of a crystal is

\[
\{ P \in P_L \mid Pn (\bullet - r_n) := n (P \cdot (\bullet - r_n)) \equiv n (\bullet - r_n) \} \quad \text{with} \quad r_n : \text{symmetry point, } \quad \bullet : \text{space argument.}
\]

The definition involves that \( r_n \) is chosen to maximize the order of \( P \) which is a — generically proper — subgroup of \( P_L \). The lattice point group \( P_L \) of smallest order which contains \( P \) gives the “crystal system” associated with \( n \). Two crystals with the same point group belong to the same crystal system but can still have two

\(^7\) \( \det (R) = +1 \)

\(^8\) Crystals with rotation axes of higher order necessarily are quasicrystals.
2.3 Symmetries of periodic crystals

Bravais lattices which are not related to each other by rescaling of their basis vectors. Bravais lattices from the same crystal system have the same “conventional unit cell”, decorated with lattice points in specific ways (cf. [KBB02, Bild 1.6]). For example, the conventional unit cell of a rectangular lattice in 2 dimensions can be decorated by a centered lattice point like in figure 2.2(c) without altering $P_L$. This results in a number of different Bravais lattices greater than the number of crystal systems. Figure 2.2(b) finally shows a structure with invariance transforms which can be described neither by a translation nor a mirror operation but only by a concatenation of both. The “space group” $S$ of a crystal contains all such pairs leaving $n$ invariant,

$$ S = \left\{ T \in R^d, P \in O(d) \left| n \left( P \cdot \bullet + T \right) \equiv n (\bullet) \right. \right\}. \quad (2.12) $$

In “symmorphic” space groups, the members of each pair $(T, P) \in S$ are symmetry operations themselves, i.e. $(T, 1) \in S$ and $(0, P) \in S$. The space group can then be written as a “direct product” of a crystallographic point group and a translation group. Structures like that in fig. 2.2(b) belong to the non-symmorphic space groups where this is not possible. [Bur66] presents a systematical derivation for $d = 3$ and its extension to arbitrary dimension. The number of distinct crystal systems, Bravais lattices, point groups and space groups is given in tab. 2.2 for $d = 2$ and $d = 3$ [Wil06].

Before moving on to the introduction into linear hydrodynamic in the next chapter 3, we introduce some further concepts that will be frequently used in later discussions. First note that from a given lattice periodic density $n'$, more complex structures $n$ of the same lattice periodicity can be easily defined by superposition of translated replicas of $n'$,

$$ n\left( r \right) := \sum_{s=1}^{B} n' (r - b^{(s)}) \quad (2.6) \quad \sum_{g \in G} n' g \sum_{s=1}^{B} e^{i g r} e^{-i g b^{(s)}}. \quad (2.13) $$

The set $\left\{ b^{(1)}, b^{(2)}, \ldots, b^{(B)} \right\}$ is called a “basis” and defines the second sum in eq. (2.13) — the “geometric form factor”. The need to abandon a unique microscopic crystal

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Note that, unlike the primitive one, this conventional unit cell contains $1 + 4 \times 1/4 = 2$ lattice points.
reference state was amply explained in the introduction chapter 1. Nonetheless, most equilibrium densities \( n \) considered in the following have an intuitive classical, defect-free low-temperature limit similar to figure 1.1(a). We will refer to that picture as the “perfect-lattice” limit/regime of \( n \). It is characterized by a so-called “Dirac comb” [Cór89],

\[
n ( \mathbf{r} ) = \sum_{s=1}^{B} \sum_{\mathbf{R} \in \mathbf{L}} \delta \left( \mathbf{r} - \mathbf{R} - \mathbf{b}^{(s)} \right)
\]

(2.14)

and yields nothing else than a reference configuration of the potential-expansion method. On that footing, \( n \) will be called “primitive” if its Wigner-Seitz cell contains exactly one particle in the perfect-lattice regime, otherwise “non-primitive”. Inversion-symmetry of \( n \) will mean that each basis position in the perfect-lattice regime is a center of inversion. The density (2.14) consists of translated replicas of a given Bravais lattice \( \mathbf{L} \) which will be referred to as “sublattices”. Finally, we introduce the so-called “Brillouin zones” which are defined on the basis of the reciprocal lattice \( \mathbf{G} \). They form a hierarchical order with the \( n \)th Brillouin zone \( \text{BZ}_n \) defined as

\[
\text{BZ}_n = \left\{ \mathbf{q} \in \mathbb{R}^d \mid \| \mathbf{q} - \mathbf{g} \| < \| \mathbf{q} \| \text{ for exactly } n - 1 \text{ points } \mathbf{g} \in \mathbf{G} \right\}.
\]

(2.15)

This definition can be easily visualized by drawing the bisectant planes to each reciprocal lattice vector \( \mathbf{g} \in \mathbf{G} \) w.r.t. to the origin (cf. figure 2.2(a)). If not further specified “Brillouin zone” (BZ) refers to the first Brillouin zone throughout this thesis. It is identical with the Wigner-Seitz cell of the reciprocal lattice.
3. Reversible linear hydrodynamics

This chapter is dedicated to the hydrodynamic approach whose reversible formulation yields elastic constants within the method of long waves. In section 3.1, we take up the equilibrium ensemble introduced in section 2.1 to explain how it can be exploited for the dynamics of small induced perturbations. On the other hand, the decay of equilibrium correlation functions becomes arbitrarily slow for a specific set of variables in the long-wavelength limit. Section 3.2 introduces a formalism to project out the dynamics of these variables within a correlation-function approach to hydrodynamics, named after its inventors Zwanzig [Zwa60; Zwa61] and Mori [Mor65b; Mor65a]. This formalism will be combined with the linear response theory for the derivation of hydrodynamic e.o.m. in chapter 5. Section 3.3 presents the phenomenological approach to hydrodynamics with a view to introducing the elastic constants. This will show how their thermodynamic definition enters into the method of long waves.

3.1. Linear response

For the harmonic potential expansion eq. (1.1) in chapter 1 to hold, we required \( \text{max}_{i,s} \| u^{(i_s)} \| \ll a \). This ensured the independence of the underlying potential \( \Phi \equiv \Phi(\{R\}) \) from the set of displacements \( \{ u^{(i_s)} \} \). Hence within this microscopic approach, the dynamical matrix is obtained from the equilibrium lattice potential. The field-theoretical formalism that generalizes these findings to the reaction of many-particle systems at finite-temperature equilibrium to small external fields is the linear response theory. This important tool for studying the equilibrium properties of many-particle systems goes back to R. Kubo [Kub57]. The general description [KTH91; Zwa01] starts with a physical system in thermodynamic equilibrium that is characterized by the time-independent Hamiltonian \( H_0 \). With \( \Gamma := \{ p_i, q_i \} \) the set of phase space variables, the corresponding stationary phase space density is denoted by \( \rho_0(\Gamma) := \rho_0 \). By assumption, \( \partial_t \rho_0 = 0 \), and the Liouville equation reads:

\[
\frac{d}{dt} \rho_0 = \frac{\partial}{\partial t} \rho_0 + i L_0 \rho_0 = i L_0 \rho_0 = 0
\]

with \( L_0 \) the Liouville operator, \( L_0 A = i \{ H_0, A \} \), and \( \{ A, B \} = \sum_i \left( \frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial B}{\partial q_i} \frac{\partial A}{\partial p_i} \right) \) the Poisson bracket.

\(^1\)For larger displacements anharmonic contributions to the expansion lead to an interaction of the phonons by so-called “umklapp processes” [MS66, chap. 25].
We now examine how the time evolution eq. (3.1) of the equilibrium phase space density is altered when applying a set \( \{ a_i \} \) of adiabatically varying weak external fields \( a_i (r, t) \). By “adiabatically” we mean that the field varies slowly enough to assume a — now time-dependent but well-defined — normalized phase space density \( \rho (\Gamma, t) =: \rho_0 + \Delta \rho (t) \). The coupling of the field \( a_i (r, t) \) to the system defines a physical observable \( A_i (r) \) through the perturbed Hamiltonian

\[
\mathcal{H} (t) = \mathcal{H}_0 - \sum_i \int d^d r \ A_i (r) \ a_i (r, t) .
\] (3.2)

With this, the Liouville equation for \( \rho (t) \) can be rewritten.

\[
\partial_t \rho (t) + i \mathcal{L} \rho (t) = 0
\] (3.3)
\[
\Leftrightarrow \partial_t \rho (t) = \partial_t \Delta \rho (t) \overset{3.2}{=} - \sum_i \int d^d r \ a_i (r, t) \ \{ A_i (t), \rho_0 + \Delta \rho (t) \} + \{ \mathcal{H}_0, \Delta \rho (t) \}
\] (3.4)

Having made use of the stationary Liouville equation (3.1) and of the bilinearity of the Poisson bracket, we assume that \( \{ A_i (r), \Delta \rho (t) \} = \mathcal{O} [a_i (r, t)] \) can be expanded in terms of the external field \( a_i (r, t) \) from the stationary case \( \Delta \rho \equiv 0 \). Hence, the last term in eq. (3.4) becomes a higher order correction \( \mathcal{O} (a^2) \) negligible in the limit of vanishing external field. With the initial condition \( \Delta \rho (t) \xrightarrow{t \to \infty} 0 \), the resulting partial differential equation is solved by

\[
\Delta \rho (t) = - \int_{-\infty}^t dt' \int d^d r' \ e^{-i(t-t')L_0} \sum_i \{ A_i (r'), \rho_0 \} a_i (r', t') .
\]

The change in expectation value of the observable \( \Delta B := B - \langle B \rangle_0 \) in the perturbed system follows as

\[
\langle \Delta B (r, t) \rangle = \int d\Gamma \ \Delta \rho (\Gamma, t) \ B (r)
\]
\[
= \int d\Gamma \ \int_{-\infty}^t dt' \int d^d r' \ e^{-i(t-t')L_0} \sum_i \{ A_i (r'), \rho_0 \} a_i (r', t') \ B (r)
\]
\[
= \int_{-\infty}^t dt' \int d^d r' \sum_i \theta (t - t') \int d\Gamma \ \overline{\{ A_i (r', t'), \rho_0 \} B (r \cdot a_i (r', t')}}
\]
\[
\overset{\chi_{\mathcal{H}A_i (r', t')}}{=} \chi_{\mathcal{H}A_i (r', t-t')}
\] (3.5)

where we introduced the dynamical susceptibility function \( \chi (\cdot, \cdot, t) \). Note its time-translational invariance inferred from the underlying equilibrium dynamics. Using integration by parts we rewrite

\[
\iint dp_s \ dq_s \ \left[ \frac{\partial A_i}{\partial p_s} \frac{\partial \rho_0}{\partial q_s} - \frac{\partial \rho_0}{\partial p_s} \frac{\partial A_i}{\partial q_s} \right] B = - \iint dp_s \ dq_s \ \left[ \frac{\partial A_i}{\partial p_s} \frac{\partial B}{\partial q_s} - \frac{\partial B}{\partial p_s} \frac{\partial A_i}{\partial q_s} \right] \rho_0
\]
3.1 Linear response

from which we can follow

\[ \chi_{BA_i}(\mathbf{r}, \mathbf{r}', t - t') = -\theta(t - t') \left( \{ B(\mathbf{r}, t), A_i(\mathbf{r}', t') \} \right)_0 . \]  

(3.6)

So the response of an observable \( B \) to a small external field \( a_i \) is given by the Poisson bracket of \( B \) with the corresponding observable \( A_i \). Under the assumption

of a canonical phase space density \( \rho_0 = \frac{1}{Z} \exp(-\beta H_0) \) with \( Z \) the canonical partition function, the Poisson bracket in the definition (3.5) of \( \chi_{BA_i}(\mathbf{r}, \mathbf{r}', t - t') \) can alternatively be written

\[ \{ A_i(\mathbf{r}', t') , \rho_0 \} = -\beta \rho_0 \frac{\partial A_i}{\partial t'}(\mathbf{r}', t') \]

which yields the classical fluctuation-dissipation theorem [Kub66]:

\[ \chi_{BA_i}(\mathbf{r}, \mathbf{r}', t - t') = \theta(t - t') \beta \frac{\partial}{\partial t'} \left( \langle B(\mathbf{r}, t) A_i(\mathbf{r}', t') \rangle_0 a_i(\mathbf{r}', t') \right) . \]

(3.7)

Before reinserting this into eq. (3.5), we restrict the external fields to vanish for \( t' > 0 \) in order to obtain the unperturbed \( t > 0 \) time evolution of an imposed small fluctuation. Bearing in mind the adiabatically slow variations of the \( a_i \), we obtain

\[ \langle \Delta B(\mathbf{r}, t) \rangle = \beta \int_{-\infty}^{\infty} dt' \int d^d r' \sum_i \theta(-t') \frac{\partial}{\partial t'} \left( \langle B(\mathbf{r}, t) A_i(\mathbf{r}', t') \rangle_0 a_i(\mathbf{r}', t') \right) . \]

The external fields can be eliminated with the equal-time correlations,

\[ \langle \Delta A_i^\ast(\mathbf{r}, t = 0) \rangle = \beta \sum_j \int d^d r' C_{A_j A_i}(\mathbf{r}, \mathbf{r}', t = 0) a_j(\mathbf{r}') \]

\[ \Leftrightarrow a_i(\mathbf{r}) = \beta^{-1} \sum_j \int d^d r' C_{A_i A_j}^{-1}(\mathbf{r}, \mathbf{r}') \left\langle \Delta A_j^\ast(\mathbf{r}') \right\rangle \]

and with the short notation \( \langle \Delta A_i^\ast(\mathbf{r}, t) \rangle = : \delta A_i^\ast(\mathbf{r}, t) \), we obtain the central result of this section

\[ \delta A_i^\ast(\mathbf{r}, t) = \sum_{j,k} \int d^d r' d^d r'' C_{A_j A_k}(\mathbf{r}, \mathbf{r}', t) C_{A_i A_k}^{-1}(\mathbf{r}', \mathbf{r}'') \delta A_k^\ast(\mathbf{r}'') . \]  

(3.8a)

By use of Plancherel’s theorem, an equivalent expression in wave-vector space is obtained,

\[ \delta A_i^\ast(\mathbf{k}, t) = \frac{1}{(2\pi)^d} \sum_{j,k} \int d^d k' d^d k'' C_{A_j A_i}(\mathbf{k}, \mathbf{k}', t) C_{A_i A_k}^{-1}(\mathbf{-k}', \mathbf{k}'') \delta A_k^\ast(\mathbf{-k}'') . \]  

(3.8b)
3.2. Zwanzig–Mori formalism

The discussion of linear response theory in the previous section 3.1 assumed a set \( S = \{ A_1 - \langle A_1 \rangle_0, A_2 - \langle A_2 \rangle_0, \ldots, A_\sigma - \langle A_\sigma \rangle_0 \} \) of equilibrium fluctuations induced by external fields in a controlled fashion. It was found that the time evolution of small fluctuations can be described perturbatively by the corresponding set of equilibrium correlation functions. The objective in this section therefore is to learn something about the time evolution of \( A_i(0) A_j(t) = C_{ij}(t) \). L. Onsager’s regression hypothesis [Ons31] will later be used to conclude from that to the time evolution of the correlation functions in eq. (3.8a). Here and henceforth, the equilibrium value of each variable will be renormalized to zero without loss of generality. Moreover, the subscript “0” will be dropped from both the equilibrium expectation value \( \langle \cdot \rangle_0 \) and the equilibrium Liouvillean \( L_0 \) in accordance with the linear response scope of this thesis. Formally,

\[
C_{ij}(t) = \langle A_i^*(0) e^{-iLt} A_j(t = 0) \rangle. \tag{3.9}
\]

The quadratic form \( \langle \cdot \langle \cdot \rangle \), defined one the Hilbert space of physical observables, fulfills all the properties of a scalar product. With this in mind, the effect of the time evolution operator \( e^{-iLt} \) in eq. (3.9) gets a geometrical interpretation: It acts on the vector \( A_j \) as a linear transform whose span will in general be disjoint from \( \text{span}(S) \).

A formal decomposition of \( e^{-iLt} \), explained in detail e.g. in [For90, chap. 5], is what follows for the rest of this section. The analysis is facilitated by moving to Laplace space, i.e. by employing to equation (3.9) the integral transform

\[
C_{ij}(z) = i \int_0^{\infty} dt e^{izt} C_{ij}(t) = \left\langle A_i^* \frac{1}{L - z} A_j \right\rangle \tag{3.10}
\]

with \( z \in \mathbb{C} \) and \( \text{Im}(z) > 0 \) to ensure convergence. \( \langle L - z \rangle^{-1} =: \mathcal{R}(z) \) is called the “resolvent (operator)”. The part of the dynamics that remains inherent to the subspace \( S \) can be found by a projection

\[
P := \sum_{i,j=1}^\sigma A_i \langle A_i^* A_j \rangle^{-1} \langle A_j^* \rangle \tag{3.11}
\]

which acts as the identity operator on the subspace \( S \) and is idempotent,

\[
P^2 = \sum_{i,j,k,l=1}^\sigma A_i \langle A_i^* A_j \rangle^{-1} \langle A_j^* A_k \rangle \langle A_k^* A_l \rangle^{-1} \langle A_l^* \rangle = \sum_{i,j,l=1}^\sigma A_i \langle A_i^* A_j \rangle^{-1} \delta_{ij} \langle A_i^* \rangle = P.
\]

Here, the Kronecker symbol was used,

\[
\delta_{ij} = \begin{cases} 1, & i = j, \\ 0, & \text{else.} \end{cases}
\]
\( Q := 1 - P \) denotes the projection onto the orthogonal complement of \( S \). Using the operator identity

\[
\frac{1}{\mathcal{X} + \mathcal{Y}} = \frac{1}{\mathcal{X}} - \frac{1}{\mathcal{X} \mathcal{Y}} \frac{1}{\mathcal{X} + \mathcal{Y}},
\]

we split up the right hand side of eq. (3.10) into two contributions

\[
C_{ij}(z) = \left( A_i^* \frac{1}{\mathcal{L} - z} A_j \right) - \left( A_i^* \frac{1}{\mathcal{L} \mathcal{Q} - z} \mathcal{L} \mathcal{P} \frac{1}{\mathcal{L} - z} A_j \right) \quad (3.12)
\]

A series expansion of the first term \( C'_{ij}(z) \) yields

\[
C'_{ij}(z) = -\frac{1}{z} \left( A_i^* \frac{1}{1 - \mathcal{Q} \mathcal{L} / z} A_j \right) = -\frac{1}{z} \left( A_i^* \sum_{n=0}^{\infty} \left( \frac{\mathcal{Q} \mathcal{L}}{z} \right)^n A_j \right)
\]

as \( \mathcal{Q} A_j = \mathcal{Q} \mathcal{P} A_j = 0 \) by construction. The second term \( C''_{ij}(z) \) can be related back to \( C_{ij}(z) \) by an expansion of \( \mathcal{P} \),

\[
C''_{ij}(z) = \left( A_i^* \frac{1}{\mathcal{L} \mathcal{Q} - z} \mathcal{L} A_k \right) C_{kl}^{-1} \left( A_j^* \frac{1}{\mathcal{L} - z} A_l \right) \quad (3.12)
\]

Before factoring out \( C(z) \), it appears natural to decompose \( C'' \) into more obviously Hermitian expressions,

\[
C'''_{ij}(z) = \frac{1}{z} \left( A_i^* \frac{z - \mathcal{L} \mathcal{Q} + \mathcal{L} \mathcal{Q}}{\mathcal{L} \mathcal{Q} - z} \mathcal{L} A_j \right) = \frac{1}{z} \left( A_i^* \left( -\mathcal{L} + \frac{\mathcal{L}^2}{\mathcal{L} \mathcal{Q} - z} \right) A_j \right)
\]

where we put two extra \( \mathcal{Q} = \mathcal{Q}^2 \) to obtain a more symmetric expression. It follows that

\[
C''_{ij}(z) = \frac{1}{z} \left( -\langle A_i^* \mathcal{L} A_k \rangle C_{kl}^{-1} + \left( A_i^* \mathcal{L} \mathcal{Q} \frac{1}{\mathcal{Q} \mathcal{L} \mathcal{Q} - z} \mathcal{Q} \mathcal{L} A_j \right) C_{kl}^{-1} \right) C_{ij}(z)
\]

which reinserted into eq. (3.12) yields after a multiplication by \( z \)

\[
[z \delta_{ij} - \Omega_{ij} + \Gamma_{ij}(z)] C_{ij}(z) = -C_{ij} \quad (3.13a)
\]

\[
\Leftrightarrow zC_{ij}(z) + C_{ij}(t = 0) - \Omega_{ij} C_{ij}(z) + \Gamma_{ij}(z) C_{ij}(z) = 0. \quad (3.13b)
\]

\(^2\)Based on this constitutive ansatz, the Zwanzig–Mori formalism is also often called “projection-operator formalism”.

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With two properties of the Laplace transform,

\[ z \mathbf{C}(z) + \mathbf{C}(t=0) = -\int_0^\infty dt \, e^{izt} \frac{\partial}{\partial t} \mathbf{C}(t) \quad (\text{partial integration}), \]

\[ \mathbf{\Gamma}(z) \cdot \mathbf{C}(z) = -\int_0^\infty dt \, e^{izt} \int_0^t dt' \, \mathbf{\Gamma}(t-t') \cdot \mathbf{C}(t') \quad (\text{convolution theorem}) \]

we transform eq. (3.13b) back to time space to find

\[
\dot{\mathbf{C}}(t) + i\mathbf{\Omega} \cdot \mathbf{C}(t) + \int_0^t dt' \, \mathbf{\Gamma}(t-t') \cdot \mathbf{C}(t') = 0. \tag{3.14}
\]

The “frequency matrix” \( \mathbf{\Omega} \) describes the reversible coupling of the correlation matrix \( \dot{\mathbf{C}}(t = t_0) \) back to itself. The property of the Liouvillian (for Hamiltonians \( \mathcal{H} \) without explicit time-dependence)

\[ \mathcal{L} = i\partial_t \]

from eq. (3.3) follows by consideration of time inversion symmetries [For90] that \( \mathbf{\Omega} \) cannot have diagonal elements (i.e. a dynamical variable cannot reversibly couple to itself). \( \mathbf{\Gamma} \) is the so-called “memory matrix” that describes how the time derivative of \( \mathbf{C} \) is related to its earlier values \( \mathbf{C}(t' < t) \). It is related to the dissemination of the information on the original correlations \( \mathbf{C}(t = 0) \) into the multitude of phase space variables.

### 3.2.1. Identification of Hydrodynamic Modes

The formal solution of eq. (3.13b),

\[ C_{ij}(z, \mathbf{k}) = \frac{C_{ij}(\mathbf{k})}{z\delta_{ij} - \Omega_{ij}(\mathbf{k}) + \Gamma_{ij}(z, \mathbf{k})}. \tag{3.15} \]

requires the inversion of \( z1 - \Omega(\mathbf{k}) + \Gamma(z, \mathbf{k}) \) - we use matrices in the denominator of a fraction to denote their inverse. For discussion of the selection criteria of the observables contained in the projection set\(^3\), we restrict ourselves to the single variable case\(^4\) which turns equation (3.15) into a scalar form

\[ C_a(z, \mathbf{k}) = \frac{C_a(\mathbf{k})}{z + \Gamma_a(z, \mathbf{k})}. \tag{3.16} \]

As argued in the last section, in such a case \( \Omega \) will vanish. Let us consider

\[ C_a(\mathbf{k}) \, \Gamma_a(z, \mathbf{k}) = \left\langle a^* \mathcal{L} Q \frac{1}{Q \mathcal{L} Q - z} Q \mathcal{L} a \right\rangle(\mathbf{k}), \tag{3.17} \]

\(^3\)We added a continuous dependency to the observables in eq. (3.15) as our application of the Zwanzig–Mori formalism will be to fields.

\(^4\)See [Mis] and references therein for the case of several variables.
3.2 Zwanzig–Mori formalism

additionally assuming that \( a ( \mathbf{k}, t ) \) is the density of a conserved quantity\(^5\) such that
\[
\partial_t a ( \mathbf{k}, t ) = - i \mathbf{k} \cdot \mathbf{j}^{(a)} ( \mathbf{k}, t ).
\]
Discussion in [For74; For90] shows that in the limit \( k \to 0 \), the projectors \( \mathcal{Q} \) can be dropped from eq. (3.17) which in the subsequent low-frequency limit \( z \to 0 \) yields a Green-Kubo like relation [Gre54; Kub57]:

\[
\lim_{z \to 0} \lim_{k \to 0} \Gamma_a ( z, \mathbf{k} ) = \lim_{z \to 0} \left[ \frac{1}{C - z} \right] ( \mathbf{k} = 0 ) \lim_{k \to 0} \frac{k_\alpha k_\beta}{C_a ( \mathbf{k} )}
\]

\[
= i \lim_{z \to 0} \int_0^\infty dt \exp(-zt) \left\{ j^{(a)*} ( t ) j^{(a)} ( \mathbf{k} = 0 ) \right\} \lim_{k \to 0} \frac{k_\alpha k_\beta}{C_a ( \mathbf{k} )}
\]

\[
= i \int_0^\infty dt \left\{ j^{(a)*} ( t ) j^{(a)} ( \mathbf{k} = 0 ) \right\} \lim_{k \to 0} \frac{k_\alpha k_\beta}{C_a ( \mathbf{k} )}.
\]

We use \( \lim_{k \to 0} C_a ( \mathbf{k} ) =: \chi^{(a)} > 0 \). Further, we make use of \( \lim_{k \to 0} \gamma^{(a)} ( \mathbf{k} ) = \delta_{\alpha\beta} \gamma^{(a)} \)
with an isotropic \( \gamma^{(a)} = \frac{1}{3} \lim_{k \to 0} \left\{ j^{(a)*} ( t ) \cdot j^{(a)} ( \mathbf{k} ) \right\} > 0 \) for simplicity. Thereby follows

\[
\lim_{z \to 0} \lim_{k \to 0} \Gamma_a ( z, \mathbf{k} ) = \lim_{k \to 0} \frac{k^2 \gamma^{(a)}}{\chi^{(a)}} = 0.
\]

In this limit, eq. (3.16) in the time domain becomes

\[
C_a ( \mathbf{k}, t ) = \left[ e^{-[k^2 \gamma^{(a)}/\chi^{(a)}+O(k^3)]t} + O \left( k^2 \right) \right] C_a ( \mathbf{k} )
\]

from which we can identify a decay time \( \left[ \tau^{(a)} ( k ) \right]^{-1} = k^2 \gamma^{(a)}/\chi^{(a)} + O \left( k^3 \right) \) that diverges in the long-wavelength limit. Note that \( \tau^{(a)} = O \left( k^{-2} \right) \) is a consequence solely of the associated conservation law. Generically, the decay time of correlation functions will show a dependency on the mean free path on all length scales, i.e. \( \tau = O \left( k^0 \right) \). Now if only the length scale of interest is large enough, the life time of correlations in \( a \) will surpass those for non-conserved variables by orders of magnitude. Hence, we have identified conservation laws as a first criterion for the selection of hydrodynamic “slow” variables. This is however not the only path to the variable \( a \) being hydrodynamic. Before exploring the second one relevant to this thesis, we take a step back and reconsider the equilibrium correlation function in the canonical ensemble

\[
C_a ( \mathbf{r} ) = \langle a^* a ( \mathbf{r} ) \rangle = \frac{1}{Z} \int d\Gamma \left| a^2 ( \mathbf{r} ) \right| \exp \left( - \beta \mathcal{H} \right)
\]

\[
= \beta^{-1} \lim_{\hbar_a \to 0} \frac{\delta h_a}{\delta h_a ( \mathbf{r} )} \frac{1}{Z} \int d\Gamma a^* ( \mathbf{r} = 0 ) \exp \left[ - \beta \left( \mathcal{H} + \int d^d r' a ( \mathbf{r} ') h_a ( \mathbf{r} ' ) \right) \right]
\]

\[
\Leftrightarrow C_a ( \mathbf{r} ) = \beta^{-1} \delta \left( a^* \right) \frac{\delta}{\delta h_a ( \mathbf{r} )} =: \beta^{-1} \chi^{(a)} ( \mathbf{r} )
\]

\(^5\)To which we refer as “conserved density”, bearing in mind that conserved is the space integral of that density — conventionally denoted by uppercase letters (e.g. \( A \) in the present context).
with \( \tilde{Z} = \int d\Gamma \exp \left[ -\beta \left( \mathcal{H} + \int d^d r' a (r') h_a (r') \right) \right] \) the partition function in the presence of a weak external field coupling to \( a \). Equation (3.20) identifies the equilibrium correlation functions with static susceptibilities. The generalization to several variables \( \{ a_1, a_2, \ldots, a_\sigma \} \) is straightforward,

\[
\chi_{ij} (r) = \frac{\delta \langle a_\sigma^* \rangle}{\delta h_{ij} (r)},
\]

and \( \chi_{ij} \) can in turn be identified with thermodynamic derivatives in the long-wavelength limit [CL10, chapter 3].

### 3.2.2. Spontaneous symmetry breaking

Equation (3.19) indicates that a divergence of the static susceptibility,

\[
\lim_{k \to 0} \chi^{(a)} (k) \propto k^{-2}
\]

influences \( \tau^{(a)} \) to the same effect as the above-mentioned conservation law. An illustrative example of slowly decaying excitations in a non-conserved density are propagating waves in antiferromagnets and liquid crystals [For90] (apparently, neither the staggered magnetization nor the director are conserved quantities). The formal derivation of diverging statical susceptibilities is based on the Goldstone theorem [GSW62]. This overview follows [Das11, chap. 5.4], where the theorem is discussed in the context of a classical solid. We begin again by considering a conserved density \( c (r, t) \), now other than \( a \).

\[
\frac{\partial}{\partial t} c (r) + \nabla \cdot j^{(c)} (r) = 0 \quad \Leftrightarrow \quad \dot{c} (k) = -ik \cdot j^{(c)} (k).
\]

The Bogoliubov inequality [Bog62]\(^6\) put for \( \dot{c} \) and \( a \) reads

\[
\langle a^* a \rangle (k) \langle \dot{c}^* \dot{c} \rangle (k) \geq |\langle \dot{c}^* a \rangle (k)|^2.
\]

Making use of the continuity equation for \( c \), this is equivalent to

\[
\chi^{(a)} (k) = \langle a^* a \rangle (k) \geq \frac{|\langle \dot{c}^* a \rangle (k)|^2}{k_\alpha k_\beta \langle j^{(c)*}_\alpha (k) j^{(c)}_\beta (k) \rangle}.
\]

(3.22)

For ease of discussion, we will assume isotropy, i.e.

\[
k_\alpha k_\beta \langle j^{(c)*}_\alpha (k) j^{(c)}_\beta (k) \rangle = \frac{1}{3} \delta_{\alpha \beta} k^2 \langle j^{(c)^2}_\beta (k) \rangle
\]

\(\text{It can be seen as the Cauchy–Schwarz inequality for the scalar product } \langle \cdot^* \cdot \rangle.\)
3.2 Zwanzig–Mori formalism

with \( j_L^{(c)}(k) = \hat{\mathbf{k}} \cdot \mathbf{j}_L^{(c)}(k) \) the longitudinal current in \( c \). Then eq. (3.22) yields a lower bound for the divergence of \( \lim_{k \to 0} \chi^{(a)}(k) \) provided that

\[
\lim_{k \to 0} \frac{|\langle \dot{c}^a \rangle (k) |^2}{\langle |j_L^{(c)}(k)|^2 \rangle} > 0. \tag{3.23}
\]

The denominator of eq. (3.23) remains finite in the long-wavelength limit if the system does not show long-range interactions. The numerator can be transformed with the fluctuation-dissipation theorem eq. (3.7),

\[
\langle \dot{c}^a (t = 0) a (t' = 0) \rangle (k) = -\frac{1}{\beta} \langle \{c^a (t = 0), a (t' = 0)\} \rangle (k). \tag{3.24}
\]

At \( k = 0 \) holds \( c(k = 0) = \int d^d r c(r) = Q = \text{const.} \) We write

\[
\{Q^*, a(k)\} =: b(k)
\]

and assume

\[
\langle b(k) \rangle = \int d\Gamma \rho_0 \{Q^*, a(k)\} \neq 0. \tag{3.25}
\]

The assumption that in eq. (3.25) \( Q^* \) can be replaced by \( c^a(k) \) in the long-wavelength limit, combined with eq. (3.24) yields

\[
\lim_{k \to 0} \langle \dot{c}^a (k) \rangle \neq 0
\]

and consequently the desired lower bound for \( \chi^{(a)}(k) \) in that limit.

Now what is the physical interpretation of the assumption in eq. (3.25)? By use of

\[
\int d\Gamma \rho_0 \{Q^*, a(k)\} = -\int d\Gamma a(k) \{Q^*, \rho_0\}
\]

from [Das11, chap. 5.4] one can follow

\[
\langle b(k) \rangle \neq 0 \Rightarrow \{Q^*, \rho_0\} \neq 0.
\]

One the other hand, \( Q^* \) itself is conserved and therefore has a vanishing Poisson bracket with the Hamiltonian

\[
\{Q^*, \mathcal{H}\} = 0.
\]

\( \mathcal{H} \) is invariant under the continuous transformation associated with \( Q \), whereas the equilibrium phase space density \( \rho_0 \) is not. Viz, the continuous symmetry of \( \mathcal{H} \) is \textit{spontaneously broken} by \( \rho_0 \).
3.3. Phenomenology and Elasticity theory

This section illustrates how the concepts of equilibrium thermodynamics can be used to derive equations of motion for mesoscopic deviations of hydrodynamic fields from equilibrium. To introduce its principles step by step, the approach is initially applied to a single-species liquid and afterwards generalized to a multi-species crystal. Before leaving the microscopic regime for the field-theoretical description, it is important to note that also the complicated phase space dynamics of a many-particle system obeys a set of conservation laws (discussed in the same context amongst others in [For90; Das11]). The microscopic densities of particles $\rho(\mathbf{r}, t) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i(t))$, momentum $\mathbf{j}(\mathbf{r}, t) = \sum_i \mathbf{p}_i(t) \delta(\mathbf{r} - \mathbf{r}_i(t))$, energy $e(\mathbf{r}, t) = \sum_i \left[ \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j}^{N} \Phi(\mathbf{r}_i - \mathbf{r}_j) \delta(\mathbf{r} - \mathbf{r}_i(t)) \right]$ obey the continuity equations

$$\frac{\partial}{\partial t} \begin{cases} \rho \\ \mathbf{j}(\mathbf{r}, t) + \nabla \cdot \mathbf{j}^{(n)}(\mathbf{r}, t) = 0 \\ e \\ \mathbf{j}^{(p)}(\mathbf{r}, t) = 0 \\ \mathbf{j}^{(e)}(\mathbf{r}, t) \end{cases}$$

(3.27)

with the microscopic currents $(\mathbf{r}_i - \mathbf{r}_j =: \mathbf{r}_{ij})$

$$j^{(n)}(\mathbf{r}, t) = \sum_i \frac{p_i}{m} \delta(\mathbf{r} - \mathbf{r}_i) = \mathbf{j}(\mathbf{r}, t)/m,$$

(3.28a)

$$j^{(p)}_{\alpha\beta}(\mathbf{r}, t) = \sum_i \frac{p_i \delta(\mathbf{r} - \mathbf{r}_i)}{m} \delta(\mathbf{r} - \mathbf{r}_i) - \frac{1}{2} \sum_{i \neq j}^{N} r_{ij,\beta} \nabla_{\alpha} \Phi(\mathbf{r}_{ij}) \Delta_{ij}(\mathbf{r})$$

(3.28b)

with $\Delta_{ij}(\mathbf{r}) = \int_0^1 d\lambda \delta\left(\mathbf{r} - \mathbf{r}_i - \frac{\lambda}{2} \mathbf{r}_j\right)$,

$$j^{(e)}(\mathbf{r}, t) = \sum_i \frac{e_i \mathbf{p}_i}{m} \delta(\mathbf{r} - \mathbf{r}_i) - \sum_{i \neq j}^{N} \frac{1}{4m} \mathbf{r}_j \nabla \Phi(\mathbf{r}_{ij}) \cdot (\mathbf{p}_i + \mathbf{p}_j) \Delta_{ij}(\mathbf{r}) \quad .$$

(3.28c)

The time-dependence of the phase space variables $\{\mathbf{r}_i, \mathbf{p}_i\}$ was omitted on the right-hand side for better readability. Additionally, $j^{(n)}$ will henceforth be substituted by $\mathbf{j}$ with eq. (3.28a). $j^{(p)}$ can be shown to be symmetric [Das11] which ensures conservation of angular momentum. The line integral in $\Delta_{ij}(\mathbf{r})$ takes into account the non-local nature of momentum and energy transport. Unless stated otherwise, we assume $\Phi$ to be of short range and approximate $\Delta_{ij}(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}_i)$ . Now, imagine a mesoscopic sample subvolume $\tilde{V} \subset V$ of the system as shown in figure 3.1, extending across a multiple of the mean free path $\lambda$ in each direction and large compared to
3.3 Phenomenology and Elasticity theory

The system is formed by a macroscopic container of volume $V$. $\tilde{V}$ marks a coarse graining volume which extends across many inter-particle distances as highlighted by the magnification to the right.

Figure 3.1.: Illustration of the length scales distinguished within the hydrodynamic description.

The range of the interaction potential but still much smaller than the system size, $\tilde{V} \ll V$. Consider the $\tilde{V}$-volume average $\tilde{n}$ of the microscopic density $\rho$ and its rate of change,

$$\tilde{n}(t) := \frac{1}{\tilde{V}} \int_{\tilde{V}} d^d r \rho(r, t),$$

$$\frac{\partial}{\partial t} \tilde{n}(t) = \frac{1}{\tilde{V}} \int_{\tilde{V}} d^d r \nabla \cdot \left[ j^{(n)}(r, t) - \tilde{j}^{(n)}(t) \right] \nabla \text{divergence theorem} \frac{1}{\tilde{V}} \int_{\partial \tilde{V}} \left[ j^{(n)} - \tilde{j}^{(n)} \right] \cdot dA$$

with $\tilde{j}^{(n)}$ the $\tilde{V}$-volume average of the particle current and $dA$ the oriented infinitesimal surface element, having applied the divergence theorem. The volume average substracted in the second line highlights that only deviations from it give overall contributions. The last equality states that changes in $\tilde{n}$ occur by microscopic processes near the surface $\partial \tilde{V}$. Before these can affect considerable parts of the mesoscopic sample subvolume $\tilde{V}$ many average collision times will have past, establishing a local thermodynamic equilibrium within $\tilde{V}$. To be strict, a similar average over a mesoscopic time interval much larger than the average collision time but small compared to macroscopic time scales needs to be performed in addition. The time dependency of the coarse grained variables is to be understood in that sense. Now, a net particle current emerging from the equilibration process would violate momentum conservation. Moreover, microscopic inhomogeneities are smoothened out rapidly. Hence, the mesoscopic volume average $\tilde{j}^{(n)}(t)$ can be assumed identical with the local thermodynamic equilibrium value of the particle current. A translation of the considered subvolume $\tilde{V}$ (on mesoscopic length scales) will lead to different values for

---

7 The reverse of that calculation is used to derive microscopic conservation laws. Emphasis here is on the meaning of conservation laws for mesoscopic dynamics.

8 A dimensionless estimate of the accuracy of this approach to fluid mechanics is given by the so-called Knudsen-number $Kn = \lambda / L$ where $\lambda$ is the mean free path and $L$ is the characteristic length of change for the flow profile, cf. [Cus97]. The subvolumina are often referred to as “fluid parcels”.
\( \tilde{n} \) and \( \tilde{j}^{(c)} \) But this means nothing else than that the mesoscopic quantities themselves are space dependent. Henceforth such “coarse-grained” quantities will be marked with a tilde,

\[
\tilde{n} (r, t), \ \tilde{j} (r, t), \ etc.
\]

bearing in mind that mesoscopic averages at \( r \) and \( t \) are considered. The original conservation laws hold equally on that coarse-grained level, and the continuity equations can be inferred,

\[
\frac{\partial}{\partial t} \tilde{n} (r, t) + \nabla \cdot \tilde{j}^{(p)} (r, t) = 0.
\]

Besides the trivial case where the currents of conserved quantities \( c \) vanish globally, \( \tilde{j}^{(c)} \equiv 0 \), any part of the system can be taken into a local rest frame by an appropriate Galilei transform. The relation of the currents \( \tilde{j}^{(c)} \) in the global rest frame — chosen to be the rest frame of the system’s center of mass — to the currents \( \tilde{j}^{(c)}_0 \) in the local rest frame (subscript “0”) can be derived from the microscopic expressions eq. (3.28):

With the canonical transformation

\[
\begin{align*}
\mathbf{p}_i & \rightarrow \mathbf{p}_{0i} = \mathbf{p}_i - m \mathbf{v} (r, t) \\
\mathbf{r}_i & \rightarrow \mathbf{r}_{0i} = \mathbf{r}_i - \mathbf{v} (r, t) t
\end{align*}
\]

and \( \tilde{n}_0 (r - \mathbf{vt}, t) = \tilde{n} (r, t) \) follows

\[
\begin{align*}
\tilde{j} (r, t) &= \tilde{j}_0 (r - \mathbf{vt}, t) + \mathbf{v} m \tilde{n} (r, t), \\
\tilde{j}^{(p)} (r, t) &= \tilde{j}^{(p)}_0 (r - \mathbf{vt}, t) + \mathbf{v} \tilde{j}_0 + \tilde{j}_0 \mathbf{v} + \mathbf{v} \mathbf{v} m \tilde{n} , \\
\tilde{j}^{(c)} (r, t) &= \tilde{j}^{(c)}_0 (r - \mathbf{vt}, t) + m \left( \tilde{j}^{(p)}_0 + \tilde{\varepsilon} I \right) \cdot \mathbf{v} + \mathbf{v} \mathbf{v} \cdot \tilde{j}_0 + \frac{1}{2} \mathbf{v}^2 \left( \tilde{j}_0 + \mathbf{v} m \tilde{n} \right).
\end{align*}
\]

Explicit occurrence of the velocity field \( \mathbf{v} \) in eq. (3.29) indicates convective transport of the respective conserved quantity. The non-convective (and linear) part of the momentum current \( \tilde{j}^{(p)}_0 \) is identical to the (negative of) the isothermal “stress tensor” \( \tilde{j}^{(p)}_0 = -\sigma \).

It shall be discussed in more detail in paragraph 3.3.2. The currents in the local rest frame \( \tilde{j}^{(c)}_0 \) are invariants of the Galilei transform and additionally restricted by the symmetry of the corresponding thermodynamic equilibrium state. As explained in [For90], the general form compatible with the point group of an isotropic liquid and physical parity requirements reads

\[
\begin{align*}
\tilde{j}_0 (r, t) &= \nabla \phi (r, t), \\
\tilde{j}^{(p)}_0 (r, t) &= p (r, t) I + n \left( \nabla \mathbf{v} + [\nabla \mathbf{v}]^T \right) (r, t) + \nabla \cdot \mathbf{v} (r, t) I , \\
\tilde{j}^{(c)}_0 (r, t) &= \nabla \phi^{(c)} (r, t).
\end{align*}
\]
The scalar fields \( \phi, \phi^{(\epsilon)} \) and the vectorial field \( \mathbf{v} \) (with a free coupling constant \( \eta \)) are related to intensive mesoscopic physical observables themselves. They give rise to currents as long as the system is spatially inhomogeneous. From stability considerations, it is intuitively clear that these currents will be directed towards a globally homogeneous system — the macroscopic equilibrium state. They can consequently be associated with irreversible processes in the system — once in a homogeneous state, mesoscopic inhomogeneities will not reoccur spontaneously.

Discussion of the physical dimension of the remaining contribution \( p(\mathbf{r}, t) \) shows

\[
\left[ \tilde{j}^{(p)} \right] = \frac{\text{momentum}}{\text{time}} \div \frac{\text{area}}{\text{area}} = \text{force} / \text{area} = \text{pressure},
\]

yielding an unsurprising physical interpretation of \( p \). In order to obtain a closed set for the dynamics of mesoscopic fluctuations, the fields introduced in equations (3.30) need to be related to \( \tilde{n}, \tilde{j} \) and \( \tilde{e} \). This can be achieved with a local formulation of thermodynamics, valid in the mesoscopic equilibrium states. As long as only the reversible dynamics is considered, that step is obsolete for the irreversible contributions in eq. (3.30). Therefore \( \tilde{j}_0 \equiv 0 \) and \( \tilde{j}^{(\epsilon)}_0 \equiv 0 \) will be assumed in the following. For the reversible component \( p \) of \( \tilde{j}^{(p)} \) we state that — with \( p_0 \) the global equilibrium pressure, \( \delta p(\mathbf{r}, t) := p(\mathbf{r}, t) - p_0 \) and \( \delta \tilde{e}, \delta \tilde{n} \) analogously — the formal thermodynamic relation

\[
\delta p(\mathbf{r}, t) = \left( \frac{\partial p}{\partial \tilde{e}} \right)_n \delta \tilde{e}(\mathbf{r}, t) + \left( \frac{\partial p}{\partial \tilde{n}} \right)_\epsilon \delta \tilde{n}(\mathbf{r}, t)
\]

completes the reversible (Euler) equations of fluid-hydrodynamics:

\[
\frac{\partial}{\partial t} \tilde{n} + \frac{1}{m} \nabla \cdot \mathbf{j} = 0, \quad (3.32a)
\]

\[
\frac{\partial}{\partial t} \mathbf{j} + \nabla \cdot \left( \frac{\mathbf{j} \mathbf{j}}{m \tilde{n}} \right) + \nabla p = 0, \quad (3.32b)
\]

\[
\frac{\partial}{\partial t} \tilde{e} + \nabla \cdot \left[ (\tilde{e} + \delta p) \frac{\mathbf{j}}{m \tilde{n}} \right] = 0. \quad (3.32c)
\]

Note the nonlinearities in the fields which are crucial for an understanding of turbulence [LL87]. For infinitesimally small deviations from equilibrium (i.e. the linear response regime), the eqs. (3.32) simplify to

\[
\frac{\partial}{\partial t} \tilde{n}(k, t) + \frac{i}{m} \mathbf{k} \cdot \mathbf{j}(k, t) = 0, \quad (3.33a)
\]

\[
\frac{\partial}{\partial t} \mathbf{j} + i \mathbf{k} \delta p(\mathbf{k}, t) = 0, \quad (3.33b)
\]

\[
\frac{\partial}{\partial t} \tilde{e}(\mathbf{k}, t) + \frac{i}{m n_0} \mathbf{k} \cdot \mathbf{j} = 0. \quad (3.33c)
\]
Here, we applied the Fourier transform to wave-vector space
\[ c(k, t) := \int d^d r \, e^{-i k \cdot r} c(r, t), \]
\[ c(r, t) = \int \frac{d^d k}{(2\pi)^d} \, e^{i k \cdot r} c(k, t) \quad \text{etc.} \]

This transform turns partial derivatives into multiplications of vector components. For example
\[ \int d^d r \, e^{-i k \cdot r} \nabla \cdot \tilde{j}(r, t) = \begin{array}{c} \text{partial} \\text{integration} \\
\int \end{array} i k \cdot \tilde{j}(k, t) \]

which shows that in the linearized eqs. (3.33) transverse momentum density fluctuations \( \tilde{j}_\perp \) with \( \tilde{j}_\perp \cdot k = 0 \) completely decouple from the other fields. In liquids, couplings of \( \tilde{j}_\perp \) arise only from the dissipative currents in eq. (3.30b). In crystals, additional, anisotropic reactive components in \( \sigma_0 \) lead to transverse sound modes as we will see later. Equations (3.33a) and (3.33c) can be combined to
\[ \frac{\partial}{\partial t} \left( \tilde{e} - \left( e_0 + p_0 \right) \tilde{n} \right) = 0. \quad (3.34) \]

This shows that the reversible linear dynamics of \( \tilde{e} \) is completely determined by that of \( \tilde{n} \). The field \( \tilde{q} \) in eq. (3.34) can be identified as the heat energy density \([KM63] \). The reversibility of eqs. (3.32) can be expressed by a continuity equation for the entropy density \( s \),
\[ \frac{d}{dt} s(r, t) = \frac{\partial}{\partial t} s(r, t) + \nabla \cdot [sv](r, t) = 0. \quad (3.35) \]

That is, entropy changes only locally (by convection). Beyond the scope of this introduction, the entropy-production formalism considers the case \( ds/dt > 0 \) to derive the irreversible components of the currents \( \tilde{j}_0^{(c)} \) by convexity arguments, see e.g. [Das11, chap. A5.1].

### 3.3.1. Hydrodynamics of periodic crystals

Following the argument in paragraph 3.2.2 and [CL10, paragraph 6.4.1], the spontaneously broken translational symmetry demands the introduction of an additional hydrodynamic field \( u(r, t) \) in a crystal. For a coarse-graining volume \( \tilde{V} \) that extends across a reasonable number of unit cells, the local average of the particle density shows the lattice-periodic nature and can be expanded in a Fourier series,
\[ \tilde{n}(r, t) = \sum_{g \in G} \tilde{n}_g(t) e^{ig \cdot r} \quad \text{(3.36)} \]
3.3 Phenomenology and Elasticity theory

with
\[ \tilde{n}_g (t) = \frac{1}{V} \int_V d^d r e^{-i g \cdot r} \rho (r, t) . \]  

(3.37)

The displacement field \( \mathbf{u} (t) \) restores the continuous symmetry of the phase \( \tilde{\varphi}_g = \varphi_{g,0} + \mathbf{g} \cdot \mathbf{u} (t) \) of the \( \tilde{n}_g \),

\[ \tilde{n}_g (t) = |\tilde{n}_g| e^{i[\tilde{\varphi}_{g,0} + \mathbf{g} \cdot \mathbf{u} (t)]} . \]  

(3.38)

Unlike for conserved hydrodynamic variables, no continuity equation can be formulated for \( \mathbf{u} \). Still the requirement that there be no reversible currents in a local rest frame (implied by Galilean invariance) yields with eqs. (3.37) and (3.38) the reversible hydrodynamic equation

\[ \frac{\partial \mathbf{u}}{\partial t} (r, t) = \mathbf{v} (r, t) = \frac{1}{\rho_0} \mathbf{j} (r, t) \]  

(3.39)

with \( mn_0 =: \rho_0 \) and \( N / V =: n_0 \).

We introduced a spatial dependence as previously for the coarse-grained fields. Note that the global averaging of the particle density \( n_0 \) neglects a spatial dependence of the particle density \( \tilde{n}_0 (r, t) \) that follows from eq. (3.37) but would yield non-linear contributions.

Having completed the reversible hydrodynamic equations of motion for single-species (unary) crystals, the scope of this thesis requires their generalization to multi-species (binary, ternary, \ldots, ”\( B \)-nary”) crystals, before finally closing them from thermodynamic considerations in the next paragraph 3.3.2. The first step is straightforward: The previous discussion of spontaneously broken translational symmetry immediately extends to several species. Maintaining eq. (3.36) and rewriting

\[ \tilde{n}_g (t) = \frac{1}{V} \int_V d^d r e^{-i g \cdot r} \sum_{s=1}^B \rho^{(s)} (r, t) = \sum_{s=1}^B |\tilde{n}_g^{(s)}| e^{i[\tilde{\varphi}_{g,0}^{(s)} + \mathbf{g} \cdot \mathbf{u} (t)]} \]

clarifies that \( \mathbf{u} \) influences the order parameter phase identically throughout all species.\(^9\) Equation (3.39) hence only changes in \( \rho_0 = \sum_s \rho_0^{(s)} \) with \( \rho_0^{(s)} := m^{(s)} n_0^{(s)} \) (cf. also the definitions in paragraph 3.3.3).

A separate particle-conservation law is obeyed for every additional species in the system. Equation (3.32a) is initially modified to

\[ \frac{\partial}{\partial t} \tilde{n}_g^{(s)} (r, t) + \frac{1}{m^{(s)}} \mathbf{\nabla} \cdot \mathbf{j}^{(s)} (r, t) = 0 \quad \iff \quad \frac{\partial}{\partial t} \underbrace{m^{(s)} \tilde{n}_g^{(s)} (r, t)}_{=: \rho^{(s)} (r, t)} = - \mathbf{\nabla} \cdot \mathbf{j}^{(s)} (r, t) \]  

(3.40)

\(^9\)In the description of eq. (3.36), the dynamics is captured by changes in the order parameters whereas the Fourier expansion remains form-invariant in a given coordinate system.

\(^{10}\)We infer the species-wise generalization of \( \rho^{(s)} \) and \( \mathbf{j}^{(s)} \) from the upper line of eq. (3.26).
where we introduced the mass density fields $\tilde{\rho}^{(s)}$. Note that unlike the total momentum $\tilde{j} = \sum_{s=1}^{B} \hat{j}^{(s)}$, the single $\hat{j}^{(s)}$ are no conserved quantities because momentum can be transferred between different species. Species-wise consideration of eq. (3.29a) yields the reversible component of $\hat{j}^{(s)}$ as

$$\nabla \tilde{\rho}^{(s)}(\mathbf{r}, t) = \hat{j}^{(s)}(\mathbf{r}, t) - \hat{j}^{(s)}(\mathbf{r}, t) \frac{\text{reversible dynamics}}{\text{total momentum}} \hat{\rho}^{(s)}(\mathbf{r}, t). \quad (3.41)$$

With $\mathbf{v} = \hat{j} / \hat{\rho}$, the reversible part of eq. (3.40) then becomes

$$\frac{\partial}{\partial t} \tilde{\rho}^{(s)}(\mathbf{r}, t) = -\frac{\hat{\rho}}{\hat{\rho}} \hat{j}(\mathbf{r}, t).$$

Finally, the coarse-grained continuity equation for the total momentum density is obtained similarly to the liquid case. The microscopic momentum current $\hat{j}^{(p)} = \sum_{a,b=1}^{B} \hat{j}^{(p),ab}$ quoted from [Das11] in eq. (3.28b) can be decomposed into species-specific components $\hat{j}^{(p),ab}$ as follows:

$$\hat{j}^{(p),ab}(\mathbf{r}, t) = \delta_{ab} \sum_{i=1}^{N(b)} \frac{P_{i}^{(b)} N(b)}{m} \mathbf{r} - \mathbf{r}_{i}^{(b)} - \frac{1}{2} \sum_{i=1}^{N(b)} \sum_{j=1}^{N(b)} \mathbf{r}_{ij}^{(ab)} \nabla \phi^{(ab)}(\mathbf{r}) \Delta_{ij}^{(ab)}(\mathbf{r}) \quad (3.42)$$

with $\mathbf{r}_{ij}^{(ab)} = \mathbf{r}_{i}^{(a)} - \mathbf{r}_{j}^{(b)}$ and $\Delta_{ij}^{(ab)}(\mathbf{r})$ generalized accordingly from $\Delta_{ij}(\mathbf{r})$ in eq. (3.28). $\phi^{(ab)}$ denotes the pair interaction potential between species $a$ and $b$. The symbol “$\nabla$” in the subscripts of the double sum signifies a logical “or” to exclude the self term where both $a = b$ and $i = j$. With the lower crystal symmetry compared to the isotropic liquid, eq. (3.30b) will now feature a higher number of independent coupling constants, subsumed in the stress tensor $\sigma$. To summarize, the reversible hydrodynamic equations of a $B$-species crystal are

$$\frac{\partial}{\partial t} \tilde{\rho}^{(s)}(\mathbf{k}, t) = -i \frac{\hat{\rho}}{\hat{\rho}} \mathbf{k} \cdot \hat{j}(\mathbf{k}, t), \quad s = 1, 2, \ldots, B, \quad (3.43a)$$

$$\frac{\partial}{\partial t} \hat{j}(\mathbf{k}, t) = -i \mathbf{k} \cdot \mathbf{\sigma}(\mathbf{k}, t), \quad (3.43b)$$

$$\frac{\partial}{\partial t} \mathbf{u}(\mathbf{k}, t) = \frac{1}{\hat{\rho}} \hat{j}(\mathbf{k}, t). \quad (3.43c)$$

As in the liquid case, no separate equation for the energy densities $\epsilon$ respectively $q$ is needed in the given limit, cf. [FC76, eq. (4.9c)]. An equation analogous to eq. (4.9d) therein can be recovered by eliminating the r.h.s. of eq. (3.43a) with eq. (3.43c),

$$\frac{\partial}{\partial t} \left[ \tilde{\rho}^{(s)}(\mathbf{k}, t) \mathbf{k}(\mathbf{k}, t) + i \hat{\rho} \mathbf{k} \cdot \mathbf{u}(\mathbf{k}, t) \right] = \frac{\partial}{\partial t} m^{(s)} \tilde{\rho}^{(s)}(\mathbf{k}, t) = 0. \quad (3.44)$$

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This implicit definition of the (point) defect densities $\delta c^{(b)}$ generalizes [WF10, eq. (1)] to

$$
\delta n^{(s)}(\mathbf{r},t) = -n_0^{(s)} \nabla \cdot \mathbf{u}(\mathbf{r},t) - \delta \tilde{c}^{(s)}(\mathbf{r},t). 
$$

(3.45)

$\delta \tilde{c}^{(s)}$ gives the contribution to the hydrodynamic density fluctuations of each species $s$ that is not due to the hydrodynamic displacement field $\mathbf{u}$. The minus sign in front of $\delta \tilde{c}^{(s)}$ follows the convention of counting vacancies positive rather than interstitials.

One step remains towards a closed formulation of the e.o.m. (3.43): The thermodynamic expansion of the stress tensor $\delta \sigma$ cited for the isotropic liquid case in eq. (3.31) needs to be generalized to crystals of several species.

### 3.3.2. Elastic constants within Thermodynamics

Under the assumption of local thermodynamic equilibrium, the hydrodynamic fields $\mathbf{u}(\mathbf{r},t), \{\tilde{n}^{(s)}(\mathbf{r},t), \tilde{c}^{(s)}(\mathbf{r},t)\}$ can be identified with quasistatic, equally long-ranged thermodynamic fluctuations $\mathbf{u}(\mathbf{r}), \{n^{(s)}(\mathbf{r}), c^{(s)}(\mathbf{r})\}$. This is due to the assumption of local thermodynamic equilibrium. Unlike the hydrodynamic field, $\mathbf{u}(\mathbf{r})$ is not defined from a spontaneously broken translational symmetry$^{11}$ but only from the fact that a (not necessarily crystalline) solid sample shows restoring forces also to particle density-conserving deformations. For the definition of $\mathbf{u}(\mathbf{r})$ we consider a continuous distribution of matter $n$ which has been smoothly (in a steady and differentiable manner) deformed with respect to a reference state. There is a one-to-one relation $\mathbf{v}$ between the position $x(\mathbf{m})$ measured for an infinitesimal element of matter $\mathbf{m}$ in the deformed and the reference state,

$$
\mathbf{v} : \{\text{“matter elements } \mathbf{m}\} \rightarrow \mathbb{R}^d, \\
\mathbf{m} \mapsto \mathbf{v}(\mathbf{m}) = x_{\text{deformed}}(\mathbf{m}) - x_{\text{reference}}(\mathbf{m}). 
$$

Each element of matter $\mathbf{m}$ can in turn be indexed by a unique coordinate $\mathbf{m}(\mathbf{r})$ for the definition

$$
\mathbf{u}(\mathbf{r}) = \mathbf{v}[\mathbf{m}(\mathbf{r})].
$$

Depending on convention, $\mathbf{m}(\mathbf{r})$ indicates that element of matter with position $\mathbf{r}$ in either the undeformed material or the deformed material. These “Lagrangian” respectively “Eulerian” coordinates can be identified with the laboratory frame before/after the deformation of a sample. Relations between both descriptions are sketched in [CL10, paragraph 6.6.3] and thoroughly discussed in [Mis], including their equivalence within linear elasticity theory.

---

$^{11}$ The continuous theory of elasticity of matter is in fact older than modern theories on its microscopic structure, dating back to the 17th century. A historical overview is quoted from [PP74] on [https://en.wikiversity.org/wiki/Introduction_to_Elasticity#Brief_Early_History_of_Theoretical_Linearized_Elasticity](https://en.wikiversity.org/wiki/Introduction_to_Elasticity#Brief_Early_History_of_Theoretical_Linearized_Elasticity)
With a definition of the displacement field \( \mathbf{u} \) at hand, the generalization of the thermodynamic expansion (3.31) is obtained from comparing it in the case of a crystal to that of a liquid. In the absence of external potentials, the internal state of the system is invariant under uniform translations and rigid rotations. Elastic deformations are hence described by the symmetrized strain tensor \( \mathbf{u} \) defined as

\[
\mathbf{u}_{\alpha\beta} = \frac{1}{2} \left[ \nabla_{\alpha} u_{\beta}(\mathbf{r}) + \nabla_{\beta} u_{\alpha}(\mathbf{r}) \right]
\] (3.46)

where \( \mathbf{r} \) is an arbitrary point inside the crystal, sufficiently far from its surface.\(^\text{12}\)

Before generalizing the expressions from [CL10, sections 6.4 to 6.6], we move to the canonical \((N,V,T)\)-ensemble for easier comparison and reference. The Helmholtz free energy density \( f \) is obtained from the internal energy \( u \) through a Legendre transform,

\[
f = u - sT \equiv f \left\{ \left\{ n^{(s)} \right\}, \mathbf{u}, T \right\}.
\]

The canonical first law of thermodynamics reads

\[
df = \sum_{s=1}^{B} \mu^{(s)} dn^{(s)} + h_{\alpha\beta} du_{\alpha\beta} - s dT
\] (3.47a)

\[
= - \sum_{s=1}^{B} \mu^{(s)} dc^{(s)} + \left( h_{\alpha\beta} - \sum_{s} \mu^{(s)} n_{0}^{(s)} \delta_{\alpha\beta} \right) du_{\alpha\beta} - s dT
\] (3.47b)

with the chemical potentials

\[
\mu^{(s)} = \left. \frac{\partial f}{\partial n^{(s)}} \right|_{u,\left\{ n^{(s)} \right\}\setminus n^{(s)}, T},
\]

and the “isodense” stress tensor

\[
h_{\alpha\beta} = \left. \frac{\partial f}{\partial u_{\alpha\beta}} \right|_{\left\{ n^{(s)} \right\}, T}.
\] (3.48)

The Cauchy, i.e. isothermal, stress tensor \( \mathbf{\sigma} \) is defined w.r.t. a strain derivative of the free energy density per particle [FC76]

\[
\sigma_{\alpha\beta} = n_{0} \frac{d \left( f \big/ n \right)}{du_{\alpha\beta}} \bigg|_{\left\{ c^{(s)} \right\}, T} = \left[ f - \sum_{s} n_{0}^{(s)} \mu^{(s)} \right] \delta_{\alpha\beta} + h_{\alpha\beta}.
\] (3.49)

In a description with point defects, density changes in the particle densities \( n^{(s)} \) can occur by both changes in \( c^{(s)} \) and changes in the trace \( u_{\alpha\alpha} \). These correspond to the two occurrences of \( \mu^{(s)} \) in eq. (3.47b). From a discussion of the work done in deforming a sample volume at constant temperature, \( \mathbf{\sigma} \) can be decomposed into a solid-specific contribution and one that is present in liquids, too. The results obtained in [CL10, section 6.6.3] yield the same as eq. (3.49) when generalized to a

\(^{12}\)Changes in \( u_{\alpha\beta} \) from altering the choice of \( \mathbf{r} \) can be related to the given expression by shorter length-scale terms of \( O \left( \nabla \nabla \nabla \mathbf{u}(\mathbf{r}) \right) \).

\(^{13}\)Note the absence of kinetic energy in the quasistatic elasticity approach. The energy density \( \epsilon \left( \left\{ n^{(s)} \right\}, \mathbf{u}, s, j \right) \) equals the internal energy density \( u \left( \left\{ n^{(s)} \right\}, \mathbf{u}, s \right) \).
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crystal of several species. By comparison with fluid thermodynamics [CL10, sec. 3.1] one finds

\[ f - \sum_s n_0^{(s)} \mu^{(s)} = -p, \]

covering the isotropic contribution to the stress tensor found in liquid thermodynamics. Consequently, \( \mathbf{h} \) characterizes the lattice specific contribution to stress not present in a liquid. To conclude, changes in \( \mathbf{\sigma} \) compared to a reference state \( \mathbf{\sigma}_0 \) are given by

\[ \delta \mathbf{\sigma} = -\delta p \mathbf{1} + d\mathbf{h} = - \left( s dP + \sum_s n_0^{(s)} d\mu^{(s)} \right) \mathbf{1} + d\mathbf{h}. \]  \hfill (3.50)

Considerations in this thesis are limited to isothermal fluctuations, such that the temperature \( T \) is treated as a constant rather than as a natural variable. In order to close the isothermal e.o.m. (3.43), \( \delta \mathbf{\sigma} \) now needs to be expressed in terms of \( \mathbf{u} \) and the \( \{ \delta n^{(s)} \} \). This is achieved from the definitions (3.48) and an expansion of the phenomenological \( f \) about the zero-strain equilibrium-state. For ease of presentation, we will initially state the general \( B \)-species expression but then restrict discussion to the binary case. There, the most general quadratic form with the scalar transformation properties required for \( f \) reads

\[ \delta f \left( \{ \delta n^{(s)} \}, u_{\alpha\beta} \right) := f \left( \{ n^{(s)} + \delta n^{(s)} \}, u_{\alpha\beta} \right) - f \left( \{ n^{(s)} \}, u_{\alpha\beta} = 0 \right) - \sum_B \mu^{(s)} \delta n^{(s)} \]

\[ = \frac{1}{2} \sum_{a,b=1}^B A^{(ab)} \frac{\delta n^{(a)}}{n_0^{(a)}} \frac{\delta n^{(b)}}{n_0^{(b)}} + \frac{1}{2} K_{\alpha\beta\gamma\delta} n_0^{(s)} u_{\alpha\beta} u_{\gamma\delta} + \sum_B D^{(s)} \frac{\delta n^{(s)}}{n_0^{(s)}}. \]  \hfill (3.51a)

The transition from density fluctuations \( \delta n^{(s)} \) to defect density fluctuations via \( \delta n^{(s)} = -n_0^{(s)} u_{\alpha\alpha} - \delta \mathbf{c}^{(s)} \) (the thermodynamic analogue of eq. (3.45)) yields

\[ \delta f \left( \{ \delta \mathbf{c}^{(s)} \}, u_{\alpha\beta} \right) = \frac{1}{2} \left[ A^{(1)} \left( \frac{\delta \mathbf{c}^{(1)}}{n_0^{(1)}} \right)^2 + 2A^{(\times)} \frac{\delta \mathbf{c}^{(1)}}{n_0^{(1)}} \frac{\delta \mathbf{c}^{(2)}}{n_0^{(2)}} + A^{(2)} \left( \frac{\delta \mathbf{c}^{(2)}}{n_0^{(2)}} \right)^2 \right] + \frac{1}{2} K_{\alpha\beta\gamma\delta} n_0^{(s)} u_{\alpha\beta} u_{\gamma\delta} + \sum_{s=1}^2 D^{(s)} \frac{\delta n^{(s)}}{n_0^{(s)}} \]  \hfill (3.51b)
The phenomenological parameters of these expansions are defined as

\[ A^{(x)} = \left. \frac{\partial^2 f}{\partial n^{(1)} \partial n^{(2)}} \right|_{u_{\alpha\beta}} \quad A^{(s)} = \left. \frac{\partial \mu^{(s)}}{\partial n^{(s)}} \right|_{n^{(s)}}, \quad B^{(s)} = \left. \frac{\partial h^{(s)}}{\partial n^{(s)}} \right|_{n^{(s)}}, \quad \sigma^{(s)} = \left. \frac{\partial D^{(s)}}{\partial n^{(s)}} \right|_{n^{(s)}} \]

(3.52a)

\[ K^{(1)}_{\alpha\beta\gamma\delta} = \frac{\partial^2 f}{\partial u_{\alpha\beta} \partial u_{\gamma\delta}} \left|_{n^{(s)}} \right. \quad K^{(2)}_{\alpha\beta\gamma\delta} = \frac{\partial^2 f}{\partial n^{(1)} \partial n^{(2)}} \left|_{n^{(s)}} \right. \]

(3.52b)

\[ D^{(s)} = \frac{1}{3} \left. \frac{\partial h^{(s)}}{\partial n^{(s)}} \right|_{n^{(s)}}, \quad \sigma^{(s)} = \left. \frac{\partial D^{(s)}}{\partial n^{(s)}} \right|_{n^{(s)}} \]

(3.52c)

\[ K^{(n)}_{\alpha\beta\gamma\delta} = K^{(n)}_{\alpha\beta\gamma\delta} = K^{(n)}_{\alpha\beta\gamma\delta} \]

We now obtain by inserting the expansion (3.51a) into the definitions eq. (3.48)

\[ \delta \mu^{(1/2)} = A^{(1/2)} \frac{\delta n^{(1/2)}}{n^{(1/2)}} + A^{(x)} \frac{\delta n^{(2/1)}}{n^{(1)}} + \frac{D^{(1/2)}}{n^{(1/2)}} u_{\alpha\beta}, \]

\[ \delta h_{\alpha\beta} = K^{(1)}_{\alpha\beta\gamma\delta} u_{\gamma\delta} + \sum_s D^{(s)} \frac{\delta n^{(s)}}{n^{(s)}} \delta_{\alpha\beta}. \]

And finally with eq. (3.50)

\[ \Rightarrow \delta \sigma_{\alpha\beta} = -2 \sum_{s=1}^2 \left( A^{(s)} + A^{(x)} \right) \frac{\delta n^{(s)}}{n^{(s)}} \delta_{\alpha\beta} + \frac{D^{(s)}}{n^{(s)}} \left( n^{(s)} u_{\gamma\delta} - \delta n^{(s)} \right) \delta_{\alpha\beta} + K^{(n)}_{\alpha\beta\gamma\delta} u_{\gamma\delta} \]

(3.53a)

\[ = 2 \sum_{s=1}^2 \left[ A^{(s)} + A^{(x)} - D^{(s)} \right] \frac{\delta c^{(s)}}{n^{(s)}} \delta_{\alpha\beta} + K^{(c)}_{\alpha\beta\gamma\delta} u_{\gamma\delta}. \]

(3.53b)

### 3.3.3. Plane-wave modes in crystals

For the identification of elastic constants in the method of long waves we need to know how the long-wavelength limit of acoustic phonons can be obtained from the
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e.o.m. (3.43): Taking the time derivative of eq. (3.43c) and inserting both eq. (3.43b) and eq. (3.53b) yields with the reversible e.o.m. (3.44)

\[
\frac{\partial^2}{\partial t^2} u_\alpha (k, t) = \frac{i}{\varrho_0} k_\beta \cdot \delta \tilde{\tilde{\sigma}}_{\beta \alpha} (k, t) = \frac{i}{\varrho_0} k_\beta \cdot \delta \tilde{\sigma}_{\alpha \beta} (k, t) ,
\]

\[
= \frac{i}{\varrho_0} k_\beta \left[ K^c_{\alpha \beta \gamma \delta} u_{\gamma \delta} (k, t) + \delta_{\alpha \beta} \sum_s B^{(s)} \frac{\delta \varepsilon^{(s)}}{n_0^{(s)}} (k, t) \right]
\]

\[
= -\frac{1}{\varrho_0} K^c_{\alpha \beta \gamma \delta} k_\beta k_\gamma u_\delta (k, t) + \frac{i}{\varrho_0} k_\alpha \sum_s B^{(s)} \frac{\delta \varepsilon^{(s)}}{n_0^{(s)}} (k, t) .
\] (3.54a)

Applying a further time derivative to eq. (3.54a) yields with eq. (3.43c) a wave equation for \( \tilde{\tilde{j}} \)

\[
\frac{\partial^2}{\partial t^2} \tilde{\tilde{j}}_\alpha (k, t) = -\frac{1}{\varrho_0} K^c_{\alpha \beta \gamma \delta} k_\beta k_\gamma \tilde{\tilde{j}}_\delta (k, t)
\] (3.54b)

which is easily shown to have acoustic plane-wave solutions with eigenfrequencies \( \lim_{k \to 0} \omega_\sigma (k) = 0 \). Note that a homogeneous wave equation (3.54a) for \( u \) is obtained only for \( \delta \varepsilon^{(s)} \equiv 0 \).

For periodic crystals with more than a single particle per primitive unit cell, there are plane-wave solutions whose eigenfrequency remains finite in the infinite-wavelength limit. A central objective of this thesis is the extension of the equations of motion in [WF10, eqs. 25] such that they yield these optical phonon modes within a statistical-mechanics approach. From the phenomenological perspective this requires a reformulation of the eqs. (3.43), taking into account specific irreversible currents. Bear in mind that this step is ad-hoc in the sense that the hydrodynamic time-scale separation does not apply to optical phonons: Their decay is mediated by microscopic processes (collisions) within the mean free-path. Thus their life time remains of the same order as the average collision time also in the infinite-wavelength limit.

Binary crystals offer a variety of well-known model systems, and for simplicity our basic considerations will be restricted to that special case. We assume a periodic crystal of particle species \( s = 1, 2 \) with masses \( m^{(s)} \) and particle densities \( \varrho_0^{(s)} = m^{(s)} n_0^{(s)} \). Analogous to eqs. (3.36) to (3.38) we introduce species-wise quantities \( n^{(s)} \), \( n_g^{(s)} \) and \( u^{(s)} \) via

\[
\tilde{n} (r) = \sum_g \tilde{n}_g e^{ig r} = \sum_{s=1}^{2} \tilde{n}^{(s)} (r)
\] (3.55)

with \( \tilde{n}^{(s)} (r) = \sum_g \tilde{n}_g^{(s)} e^{ig r} \).

Discussion of the optical-mode solution at infinite wavelength within the potential-expansion method shows an opposite movement of both species such that the center of mass of the system is at rest. We conclude that for an ad-hoc hydrodynamic
description of optical phonons — on microscopic time scales — the local rest frame needs not be the same for both species. Then eq. (3.39) generalizes to
\[ \frac{\partial \mathbf{u}^{(s)}}{\partial t} (\mathbf{r}, t) = \mathbf{v}^{(s)} (\mathbf{r}, t) \approx \frac{1}{\varrho_0^{(s)}} \mathbf{j}^{(s)} (\mathbf{r}, t) . \] (3.56)

With the same reasoning eq. (3.40) keeps its originally species-wise formulation,
\[ \frac{\partial}{\partial t} \tilde{\mathbf{v}}^{(s)} (\mathbf{r}, t) = -i \mathbf{\nabla} \cdot \mathbf{j}^{(s)} (\mathbf{r}, t) . \] (3.40)

From the requirement that eq. (3.43c) still holds, we infer a relation between \( \mathbf{u} \) and the \( \mathbf{u}^{(s)} \)
\[ \mathbf{u} (\mathbf{r}, t) = \sum_{s=1}^{B} \frac{\varrho_0^{(s)}}{\varrho_0} \mathbf{u}^{(s)} (\mathbf{r}, t) \] (3.57)
so that \( \mathbf{u} \) can be read as a center-of-mass displacement field. The transformation to absolute and relative displacement fields is completed with
\[ \mathbf{b} (\mathbf{r}, t) := \frac{1}{\varrho_0} \left[ \frac{\varrho_0^{(1)}}{\varrho_0} + \frac{\varrho_0^{(2)}}{\varrho_0} \right] \left[ \mathbf{u}^{(1)} (\mathbf{r}, t) - \mathbf{u}^{(2)} (\mathbf{r}, t) \right], \] \( \mathbf{r} \) “sufficiently far inside sample”.

One factor \( \varrho_0 \) was written out to highlight the resemblance of the remaining fraction to a reduced mass density and, more generally, of the discussion to that of a two-body problem. The invariance w.r.t. homogeneous translations and rotations which motivated the definition of the symmetrized strain tensor \( \mathbf{u} \) does not hold for relative homogeneous movements of the two species. This explains why the “optical strain” \( \mathbf{b} \) is in leading spatial order defined as constant vector. With the explicit consideration of this purely microscopic\(^{14} \) quantity, the total differential (3.47a) generalizes to
\[ df \rightarrow df' = \sum_{s=1}^{B} \mu^{(s)} d\mu^{(s)} + \kappa_{\alpha\beta} d\mu_{\alpha\beta} - s' dT + s_d d\varrho_a \]
with the “optical stress” \( s_a = \frac{\partial f}{\partial \varrho_a} \bigg|_{u, \{x^{(s)}\}, T, b} \).

Quantities redefined within this ad-hoc approach will be marked by a prime for the remainder of this section. It is of central importance for later discussion to note that the inclusion of \( \mathbf{b} \) into the free energy density \( f \) requires to add an additional constraint also to the definition of the stress tensor \( \sigma \),
\[ \sigma \rightarrow \sigma' = n_0 \frac{d (f / n)}{d \mathbf{u}} \bigg|_{\{x^{(s)}\}, T, b} . \]

\(^{14} \)Within a theory of elasticity treating a sample as a continuous distribution of matter there is no clear picture of “relative displacement” — maybe not even for a binary system in general.
The same applies to \( h' \) and the \( \mu^{(s)'} \) from eq. (3.48). The expansion (3.51a) in turn needs to be extended by two coupling terms

\[
\delta f' \left( \delta n^{(1)}, \delta n^{(2)}, u_{\alpha\beta}, \delta b \right) = \delta f \left( \delta n^{(1)}, \delta n^{(2)}, u_{\alpha\beta} \right) + X_{\alpha\beta\gamma} u_{\alpha\beta} \delta b_{\gamma} + Y_{\alpha\beta} \delta b_{\alpha} \delta b_{\beta} \quad (3.58)
\]

with

\[
X_{\alpha\beta\gamma} = \frac{\partial h_{\alpha\beta}}{\partial \gamma} \bigg|_{\{n^{(r)}\}_{u_{\alpha\beta}}}, \quad Y_{\alpha\beta} = \frac{\partial f}{\partial \delta b_{\alpha} \delta b_{\beta}} \bigg|_{\{n^{(r)}\}_{u_{\alpha\beta}}}
\]

Additional couplings to \( b \) from the scalar (defect) density fluctuations are ruled out by symmetry. Moreover, in crystals with a center of inversion, i.e. a point \( r_0 \in \mathbb{R}^d \) with \( n^{(s)} (\cdot) \equiv n^{(s)} (2r_0 - \cdot) \ \forall s \in \{1, 2, \ldots, B\}, \ X \) vanishes for symmetry reasons.

The expansion (3.53) of the stress tensor generalizes to

\[
\delta \sigma_{\alpha\beta} = \delta \sigma'_{\alpha\beta} + X_{\alpha\beta\gamma} \delta b_{\gamma} \quad (3.59)
\]

which yields an additional coupling in the generalized e.o.m. (3.43b)

\[
\frac{\partial}{\partial t} \tilde{j}_{\alpha} (k, t) = i k_{\beta} \left[ \delta \sigma'_{\alpha\beta} (k, t) + X_{\alpha\beta\gamma} \delta b_{\gamma} (k, t) \right] . \quad (3.60a)
\]

The additional optical e.o.m. is obtained by expressing the optical stress \( s \) in terms of the generalized expansion (3.58),

\[
\frac{\partial}{\partial t} \varrho_0 \delta b_{\alpha} (k, t) = Y_{\alpha\beta} \delta b_{\beta} (k, t) + X_{\alpha\gamma\alpha} u_{\beta\gamma} (k, t) \ . \quad (3.60b)
\]

In order to treat common and relative movement of both species on equal footing we introduce a weighted relative momentum density

\[
\Delta \tilde{j}_{\alpha} (k, t) := \frac{1}{\varrho_0} \left[ \varrho_0^{(2)} \tilde{j}_{\alpha}^{(1)} (k, t) - \varrho_0^{(1)} \tilde{j}_{\alpha}^{(2)} (k, t) \right] \quad (3.56)
\]

\[
\Rightarrow \frac{\partial}{\partial t} \Delta \tilde{j}_{\alpha} (k, t) = \frac{1}{\varrho_0} \left[ Y_{\alpha\beta} \Delta \tilde{j}_{\beta} (k, t) + i X_{\alpha\gamma\alpha} k_{\beta} \tilde{j}_{\gamma} (k, t) \right] \quad (3.60c)
\]

and examine to what extent the form of the wave equation (3.54b) is recovered from the eqs. (3.60). Mutual substitution together with the expression (3.59) for \( \delta \sigma' \) yields up to \( \mathcal{O} (k^2) \)

\[
\frac{\partial^2}{\partial t^2} \left( \frac{\tilde{j}_{\alpha}}{\Delta \tilde{j}_{\alpha}} \right) (k, t) = \frac{1}{\varrho_0} \begin{pmatrix}
-K_{\alpha\beta\gamma\delta} k_{\delta} k_{\beta} & i \varrho_0 X_{\alpha\beta\gamma} k_{\beta} \\
 i Y_{\alpha\beta} X_{\gamma\delta\beta} k_{\delta} & Y_{\alpha\beta} Y_{\beta\gamma} + X_{\beta\alpha} X_{\delta\gamma} k_{\delta} k_{\beta}
\end{pmatrix} \left( \frac{\tilde{j}_{\gamma}}{\Delta \tilde{j}_{\gamma}} \right) (k, t) . \quad (3.61)
\]

As will be shown in a similar analysis in paragraph 5.3.2 (cf. eq. (5.31)), eq. (3.61) ensures the existence of acoustic phonon modes. The nontrivial part both there and here is the occurrence of relevant couplings between total and relative momentum density. We will not go into the approximate diagonalization of eq. (3.61) which
presumably could be transferred from appendix C. However, as will be illustrated in paragraph 8.2, note that the elastic coefficients obtained with the coupling terms suppressed,

\[ K_{\alpha\beta\gamma\delta}^{c} = \frac{\partial f}{\partial u_{\alpha\beta} \partial u_{\gamma\delta}} \{ c(\alpha) \}, b \]

will in general lie above, i.e. be “harder than” the conventional phenomenological coefficients from eq. (3.52b). With this, a supposed contradiction of eq. (3.61) to Fleming and Cohen’s phenomenological wave equation [FC76, eq. (4.10)] can be resolved, provided that the acoustic eigenvectors of eq. (3.61) differ from the total momentum \( \hat{\mathbf{j}} \) only by terms of \( O(k) \).

What is more: Only by employing the correct physical elastic constants rather than \( K_{\alpha\beta\gamma\delta}^{n} / c \) can the total momentum density \( \hat{\mathbf{j}} \) be assumed the acoustic eigenvector — correct up to \( O(q^0) \). The conceptual difference between Fleming and Cohen’s elastic coefficients \( C \) respectively \( K_{\alpha\beta\gamma\delta}^{n} / c \) and the ad-hoc tensor \( K_{\alpha\beta\gamma\delta}^{c} \) is the explicit consideration of a microscopic non-hydrodynamic quantity for the latter. All couplings to such quantities are included in the unprimed coefficients by the assumption of instantaneous relaxation to their equilibrium value at (infinitesimal) external strain. The internal strain variable \( b \) is only an example for such a quantity which can be identified with the basis vector in a binary Bravais lattice. It does however have the unique feature to persist even in the potential expansion ansatz as the only microscopic parameter needed to characterize the equilibrium density of a given Bravais lattice.

A self-consistent version of eq. (3.61) would have to be extended to include an additional current for every independent parameter involved in the description of the equilibrium densities \( n^{(s)} \).\textsuperscript{15} Chapter 5 will consider the reversible, isothermal hydrodynamic e.o.m. within the Zwanzig–Mori approach, again with special consideration of relative — “optical” — dynamics of different species.

\textsuperscript{15}Generically, this is an infinite set of currents isomorphic to the set of all order parameters \( \{ n^{(s)} \} \).

As described in paragraph 3.3.3, elastic constants can be obtained from the eigenvalues of the wave equation in the long-wavelength limit $q \to 0$. This identification is based on the expansion (3.51) of the (Helmholtz) free energy $f$ density in terms of the linear strain $u_{\alpha\beta}$. The linear strain in turn is related to the displacement field $u$ in the hydrodynamic limit (cf. paragraph 3.3.2). At the same time paragraph 3.3.2 itself forms a self-contained, static approach to crystal elasticity. On top of statistical mechanics, the following two chapters 5 and 6 will use Density Functional Theory to derive expressions for the elastic constants in the dynamic respectively static approach. This means that both will more or less explicitly make use of an expression for the free energy in terms of the equilibrium densities,

$$ F \equiv F \left[ \{ n^{(s)}(r) \} \right]. $$

This proceeding is based on a theorem proven by Hohenberg and Kohn [HK64] and generalized to finite temperature by Mermin [Mer65]. It is reviewed in a classical context by [Eva79] from where we now recapitulate its central aspects.

For a given many-body Hamiltonian $H$ and external potentials $\{ \Psi^{(s)} \}$ the theorem states the existence of a unique functional $\tilde{\Omega}[\{ \eta^{(s)} \}]$ whose global minimum equals the grand potential $\Omega$ and is assumed for the equilibrium densities $\{ n^{(s)} \}$,

$$ \min_{\eta^{(s)}} \tilde{\Omega} \left[ \{ \eta^{(s)} \} \right] = \tilde{\Omega} \left[ \{ n^{(s)} \} \right] = \Omega. \quad (4.1) $$

That functional is given by

$$ \tilde{\Omega} \left[ \{ \eta^{(s)} \} \right] = \sum_s \int d^d r \, n^{(s)}(r) \, \Psi^{(s)}(r) + \tilde{F} \left[ \{ \eta^{(s)} \} \right] - \sum_s \mu^{(s)} \int d^d r \, \eta^{(s)}(r). \quad (4.2) $$

We will henceforth assume vanishing external potentials $\Psi^{(s)} \equiv 0$. Now the functional $\tilde{F}$ can be related to the free energy $F$. Namely, eq. (4.2) at equilibrium takes the form of a Legendre transform with $\tilde{F} \left[ \{ \eta^{(s)} = n^{(s)} \} \right] = F$. From eq. (4.2), the minimization of $\tilde{\Omega}$ is equivalent to the minimization of $\tilde{F}$ under the constraint of constant total particle numbers $\{ N^{(s)} \}$. The Lagrange multipliers are the chemical potentials $\mu^{(s)}$ which follow from (cf. eq. (3.48))

$$ \frac{\delta F}{\delta n^{(s)}(r)} = \mu^{(s)}. \quad (4.3) $$
Chapter 4 Framework of Density Functional Theory

Following [Eva79, §3], the functional \( \tilde{F} \) can be further exploited to characterize the particle interactions at equilibrium by a “hierarchy” of functional derivatives:

\[
C^{(s_1...s_r)} \left( \mathbf{r}_1, \ldots, \mathbf{r}_\ell; \{ n^{(s)} \} \right) = \beta \frac{\delta^r \tilde{F} \left[ \{ n^{(s)} \} \right]}{\delta n^{(s_1)} (\mathbf{r}_1) \ldots \delta n^{(s_\ell)} (\mathbf{r}_\ell)}
\]  \hspace{1cm} (4.4)

is the \( r \)-th order functional derivative of the free energy functional\(^1\) \( \tilde{F} \) at the particle densities \( \{ n^{(s)} \} \).\(^2\) As a convention, we will omit the densities argument if evaluated at equilibrium \( \{ n^{(s)} = n^{(s)} \} \). It is then convenient to decompose \( F \) into its — non-interacting and well-known — ideal-gas contribution and an excess part due to particle interactions, \( F = F_{\text{ideal gas}} + F_{\text{ex}} \). The former is given by

\[
F_{\text{ideal gas}} \left[ \{ n^{(s)} \} \right] = k_B T \sum_{s=1}^B \int d^d r n^{(s)} (\mathbf{r}) \left\{ \ln \left[ n^{(s)} (\mathbf{r}) \right] \frac{\lambda_s^3}{3} - 1 \right\},
\]  \hspace{1cm} (4.5)

the latter yields the “\( r \)-th order direct correlation functions” \( c^{(s_1...s_r)} \) from eq. (4.4) with a minus sign by convention,

\[
c^{(s_1...s_r)} \left( \mathbf{r}_1, \ldots, \mathbf{r}_\ell; \{ n^{(s)} \} \right) = -\beta \frac{\delta^r F_{\text{ex}} \left[ \{ n^{(s)} \} \right]}{\delta n^{(s_1)} (\mathbf{r}_1) \ldots \delta n^{(s_\ell)} (\mathbf{r}_\ell)}.
\]  \hspace{1cm} (4.6)

Similar to the second spatial derivative of the pair potential \( \Phi \) in the potential expansion approach (cf. eq. (1.1)), the second functional derivative \( C^{(ab)} \) will be crucial for small deviations from the thermodynamic equilibrium state. Understood as a \( B \times B \)-matrix, \( C^{(ab)} \) is symmetric in the species indices by construction and diagonal in its ideal gas part because ideal-gas particles do not interact,

\[
C^{(ab)} (\mathbf{r}, \mathbf{r}') = C^{(ba)} (\mathbf{r}', \mathbf{r}) = \delta_{ab} \frac{\delta (\mathbf{r} - \mathbf{r}')}{n^{(a)} (\mathbf{r})} - c^{(ab)} (\mathbf{r}, \mathbf{r}')
\]  \hspace{1cm} (4.7)

with \( \mathbf{r} - \mathbf{r}' =: \Delta \mathbf{r} \). The central objective of Density Functional Theory (DFT) is to work out accurate approximations to the unknown density functional \( \tilde{F} \). It finds broad applications within quantum mechanical descriptions for materials science. An early approach of classical DFT to liquid-crystal phase transitions will be used in section 7.1.

---

\(^1\) We will drop the distinction between \( \tilde{F} \) and \( F \) as well as \( \eta \) and \( n \) for ease of notation. Bear in mind that exact physical statements follow from \( \tilde{F} \) only at the true equilibrium densities \( \{ n^{(s)} \} \).

\(^2\) For a brief introduction into use of functional derivatives see [ED11, appendix A] or [GR96, section 2.3].
Part II.

Evaluation for Periodic crystals
5. Equations of motion

While the phenomenological field theory of hydrodynamics from section 3.3 deliberately neglects the microscopic constituents of a flowing medium, the Zwanzig–Mori formalism (section 3.2) takes as its starting point the complete microscopic dynamics. Much of the following will be in parallel with the discussion in [WF10] for the case of single-component crystals. Solution of the e.o.m. (1.2) of the potential-expansion method leads to optical optical phonons in non-primitive crystals. Unless stated otherwise, we will assume that each particle in the basis belongs to a distinct particle species. This facilitates the approach by enabling one to introduce microscopic quantities in a species-wise fashion. The agenda is, in principle, straightforward: We identify the dynamical variables in the next section, derive the generalized Zwanzig–Mori e.o.m. and the dynamical block matrix $\Lambda$ in section 5.2 and discuss its properties in section 5.3. An ansatz to obtain optical phonons for single-species non-primitive crystals like diamond is pointed out in section 8.1.

5.1. Identification of hydrodynamic variables

We recall the definitions from section 3.3 for species $s = 1, 2, \ldots, B$:

- microscopic particle densities $\rho^{(s)}(r, t) = \sum_{i=1}^{N^{(s)}} \delta \left( \mathbf{r}^{(s)}_i(t) - \mathbf{r} \right)$,
- average particle densities $n^{(s)}(r) = \langle \rho^{(s)}(r, t) \rangle_{\text{can.}} = \sum_{g \in G} n^{(s)}_g e^{ig \cdot r}$, with $n^{(s)}_k = \frac{1}{V} \langle \rho^{(s)}(k) \rangle$, (5.1)
- and microscopic momentum densities $j^{(s)}(r, t) = \sum_i p^{(s)}_i(t) \delta \left( \mathbf{r} - \mathbf{r}^{(s)}_i(t) \right)$.

The total particle and momentum density $\rho$ and $j$ are defined as $\rho = \sum_{s=1}^{B} \rho^{(s)}$ and $j = \sum_{s=1}^{B} j^{(s)}$ respectively. As in phenomenological hydrodynamics, the dynamics is determined by deviations from the equilibrium densities. We write $\rho^{(s)}(r, t) - n^{(s)}(r) =: \delta \rho^{(s)}(r, t)$ and $\delta \rho$ accordingly.\footnote{Note this exception from the significance of the $\delta$-notation for linear response averages introduced in section 3.1.} In a periodic crystal, all species share a
single Bravais lattice \( L \), generically shifted w.r.t. a common origin by basis vectors \( b^{(s)} \). [WF10, eqs. (7) and (8)] can thus be put species-wise,

\[
\rho^{(s)}(r, t) = \sum_g \int_{1^{*}\text{BZ}} \frac{d^3q}{(2\pi)^d} e^{i(q \cdot r)} \rho^{(s)}_g(q, t) \quad \text{with} \quad \rho^{(s)}_g(q, t) := \rho^{(s)}(g + q, t) .
\]

\( \delta \rho^{(s)}(q, t) = \rho^{(s)}_g(q, t) - n^{(s)}(g + q) \) is introduced accordingly. With the Liouville operator \( \mathcal{L} = -i\partial_t \), [WF10, eq. (17)] generalizes to

\[
\mathcal{L} \delta \rho^{(s)}(g + q, t) = -i\partial_t \rho^{(s)}_g(q, t) = - \frac{(g + q)}{m^{(s)}} \cdot j^{(s)}(g + q, t) \quad (5.2)
\]

The Bogoliubov inequality [WF10, eq. (13)] is rewritten in species-wise manner for the (particle) density fluctuations \( \delta \rho^{(s)} \) while maintaining the projection on the total momentum \( j \),

\[
\left\langle \left| \delta \rho^{(s)}_g(q) \right|^2 \right\rangle \geq \left| \frac{\left\langle j^{(s)}_a(k) \mathcal{L} \delta \rho^{(s)}_g(q) \right\rangle}{\left\langle \mathcal{L} j^{(s)}_a(k) \right\rangle^2} \right|^2 . \quad (5.3)
\]

The equipartition theorem [WF10, eq. (15)] becomes

\[
\left\langle [\pi^{(a)}_i, \pi^{(b)}_j] \right\rangle = m^{(a)} k_B T \delta_{ij} \delta_{ab} \mathbb{1}_d . \quad (5.4)
\]

M. Fuchs pointed out\(^2\) that — besides for \( k = k' \) — the momentum-momentum correlations \( \left\langle j^{(a)*}_a(k) j^{(b)}_{k'}(k') \right\rangle \) also do not vanish for \( k - k' \in G \). Together with eq. (5.4), [WF10, eq. (17)] is consequently generalized to

\[
\left\langle j^{(a)*}_a(k = g + q) j^{(b)}(k' = g' + q') \right\rangle = \delta_{ab} \left\langle \sum_{i=1}^{N^{(a)}} p^{(a)}_i p^{(a)}_i e^{i(k - k')} \right\rangle
\]

\[
= m^{(a)} V k_B T n^{(a)}_{g - k} \delta_{q, q'} \delta_{ab} \mathbb{1}_d
\]

\[
= m^{(a)} V k_B T n^{(a)}_{g - q} \delta_{q, q'} \delta_{ab} \mathbb{1}_d \quad (5.5)
\]

The rewriting of the two arguments \( k, k' \) is based on the decomposition into a reciprocal lattice vector \( g, g' \) and a vector from the first Brillouin zone \( q, q' \). The letter \( q \) will henceforth be reserved to vectors from the first BZ. Note this is possible only for periodic crystals where it will strongly simplify the long-wavelength limit, restricting \( k \) and \( k' \) to the first Brillouin zone. With eqs. (5.5) and (5.2), the numerator of the Bogoliubov inequality (5.3) becomes

\[
\left| \left\langle j^{(a)*}_a(k) \mathcal{L} \delta \rho^{(s)}_g(q) \right\rangle \right|^2 = \frac{(g + q)_\beta}{m^{(s)}} \left| \left\langle j^{(a)*}_a(k) \right. \right. \left. \left. j^{(s)}_{\beta}(g + q, t) \right\rangle \right|^2
\]

\[
= |(g + q)_\alpha V k_B T|^2 \left| n^{(s)}_{g + q - k} \right|^2 .
\]

\(^2\)unpublished notes, March 2016
5.2 Formulation of the equations of motion

The denominator is simplified like [WF10, eq. (19)] with the microscopic continuity equation (3.27) and the simplification of isotropic stress-stress correlations $R > 0$,

$$\langle |L_{j\alpha}(k)|^2 \rangle \sim Rk^2.$$  

$k$ can be chosen such that $g + q = G + k$ with an arbitrary $G \in G$ so that we finally obtain the analogue of [WF10, eq. (21)] for multiple species:

$$\langle \delta \rho_{G}^{(s)}(k) \rangle \geq \frac{(G + k)^2 (V k_B T)^2 |\nu_{G}^{(s)}|^2}{Rk^2}$$  

which yields a divergence in the limit $k \to 0$ for each $G \in G \setminus \{0\}$ and $s = 1, 2, \ldots, B$. Consequently, the whole of the linear response density fluctuations $\langle \delta \rho_{G}^{(s)} \rangle_{\text{lin. resp.}}$ enters the set of long-range correlated and therefore hydrodynamic variables.

5.2. Formulation of the equations of motion

Having identified hydrodynamic variables on the microscopic level, we can now proceed towards a generalization of the Zwanzig–Mori equations of motion (e.o.m.) to several species. It is important to see how the concepts of linear response (cf. sec. 3.1) and the projection operator/Zwanzig–Mori formalism (sec. 3.2) can be combined to obtain the e.o.m. for small and slow deviations from equilibrium of the dynamical variables $\{A_i(r, t)\}$. Small induced macroscopic fluctuations of the latter have been related to their correlation functions $\Delta A_i(r, t) \Delta A_j(r', t')$ by eq. (3.8). The e.o.m. for microscopic correlation functions $\langle A_i^\ast(r, t) A_j(r', t') \rangle$ is given by eq. (3.14). Onsager’s regression hypothesis states that the correlation functions in both situations are governed by the same dynamics. Taking the time derivative of eq. (3.8) and inserting eq. (3.14) yields

$$\frac{\partial}{\partial t} \delta A_i^\ast(k, t) = - \sum_j \int d^d k' \left( i \Omega_{ij} \left(k, k'\right) \delta A_j^\ast \left(k', t\right) + \int_0^t dt' \Gamma_{ij} \left(k, k', t - t'\right) \delta A_j^\ast \left(k', t'\right) \right)$$  

$$\frac{\partial}{\partial t} \delta A_i^\ast(k, t) = - \sum_j \int d^d k' \left( i \Omega_{ij} \left(k, k'\right) \delta A_j^\ast \left(k', t\right) + \int_0^t dt' \Gamma_{ij} \left(k, k', t - t'\right) \delta A_j^\ast \left(k', t'\right) \right)$$  

$$\Omega_{ij} \left(k, k'\right) = \sum_h \int d^d k'' \frac{\langle A_i^\ast(k) L A_h \left(k''\right) \rangle}{\langle A_h^\ast \left(k''\right) A_j \left(k'\right) \rangle},$$  

with

$$\Gamma_{ij} \left(k, k', t\right) = \sum_h \int d^d k'' \frac{\langle A_i^\ast(k) L Q e^{-iQ \cdot \xi} Q L A_h \left(k''\right) \rangle}{\langle A_h^\ast \left(k''\right) A_j \left(k'\right) \rangle}.$$  

These expressions will be simplified for periodic crystals: The arguments $k, k'$ can be decomposed like in eq. (5.5) and in the long-wavelength limit be restricted to the
first BZ (the reciprocal space integrals in eqs. (5.7) and (5.8) are then also integrals over the first BZ). Hydrodynamics additionally requires the projected set \( \{ \delta \mathbf{A}_i \} \) to contain all variables showing slow dynamics. In previous works \cite{SE93, WF10} it has been argued that a frequency matrix \( \Omega \) constructed that way will describe the full reversible dynamics in the long-wavelength limit \( \mathbf{k} \rightarrow \mathbf{0} \), i.e. the purely dissipative memory matrix \( \mathbf{\Gamma} \) can be neglected. We will adopt this statement as a working hypothesis and comment on potential exceptions in section A.1.

**Working hypothesis 1:** In the long-wavelength limit \( \mathbf{k} \rightarrow \mathbf{0} \), no reversible contributions are contained in the memory matrix \( \mathbf{\Gamma} \) if the Zwanzig–Mori formalism is applied to crystals with the exact full set of hydrodynamic variables (none missing and none dispensable).

An aspect peculiar to this thesis still is that the description of optical phonons requires the inclusion of non-hydrodynamic variables into the set of projected ones. As a second working hypothesis, we extend the convenient decomposition into a reversible frequency matrix \( \Omega \) and a dissipative memory matrix \( \mathbf{\Gamma} \) to this non-generic application of the Zwanzig–Mori formalism.

**Working hypothesis 2:** The Working hypothesis 1 holds also for projectors which contain additional non-slow variables beyond the full hydrodynamic set.

A physical argument is used in appendix A to underpin Working hypothesis 2. An outlook to the findings of this chapter may serve to understand the motivation behind the formulation of these working hypotheses: The frequency matrix obtained in the following, defined from a set including a non-hydrodynamic relative momentum density \( \Delta \mathbf{j} \), will yield couplings between \( \Delta \mathbf{j} \) and the total momentum density \( \delta \mathbf{j} \) which are relevant to the hydrodynamic limit. This means that the proper hydrodynamic Zwanzig–Mori formalism — based on Working hypothesis 1 — yields other results than the non-generic one employed in the following. Provided that Working hypothesis 2 is true, both approaches should yield the same reversible dynamics in the hydrodynamic limit. This contradiction can then only be resolved if either Working hypothesis 1 or its assumptions are false (for binary periodic crystals).

Provided the validity of the announced physical argument, this justifies Working hypothesis 2 and lets us return to the equations of motion with greater confidence. The set \( \mathbf{A} \) of dynamical variables consists of the momentum densities \( \{ \mathbf{j}^{(s)} \} \) and the order parameters \( \{ \delta \rho_g^{(s)} \} \) of each species. The symmetry-restoring variables identified in section 5.1 are fully contained. So are the conserved particle densities \( \{ \delta \rho_g^{(s)} \}_{\mathbf{g}=\mathbf{0}} \) and the total momentum \( \mathbf{j} = \sum_s \mathbf{j}^{(s)} \). We introduce the notation \( \delta \mu_g^{(s)} = \langle \delta \rho_g^{(s)} \rangle_{\text{lin. resp.}} \) to distinguish the expectation value of the small induced macroscopic fluctuation from the microscopic density fluctuations \( \delta \rho_g^{(s)} \). With the scope of this thesis in mind, we omit the superscript “lin. resp.” from all expectation values “\( \langle \cdot \rangle_{\text{lin. resp.}} \)” in the following. Considering only the frequency matrix \( \Omega \), we obtain from eqs. (5.7) and (5.8):
5.2 Formulation of the equations of motion

\[
\frac{\partial}{\partial t} \delta n^{(s)}_{g}(\mathbf{q}, t) = i \sum_{s', s''} \int d^d k' d^d k'' \left( \frac{\langle \delta \rho^{(s')}_{g} (\mathbf{q}) \mathcal{L}_{j^{(s')}_{\alpha}} (k') \rangle}{\langle j^{(s')}_{\alpha} (k') \rangle} \right)^{*} \delta j^{(s'')}_{\beta}(k'', t)
\]

\[
= -i \sum_{s', s''} \sum_{s' \neq s''} \int d^d q' d^d q'' \frac{(g + q \gamma)}{m^{(s)}} \left( \frac{\langle j^{(s')}_{g, \gamma} (q', t) j^{(s'')}_{g, \alpha} (q'') \rangle}{\langle j^{(s')}_{g, \alpha} (q') \rangle \langle j^{(s'')}_{g, \beta} (q'') \rangle} \right)^{*} \delta j^{(s'')}_{g, \beta}(q'', t)
\]

\[
= -i \frac{(g + q \gamma)}{m^{(s)}} \delta j^{(s)}_{g, \alpha}(\mathbf{q}, t), \quad (5.9a)
\]

\[
\frac{\partial}{\partial t} \delta j^{(s)}_{g, \alpha}(\mathbf{q}, t) = i \sum_{s', s''} \int d^d k' d^d k'' \left( \frac{\langle j^{(s')}_{g, \alpha} (q) \mathcal{L}_{\delta \rho^{(s')}} (k') \rangle}{\langle \delta \rho^{(s')}_{g} (k') \rangle} \right)^{*} \delta n^{(s'')}_{g}(k'', t)
\]

\[
= -i \sum_{s', s''} \sum_{s' \neq s''} \int d^d q' d^d q'' \frac{(g' + q') \gamma}{m^{(s')}} \left( \frac{\langle j^{(s')}_{g, \gamma} (q', \mathbf{q}) \rangle}{\langle \delta \rho^{(s')}_{g, \gamma} (q', \mathbf{q}) \rangle} \right)^{*} \delta n^{(s'')}_{g}(q'', t)
\]

\[
= -i \sum_{s'} (g' + q) \alpha n^{(s')}_{g, \gamma} \langle j^{(s')}_{g, \gamma} (q) \rangle \delta n^{(s'')}_{g, \beta}(\mathbf{q}), \quad (5.9b)
\]

The inverse of the density-density correlation matrix \( \mathbf{J} \) is defined via (cf. [WF10, eq. (24)])

\[
V_{k\bar{k}} T \mathbf{d}_{g} \mathbf{d}_{ab} = \sum_{s} \left( \delta \rho^{(s)}_{g} (q) \right) \delta \rho^{(s)}_{g} (q) \right) \mathbf{d}_{g}^{(s)} (q). \quad (5.10)
\]

It is already given with a single BZ argument \( \mathbf{q} \) which will be shown in paragraph 5.3.1. Together with eq. (5.5) this makes clear that only quantities with equal BZ wave vector \( \mathbf{q} \) couple in eq. (5.9) and why the second spatial argument could be dropped in appendix A. Due to time-inversion arguments (cf. section 3.2), only couplings between density fluctuations \( \delta n^{(s)}_{g} \) and momentum density fluctuations \( \delta j^{(s)}_{g} \) arise in eqs. (5.9). Still, the frequency matrix \( \mathbf{J} (\mathbf{q}) \) found from that includes additional couplings to the momentum densities \( \delta j^{(s)}_{g} \) \( \not\in \mathbf{A} \). A closed set of e.o.m. for the variables in \( \mathbf{A} \) is obtained by neglecting contributions of \( j^{(s)}(\mathbf{k}, \cdot) \) for \( \mathbf{k} \) outside the first BZ,

\[
\mathbf{k} \not\in 1^{st} \text{BZ} \Leftrightarrow j^{(s)}(\mathbf{k}, \cdot) \frac{1}{T} = 0, \ s = 1, \ldots, B.
\]

This can be motivated from a physical point of view: The currents \( j^{(s)} \) can show slow decay only at length scales much larger than the unit-cell size and will equilibrate quickly at shorter length scales. Consequently, the integrations in eq. (5.9a) can be restricted to the first BZ from the beginning. The summations over \( \mathbf{g}' \) and \( \mathbf{g}'' \) then vanish from the calculations in eq. (5.9a), yielding only a coupling to \( \delta j^{(s)}_{g=0} (\mathbf{q}) = \delta j^{(s)} (\mathbf{q}) \). The extension of the linear, dissipationless and isothermal e.o.m. [WF10, eq. (25)] follows as
\[
\partial_t \delta n_{g}^{(s)}(q, t) = i \left( \frac{\langle \delta \rho_{g}^{(s)}(q) \mathcal{L} j_{\alpha}(q) \rangle}{\langle j_{\alpha}^{*}(q) \mathcal{J}_{\beta}(q) \rangle} \right)^* \delta j_{\beta}(q, t)
\]
\[
= -i n_{g}^{(s)}(g + q) \cdot \frac{\delta j_{\alpha}(q, t)}{\varrho_{0}^{(s)}}, \tag{5.11a}
\]
\[
\partial_t \delta j_{\alpha}(q, t) = i \sum_{c,b=1}^{B} \sum_{g' \in G} \left( \frac{\langle \delta j_{\alpha}^{(c)}(q) \mathcal{J} \delta \rho_{g}^{(c)}(q) \rangle}{\langle \delta \rho_{g}^{(c)}(q) \delta \rho_{g}^{(b)}(q) \rangle} \right)^* \delta n_{g}^{(b)}(q, t)
\]
\[
= -i \sum_{g' \in G, g, a, b} (g' + q) n_{g}^{(a)*} j_{g_{g}^{(a)b}}^{(ab)*}(q) \delta n_{g}^{(b)}(q, t). \tag{5.11b}
\]

Note that eq. (5.11b) is not a purely hydrodynamic equation. It was already pointed out in paragraph 3.3.3 that \( j^{(s)} \), unlike the total momentum density \( j \), separately are not related to a conserved quantity. However, eq. (5.11b) reduces to [WF10, eq. (24b)] in the single-species case \( B = 1 \). Furthermore, an equation for the total momentum density can be easily obtained from eq. (5.11b):
\[
\frac{\partial}{\partial t} j(q) = \partial_t \sum_{a} \delta j_{\alpha}(q, t) = -i \sum_{g', g, a, b} (g' + q) n_{g}^{(a)*} j_{g_{g}^{(a)b}}^{(ab)*}(q) \delta n_{g}^{(b)}(q, t). \tag{5.12}
\]

This shows that eqs. (5.11) take into account the complete set of hydrodynamic variables that is of interest in the reversible case. These variables form a set for which the time-scale separation argument discussed in paragraph 3.2.1 holds and whose dynamics is therefore distinct from the remaining fast dynamics in the long-wavelength limit. No criterion of similar rigor can be given for the additional components included into eq. (5.11b). A good candidate for e.o.m. including optical phonons will be one that reproduces the dynamical matrix \( D \) from eq. (1.2) in the perfect-lattice regime. An e.o.m. of similar form is easily obtained from eq. (5.11) by taking the time derivative and subsequently inserting eq. (5.11a),
\[
\partial_{\alpha}^{2} \delta j_{\alpha}(q, t) = - \sum_{b} A_{ab}^{(ab)} \cdot \frac{\delta j_{\alpha}^{(b)}}{\varrho_{0}}(q, t), \tag{5.12}
\]
where we introduced the dynamical (block) matrix
\[
\Lambda(q) = \left( \begin{array}{cccc}
\Lambda^{(11)} & \Lambda^{(12)} & \ldots & \Lambda^{(1B)} \\
\Lambda^{(21)} & \Lambda^{(22)} & \ldots & \Lambda^{(2B)} \\
\vdots & \vdots & \ddots & \vdots \\
\Lambda^{(B1)} & \Lambda^{(B2)} & \ldots & \Lambda^{(BB)}
\end{array} \right) \tag{5.13}
\]
5.3 Properties of the dynamical block matrix \( \Lambda \)

with the matrix blocks

\[
A_{\alpha \beta}^{(ab)}(q) = \frac{\partial_{q}^{(a)}}{\partial_{q}^{(b)}} \sum_{g \cdot g'} \left( g^{(a)} + q \right) n^{(a)}_{g'} \left( g^{(b)} \right) n_{g} \left( g + q \right) = \frac{\partial_{q}^{(a)}}{\partial_{q}^{(b)}} A_{\beta \alpha}^{(ab)*}(q). \tag{5.14}
\]

Equation (5.12) poses an eigenvalue problem; the ansatz

\[
\delta j_{i}^{(1)}(q, t) = e^{i \omega(q) t} \delta j_{i}^{(1)}(q)
\]

yields

\[
0 = \begin{pmatrix}
\Lambda^{(11)} & \Lambda^{(12)} & \cdots & \Lambda^{(1B)} \\
\Lambda^{(21)} & \Lambda^{(22)} & \cdots & \Lambda^{(2B)} \\
\vdots & \vdots & \ddots & \vdots \\
\Lambda^{(B1)} & \Lambda^{(B2)} & \cdots & \Lambda^{(BB)}
\end{pmatrix} (q) - \frac{\partial_{q}^{2} \omega^{2}(q)}{= \lambda(q)} \mathbb{I}_{Bd} \begin{pmatrix}
\delta j^{(1)} \\
\delta j^{(2)} \\
\vdots \\
\delta j^{(B)}
\end{pmatrix} (q). \tag{5.15}
\]

Bear in mind that \( \Lambda \sim \partial_{q} D \) differs from the conventional (“physical”) dynamical matrix by a constant factor \( \partial_{q} \). Its eigenvalues \( \lambda_{\sigma}(q) \) are related to the squared physical eigenfrequencies \( \omega^{2}_{\sigma}(q) \) by the same factor. Unless specified otherwise “dynamical matrix” will refer to \( \Lambda \). All questions concerning existence and properties of the desired acoustic and optical solutions to this equation require discussion of the dynamical matrix. This is the subject of the following section.

5.3. Properties of the dynamical block matrix \( \Lambda \)

Examining the existence of solutions to eq. (5.15) is tantamount to asking whether \( \Lambda(q) \), at an arbitrary but fixed value of \( q \), can be diagonalized. The linear coordinate transforms \( T(q) \) relevant to this can be represented as (invertible) \( Bd \)-square matrices. The momentum-density components \( j^{(s)}(q) \) and the dynamical matrix \( \Lambda(q) \) transform as\(^3\)

\[
\delta j_{\alpha}^{(a)} \rightarrow T \delta j_{\alpha}^{(a)} = \sum_{s} T_{\alpha \beta}^{(as)} \delta j_{\beta}^{(s)}, \tag{5.16a}
\]

\[
A_{\alpha \beta}^{(ab)} \rightarrow T A_{\alpha \beta}^{(ab)} = \sum_{s, s'} T_{\alpha \gamma}^{(as)} A_{\gamma \delta}^{(ss')} T_{\delta \beta}^{(s'b)}. \tag{5.16b}
\]

We introduced a left superscript to denote the \( T \)-transformed variables \( T \delta j_{\alpha}^{(a)} \) and dynamical matrix \( T \Lambda \). Note that the indices in \( T \delta j_{\alpha}^{(a)} \) generally loose the original

\(^3\)In the following, the arguments \( q \) are omitted to shorten notation.
interpretation as $a^{\text{th}}$ cartesian component of the $a^{\text{th}}$-species contribution. However, if $T$ can be written as a Kronecker product/ matrix direct product,

$$T_{\alpha\beta}^{(ab)} = [t \otimes R]_{\alpha\beta}^{(ab)} = t^{(ab)} R_{\alpha\beta}$$

with a $B \times B$ matrix $t$ and a $d \times d$ matrix $R$, there exist separate inverse matrices for $t$ and $R$ [Loa00]. If $t = 1_B$ then only the cartesian coordinates are transformed, leaving the basis of the physical variables invariant. Transforms of the physical variables alone with $R = 1_d$ are the complementary case and will be used in the following sections to show the diagonalizability of $A$ and the presence of $d$ acoustic phonon branches.

### 5.3.1. Inverse of the density-density correlation matrix

The defining relation (5.10) for the inverse density-density correlation matrix $\rho_{g,g}^{(ab)}(q)$ was only implicit. We follow [WF10, sec. IV.A] to an explicit expression. For periodic crystals, the density-density correlations between arbitrary species are periodic on the same Bravais lattice. [WF10, eq. (45)] then becomes a set of Fourier series [MA97]

$$\left\langle \delta \rho^{(a)}(r) \delta \rho^{(b)}(r') \right\rangle = \sum_ge^{igR} \delta n_g^{(ab)}(\Delta r)$$

with coordinates centered $R := \frac{r + r'}{2}$ (5.17)

and the Fourier coefficients

$$\delta n_g^{(ab)}(\Delta r) = \frac{1}{V} \int d^dR e^{-igR} \left\langle \delta \rho^{(a)}(R + \frac{\Delta r}{2}) \delta \rho^{(b)}(R - \frac{\Delta r}{2}) \right\rangle.$$ (5.18)

The identity form of the Ornstein–Zernike equation, [WF10, eq. (48)] can be generalized from the discussion of fluid mixtures [Bax70] and [Eva79, § 3]. With our notation for the average densities $\{n^{(s)}\}$ and the chemical potentials $\{\mu^{(s)}\}$ we infer

$$\frac{\delta n^{(a)}(r)}{\delta \mu^{(b)}(r')} = \left\langle \delta \rho^{(a)}(r) \delta \rho^{(b)}(r') \right\rangle$$

and

$$\frac{\delta \mu^{(a)}(r)}{\delta n^{(b)}(r')} = \frac{\delta^2 F \left[ \{n^{(s)}\} \right]}{\delta n^{(a)}(r) \delta n^{(b)}(r')} = C^{(ab)}(r, r').$$

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5.3 Properties of the dynamical block matrix $\mathbf{\Lambda}$

$C^{(ab)}$ was introduced in eq. (4.7). From that definition also follows

$$ C^{(ab)} \left( \mathbf{P} \cdot (\mathbf{r} + \mathbf{T}) , \mathbf{P} \cdot (\mathbf{r}' + \mathbf{T}) \right) = C^{(ab)} (\mathbf{r}, \mathbf{r}') \quad \forall \ (\mathbf{T}, \mathbf{P}) \in \mathbf{S}. \quad (5.20) $$

$\mathbf{S}$ is the space group of the given system that was introduced in the definition (2.12). Equation (5.20) states that $C^{(ab)}$ inherits the space group of the given system for simultaneous transformations of both of its arguments. This statement can easily be generalized to higher order functional derivatives of $\mathbf{F}$. Its proof follows from the definition of the functional derivative in combination with the definition (2.12) of $\mathbf{S}$. The lattice periodicity can be exploited for an expansion of $C^{(ab)}$ and in particular $c^{(ab)}$ into a Fourier series (cf. [MA97]),

$$ C^{(ab)} (\mathbf{r}, \mathbf{r}') = \sum_{\mathbf{g} \in \mathbf{G}} e^{i \mathbf{g} \cdot \mathbf{R}} C^{(ab)}_{\mathbf{g}} (\Delta \mathbf{r}) \quad (5.21) $$

with $C^{(ab)}_{\mathbf{g}} (\Delta \mathbf{r}) = \frac{1}{V} \int_{\text{primitive unit cell}} d^d \mathbf{R} e^{-i \mathbf{g} \cdot \mathbf{R}} C^{(ab)} \left( \mathbf{R} + \frac{\Delta \mathbf{r}}{2}, \mathbf{R} - \frac{\Delta \mathbf{r}}{2} \right).$

Equations (5.19a) and (5.19b) pose mutually inverse relations that can, in parallel with [RW02, sec. 4.2], be combined with the chain rule of functional calculus,

$$ \delta_{ab} \delta (\mathbf{r} - \mathbf{r}'') = \sum_{\mathbf{s}} \int d^d \mathbf{r}' \left( \delta \rho^{(a)} (\mathbf{r}) \delta \rho^{(s)} (\mathbf{r}') \right) C^{(ab)} (\mathbf{r}', \mathbf{r}''). \quad (5.22) $$

This is the generalization of the Ornstein–Zernike equation [WF10, eq. (50)] to several species. But for a constant, the l.h.s. of this relation (5.22) matches the l.h.s. of eq. (5.10). The species indices do not alter the discussion made in [WF10, eqs. (50) to (53)] so that $\mathbf{J}$ follows as

$$ J^{(ab)}_{\mathbf{g} \cdot \mathbf{g}'} (\mathbf{q}) = \frac{k_B T}{V} \int d^d \mathbf{r} d^d \mathbf{r}' e^{i \mathbf{g} \cdot \mathbf{r}} e^{-i \mathbf{g}' \cdot \mathbf{r}'} e^{i \mathbf{q} \cdot \Delta \mathbf{r}} C^{(ab)} (\mathbf{r}, \mathbf{r}') \quad (5.23a) $$

$$ = J^{(ba)}_{\mathbf{g}' \cdot \mathbf{g} - \mathbf{q}} (-\mathbf{q}) = J^{(ba)}_{\mathbf{g} \cdot \mathbf{g}'} (\mathbf{q}). \quad (5.23b) $$

The second equality in eq. (5.23b) can be considered as self-adjointness if $\mathbf{J}$ is considered a matrix with indices $(a, \mathbf{g}), (b, \mathbf{g}')$. These properties can be exploited for the discussion of $\mathbf{\Lambda}$ by rescaling the observables,

$$ \delta \mathbf{j}^{(s)} \rightarrow \mathbf{S} \delta \mathbf{j}^{(s)} = \sqrt{\frac{\rho_0}{\rho_0^{(s)}}} \delta \mathbf{j}^{(s)}. \quad (5.24) $$

The transformation matrix $\mathbf{S}$ is diagonal in both species and spatial indices,

$$ \mathbf{S}^{(ab)} = \delta_{ab} \sqrt{\frac{\rho_0}{\rho_0^{(a)}}} \mathbf{I}_d $$

and transforms $\mathbf{\Lambda}$ as

$$ \mathbf{S} \mathbf{A}^{(ab)} (\mathbf{q}) = \frac{\rho_0}{\rho_0^{(ab)}} \sum_{\mathbf{g}'} (\mathbf{g}' + \mathbf{q}) n^{(a)*}_{\mathbf{g}'} J^{(ab)*}_{\mathbf{g} \cdot \mathbf{g}'} (\mathbf{q}) n^{(b)}_{\mathbf{g}} (\mathbf{g} + \mathbf{q}) \quad (5.25) $$

53
with the shorthand $\sqrt{\theta_0^{(a)} \theta_0^{(b)}} =: \theta_0^{(ab)}$. Note the invariance of the diagonal blocks $A^{(ab)}$ under $S$. Consideration of the adjoint $S^g = S^{T*}$ yields

$$S A^{(ba)*}_{a\beta} (q) = \frac{\theta_0^{(ab)}}{\theta_0^{(a)}} \sum_{g, g'} (g' + q)_\beta n^{(b)}_{g} j^{(ba)}_{g, g'} (q) n^{(a)*}_{g'} (g + q)_\alpha = S A^{(ab)}_{\alpha \beta} (q) \frac{\theta_0^{(ab)}}{\theta_0^{(a)}} \sum_{g, g'} (g + q)_\alpha n^{(a)*}_{g} j^{(ba)*}_{g, g'} (-q) n^{(b)}_{g'} (g' + q)_\beta \quad (5.26)$$

In the last line, $n^{(a)*}_{g} = n^{(-s)}_{g}$ was used. The first part of eq. (5.26) signifies the self-adjointness of $S^g$, the lower half its antisymmetry in $q$. It follows immediately that $S^g$ and consequently $\Lambda$ has a set of real $q$-dependent eigenvalues $\{\omega(s)(q)\}$ with only even powers in $q$, $\omega(s)(q) = \omega(s)(-q)$. Besides these analytical results, the transform $S$ also facilitates the numerical diagonalization of $\Lambda$ with more efficient algorithms at hand for the self-adjoint case (cf. paragraph 7.1.2).

Before proceeding to the discussion of the long-wavelength limit of $\Lambda$, it seems worthwhile to point out that the Fourier expansions (5.17) and (5.21) allow to reshape eq. (5.22):

$$\delta_{ab} (\Delta r) = \sum_s \int d^d r' \sum_{g, g'} e^{i g' \cdot \frac{r + \Delta r}{2}} \delta n^{(as)}_{g} (-r') e^{i g' \cdot \frac{r + \Delta r}{2}} C^{(sb)}_{g'} (r' + \Delta r)$$

$$= \sum_s \int d^d r' \sum_{g, g'} e^{-i \frac{g + g'}{2} \cdot r'} e^{i g' \cdot \frac{r + \Delta r}{2}} \delta n^{(as)}_{g} (r') C^{(sb)}_{g'} (\Delta r - r') \int d^d R$$

$$V \delta_{ab} (\Delta r) = \sum_s \int d^d r' \sum_{g} e^{i g' \cdot \frac{r'}{2}} \delta n^{(as)}_{g} (r') C^{(sb)}_{g} (\Delta r - r') \int d^d R$$

This might serve as a starting point to integral-equation theories for periodic crystals in the spirit of [RS04, cf. eq. (31)].

### 5.3.2. Existence of acoustic modes

The characterization of the long-wavelength modes requires a diagonalization of $\Lambda (q)$ up to the leading orders in $q$ of these modes, i.e. up to $O(q^0)$ for optical and $O(q^2)$ for acoustic phonons. In view of the wave equation (3.54b) from paragraph 3.3.3, the
5.3 Properties of the dynamical block matrix $\Lambda$

eigenvector of the acoustic modes in the limit $q \to 0$ has to be the total momentum density $\delta j$. In a uniformly moving sample, each species contributes to $\delta j$ according to its fraction of the total mass density $\varrho_0$. The $B - 1$ observables complementary to $\delta j$ are introduced as deviation from that fraction, i.e.

$$\Delta j^{(s)} := \delta j^{(s)} - \frac{\varrho_0^{(s)}}{\varrho_0} \delta j, \quad s = 1, 2, \ldots, B - 1.$$  

These considerations can be combined into a second variable transform $P$,

$$\delta j^{(s)} \to P \delta j^{(s)} = \left\{ \begin{array}{ll} \delta j, & s = 1, \\ \Delta j^{(s-1)}, & s = 2, 3, \ldots, B \end{array} \right.$$  

with

$$P = \frac{1}{\varrho_0} \begin{pmatrix} \varrho_0 & \varrho_0 & \ldots & \varrho_0 & \varrho_0 \\ \varrho_0 - \varrho_0^{(1)} & -\varrho_0^{(1)} & \ldots & -\varrho_0^{(1)} & -\varrho_0^{(1)} \\ -\varrho_0^{(2)} & \varrho_0 - \varrho_0^{(2)} & \ldots & -\varrho_0^{(2)} & -\varrho_0^{(2)} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ -\varrho_0^{(B-1)} & -\varrho_0^{(B-1)} & \ldots & \varrho_0 - \varrho_0^{(B-1)} & -\varrho_0^{(B-1)} \end{pmatrix} \otimes I_d$$

$$= \frac{1}{\varrho_0} \begin{pmatrix} \varrho_0 & \varrho_0 \\ \varrho_0 1^{B-1} - M & -\varrho_0 \end{pmatrix}, \quad P^{-1} = \frac{1}{\varrho_0} \begin{pmatrix} \varrho_0 & \varrho_0 1^{B-1} \\ \varrho_0^{(B)} & -\varrho_0 \end{pmatrix}.$$  \hfill (5.27)

The compact notation (5.27) introduced the two $(B - 1)$-component vectors

$$\varrho_0 = \left( \begin{array}{cccc} \varrho_0 & \varrho_0 & \ldots & \varrho_0 \end{array} \right) \otimes I_d, \quad \varrho_0^{\|} = \left( \begin{array}{cccc} \varrho_0^{(1)} & \varrho_0^{(2)} & \ldots & \varrho_0^{(B-1)} \end{array} \right)^T \otimes I_d$$  

and

$$M = \left( \begin{array}{cccc} \varrho_0^{(1)} & \varrho_0^{(1)} & \ldots & \varrho_0^{(1)} \\ \varrho_0^{(2)} & \varrho_0^{(2)} & \ldots & \varrho_0^{(2)} \\ \vdots & \vdots & \ddots & \vdots \\ \varrho_0^{(B-1)} & \varrho_0^{(B-1)} & \ldots & \varrho_0^{(B-1)} \end{array} \right) \otimes I_d = \frac{1}{\varrho_0} \varrho_0^{\|} \varrho_0.$$  

Making use of

$$M \cdot \varrho_0^{\|} = \left( \varrho_0 - \varrho_0^{(B)} \right) \varrho_0^{\|} \quad \text{and} \quad \varrho_0 \cdot M = \left( \varrho_0 - \varrho_0^{(B)} \right) \varrho_0,$$
it can be easily verified with that the identity $\mathbf{P} \cdot \mathbf{P}^{-1} = \mathbf{1}_{Bd} = \mathbf{P}^{-1} \cdot \mathbf{P}$ for eq. (5.27) holds indeed. The transformed dynamical matrix $\mathbf{P}\mathbf{A}$ is best given by its blocks

$$\mathbf{P}\mathbf{A} = \mathbf{P} \cdot \mathbf{A} \cdot \mathbf{P}^{-1} = \begin{pmatrix}
\mathbf{P} \mathbf{A}^{(11)} & \mathbf{P} \mathbf{A}^{(12)} & \mathbf{P} \mathbf{A}^{(13)} & \cdots & \mathbf{P} \mathbf{A}^{(1B)} \\
\mathbf{P} \mathbf{A}^{(21)} & \mathbf{P} \mathbf{A}^{(22)} & \mathbf{P} \mathbf{A}^{(23)} & \cdots & \mathbf{P} \mathbf{A}^{(2B)} \\
\mathbf{P} \mathbf{A}^{(31)} & \mathbf{P} \mathbf{A}^{(32)} & \mathbf{P} \mathbf{A}^{(33)} & \cdots & \mathbf{P} \mathbf{A}^{(3B)} \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
\mathbf{P} \mathbf{A}^{(B1)} & \mathbf{P} \mathbf{A}^{(B2)} & \mathbf{P} \mathbf{A}^{(B3)} & \cdots & \mathbf{P} \mathbf{A}^{(BB)}
\end{pmatrix}$$

(5.28)

where the last line introduced physically motivated submatrices of $\mathbf{P}\mathbf{A}$: $\mathbf{P} A^{(tot)}$ describes the internal coupling of the total-momentum subspace, $\mathbf{P} \mathbf{A}$ the same for the subspace spanned by $\{\Delta j^{(1)}, \Delta j^{(2)}, \ldots, \Delta j^{(B-1)}\}$, $\mathbf{P} \mathbf{A}^{(c)}$ and $\mathbf{P} \mathbf{A}^{(c)}$ the mutual couplings between $\Delta j$ and the $\Delta j^{(c)}$. Evaluation of $\mathbf{P}\mathbf{A}$ yields

$$\mathbf{P} A^{(tot)} = \mathbf{P} A^{(11)} = \frac{1}{\theta_0} \sum_{a,b=1}^{B} A^{(ab)} \theta_0^{(b)},$$

(5.29a)

$$\mathbf{P} A^{(b)} = \mathbf{P} A^{(1,b+1)} = \sum_{s=1}^{B} \left( A^{(sb)} - A^{(sB)} \right),$$

(5.29b)

$$\mathbf{P} A^{(a)} = \mathbf{P} A^{(a+1,1)} = \frac{1}{\theta_0} \sum_{s} \left( A^{(as)} - \sum_{s'} \frac{\theta_0^{(a)}}{\theta_0} A^{(s')} \theta_0^{(s)} \right),$$

(5.29c)

$$\mathbf{P} A^{(ab)} = \mathbf{P} A^{(a+1,b+1)} = A^{(ab)} - A^{(aB)} + \frac{\theta_0^{(a)}}{\theta_0} \sum_{s} \left( A^{(sB)} - A^{(sb)} \right).$$

(5.29d)

Using $A^{(ab)} = \frac{\theta_0^{(a)}}{\theta_0^{(b)}} A^{(ba)}$, we obtain the following relation between $\mathbf{P} A^{(c)}$ and $\mathbf{P} A^{(c)}$:

$$\sum_{b=1}^{B-1} \frac{\theta_0^{(b)}}{\theta_0} \mathbf{P} A^{(b)} = \sum_{s,b=1}^{B} A^{(s,b)} \theta_0^{(b)} \theta_0^{(s)} - \sum_{s} A^{(sB)}$$

$$= \frac{\theta_0}{\theta_0^{(B)}} \sum_{a=1}^{B-1} \mathbf{P} A^{(a)}.$$

(5.30)
5.3 Properties of the dynamical block matrix $\mathbf{A}$

The expressions (5.28) to (5.30) evaluated for the binary case $B = 2$ give an instructive example:

$$
\mathbf{P} = \frac{1}{\theta_0} \left( \begin{array}{cc}
\theta_0 & \theta_0 \\
\theta_0 & -\theta_0
\end{array} \right) \otimes \mathbf{1}_d, \quad \mathbf{P}^{-1} = \frac{1}{\theta_0} \left( \begin{array}{cc}
\theta_0 & \theta_0 \\
\theta_0 & -\theta_0
\end{array} \right) \otimes \mathbf{1}_d.
$$

$$
\mathbf{P} \mathbf{A} = \frac{1}{\theta_0} \left( \sum_{a,b} \mathbf{A}^{(ab)} \mathbf{A}^{(b)} \mathbf{A}^{(12)} + \mathbf{A}^{(22)} - \mathbf{A}^{(12)} \right) \otimes \mathbf{1}_d.
$$

(5.31)

This can be put into a self-adjoint form with a modification of $\mathbf{P}$ by an additional transform

$$
\mathbf{P}_2 := \frac{1}{\theta_0} \left( \begin{array}{cc}
\theta_0 & 0 \\
0 & \theta_0
\end{array} \right) \otimes \mathbf{1}_d \cdot \mathbf{P} = \frac{1}{\theta_0} \left( \begin{array}{cc}
\theta_0 & \theta_0 \\
\theta_0 & -\theta_0
\end{array} \right) \otimes \mathbf{1}_d,
$$

$$
\mathbf{P}_2 \mathbf{A} = \frac{1}{\theta_0} \left( \sum_{a,b} \mathbf{A}^{(ab)} \mathbf{A}^{(b)} \mathbf{A}^{(12)} \mathbf{A}^{(11)} + \mathbf{A}^{(22)} - \mathbf{A}^{(12)} \mathbf{A}^{(12)} \right) \otimes \mathbf{1}_d.
$$

(5.32)

The block $\mathbf{P} \mathbf{A}^{(tot)}$ characterizes the $\delta \mathbf{j} - \delta \mathbf{j}$ coupling and reduces to the wave equation [WF10, eq. (26)] in the single-species case. For the discussion of the low-$q$ limit of $\mathbf{P} \mathbf{A}$, it needs to be given a more explicit form. The rewriting is facilitated by splitting up $\mathbf{A}$ into an ideal gas part $\mathbf{A}_{id}$ and an excess part $\mathbf{A}_{ex}$, according to the decomposition of $C^{(ab)}$ in eq. (4.7). The former can then be rewritten with the translational Lovett, Mou, Buff, Wertheim (LMBW) equation [LMB76; Wer76], generalized to a multi-component system [IF97],

$$
\nabla \left[ \ln n^{(a)} (\mathbf{r}) + \beta V_{ext}^{(a)} (\mathbf{r}) \right] = \sum_b \int d^d r' c^{(ab)} (\mathbf{r}, \mathbf{r}') \nabla' n^{(b)} (\mathbf{r}')
$$

(5.33)

and employed at vanishing external potential $V_{ext}^{(a)} \equiv 0$. Together with eqs. (4.7)

---

5 This step might as well have been taken in the original definition of $\mathbf{A}$. Its use however seems to be peculiar to the binary case where the “average statement” eq. (5.30) turns into a simple relation between the to off-diagonal blocks.

6 This relation is based on the expansion of $V^{\text{ext}} \left[ \{ n^{(s)} \} \right]$ in an infinitesimal global displacement of the sample. See [WF10, sec. IV.B. and references therein] for a general discussion.
and (5.23a), \( \Lambda_{id} \) becomes

\[
\Lambda_{\alpha\beta, id}^{(ab)}(q) = \\
= \delta_{ab} \frac{\theta_0}{V} \frac{k_BT}{\rho_0^{(a)}} \int d^4r \frac{1}{n^{(a)}(r)} \left( (i \nabla + q)_\alpha n^{(a)}(r) \right) \left( (-i \nabla + q)_\beta n^{(a)}(r) \right)
\]

\[
= \delta_{ab} \frac{k_BT}{\rho_0^{(a)}} \left\{ N^{(a)} q_\alpha q_\beta + \\
+ \frac{1}{2} \int d^4r \left[ \left( (i \nabla + q)_\alpha n^{(a)}(r) \right) (-i \nabla)_\beta n^{(a)}(r) + q_\beta n^{(a)}(r) i\nabla_\alpha \ln n^{(a)}(r) + \\
+ \left( (-i \nabla + q)_\beta n^{(a)}(r) \right) i\nabla_\alpha \ln n^{(a)}(r) + q_\alpha n^{(a)}(r) (-i \nabla)_\beta \ln n^{(a)}(r) \right] \right\}
\]

\[
= \delta_{ab} \frac{k_BT}{\rho_0^{(a)}} \left\{ N^{(a)} q_\alpha q_\beta + \sum_{\ell} \int d^4r d^4r' \times \\
\times \left[ (i \nabla + q)_\alpha n^{(a)}(r) c^{(a\ell)}(r, r') (-i \nabla')_\beta n^{(\ell)}(r') + q_\beta n^{(a)}(r) c^{(a\ell)}(r, r') i\nabla'_\alpha n^{(\ell)}(r') + \\
- (i \nabla - q)_\beta n^{(a)}(r) c^{(a\ell)}(r, r') (+i \nabla')_\alpha n^{(\ell)}(r') - q_\alpha n^{(a)}(r) c^{(a\ell)}(r, r') i\nabla'_\beta n^{(\ell)}(r') \right] \right\}.
\]

Equation (5.34) made use of the identity \( \sum_g g^{(x)} e^{i\mathbf{g} \mathbf{r}} = -i \nabla n^{(x)}(\mathbf{r}) \) to contract the reciprocal lattice sums. (5.35) symmetrized the expression so that the self-adjointness of \( \Lambda^{(aa)} \) remains visible after applying eq. (5.33) to the four underlined terms. The excess part \( \Lambda_{ex} \) simply reads

\[
\Lambda_{\alpha\beta, ex}^{(ab)} = -k_BT \rho_0^{(b)} \int d^4r d^4r' (i \nabla_\alpha + q_\alpha) n^{(a)}(r) c^{(ab)}(r, r') (-i \nabla' + q)_\beta n^{(b)}(r') e^{-i\mathbf{q} \cdot \Delta\mathbf{r}}
\]

and combines with eq. (5.36) to

\[
\Lambda_{\alpha\beta}^{(ab)}(q) = \frac{N^{(a)} \rho_0}{\beta V \rho_0^{(a)}} q_\alpha q_\beta \delta_{ab} + \frac{\rho_0}{V} \int d^4r d^4r' \left\{ \delta_{ab} \frac{1}{2\rho_0^{(a)}} \sum_{\ell} c^{(a\ell)}(r, r') \times \\
\times \left[ (i \nabla + q)_\alpha n^{(a)}(r) (-i \nabla' + q)_\beta n^{(\ell)}(r') + q_\beta n^{(a)}(r) n^{(\ell)}(r') + \\
- (i \nabla - q)_\beta n^{(a)}(r) (+i \nabla')_\alpha n^{(\ell)}(r') - q_\alpha n^{(a)}(r) n^{(\ell)}(r') \right] + \\
- \frac{1}{\rho_0^{(a)}} (i \nabla + q)_\alpha n^{(a)}(r) c^{(ab)}(r, r') (-i \nabla' + q)_\beta n^{(b)}(r') e^{-i\mathbf{q} \cdot \Delta\mathbf{r}} \right\}.
\]

Note from this explicit form that the real and imaginary part of \( \Lambda(q) \) contain only
even respectively odd orders in \( q \). With the intermediate step

\[
\frac{1}{\theta_0} \sum_b \Lambda^{(ab)} \frac{\theta_0}{\beta} = \frac{n_0^{(a)}}{\beta} q q + \frac{1}{\beta V} \sum_b \int \int d^d r \, d^d r' c^{(ab)} (r, r') \times
\]

\[
\left[ (1 - e^{-i q \cdot \Delta r}) (i \nabla + q) n^{(a)} (r) (-i \nabla' + q) n^{(b)} (r') - q q n^{(a)} (r) n^{(b)} (r') \right].
\]

(5.38)

\( \mathcal{P} A^{(\text{tot})} \) in eq. (5.28) now becomes

\[
\mathcal{P} A^{(\text{tot})} (q) = \frac{n_0^{(a)}}{\beta} q q + \frac{1}{\beta V} \sum_{a,b} \int \int d^d r \, d^d r' c^{(ab)} (r, r') \times
\]

\[
\left[ (1 - e^{-i q \cdot \Delta r}) (i \nabla + q) n^{(a)} (r) (-i \nabla' + q) n^{(b)} (r') - q q n^{(a)} (r) n^{(b)} (r') \right].
\]

(5.39)

The \( \mathcal{O} (q^0) \)-contribution vanished already in eq. (5.38) which was only summed over to obtain eq. (5.39). The contributions linear in \( q \) can be eliminated with a reverse application of the translational LMBW-equation (5.33). Consider only the linear order in \( q \) of \( \mathcal{P} A^{(\text{tot})} (q) \),

\[
\mathcal{P} A^{(\text{tot})} (q) = i \frac{1}{\beta V} q \gamma \cdot \sum_{a,b} \int \int d^d r \, d^d r' c^{(ab)} (r, r') (r - r') \gamma \nabla n^{(a)} (r) \nabla' n^{(b)} (r') + \mathcal{O} (q^2)
\]

and rewrite the first integral contribution

\[
\sum_{a,b} \int \int d^d r \, d^d r' c^{(ab)} (r, r') r_\gamma \nabla n^{(a)} (r) \nabla' n^{(b)} (r') =
\]

\[
= \sum_a \int d^d r \, r_\gamma \nabla n^{(a)} (r) \sum_b \int d^d r' c^{(ab)} (r, r') \nabla' n^{(b)} (r')
\]

(5.33)

\[
= \sum_a \int d^d r \, r_\gamma \nabla n^{(a)} (r) \nabla \ln \left[ n^{(a)} (r) \right]
\]

(5.40a)

and similarly,

\[
\sum_{a,b} \int \int d^d r \, d^d r' c^{(ab)} (r, r') r'_\gamma \nabla n^{(a)} (r) \nabla' n^{(b)} (r') =
\]

\[
= \sum_b \int d^d r' \, r'_\gamma \nabla n^{(b)} (r') \nabla \ln \left[ n^{(b)} (r') \right].
\]

(5.40b)

Equations (5.40) in combination yield

\[
\mathcal{P} A^{(\text{tot})} (q) = \mathcal{O} (q^2).
\]

(5.41)

The presence of a linear order in \( q \) in \( \mathcal{P} A^{(\text{tot})} \) can be ruled out by a different reasoning without eq. (5.33). This will be shown in appendix B. In many cases either of these two approaches is obsolete: If the system has a center of inversion appropriate substitutions of the integration variables in eq. (5.39) yield \( \mathcal{P} A^{(\text{tot})} (q) = \mathcal{P} A^{(\text{tot})} (-q) = \mathcal{O} (q^2) \).
The identification of this $d$-dimensional block is a necessary condition for the existence of acoustic mode solutions to eq. (5.12). Sufficient will be to show in addition that both $\mathbf{p} \mathbf{A}^{(1)}$ and $\mathbf{m} \mathbf{A}^{(1)} = \mathcal{O}(q)$. This can be understood from the definition of the determinant of a $D$-dimensional square-matrix $\mathbf{M}$ (Leibniz formula)

$$
\det \mathbf{M} = \sum_\pi \text{sgn} \pi M_{\pi(1),1} M_{\pi(2),2} \ldots M_{\pi(D),D}
$$

(5.42)

with $\pi$ a permutation of $(1,2,\ldots,D)$. It yields the characteristic polynomial of $\mathbf{p} \mathbf{A}$,

$$
\det \left[ \mathbf{p} \mathbf{A}(q) - \lambda \mathbf{I}_{Bd} \right] = \det \left[ \mathbf{p} \mathbf{A}^{(\text{tot})}(q) - \lambda \mathbf{I}_d \right] \det \left[ \mathbf{p} \mathbf{A}(q) - \lambda \mathbf{I}_{Bd-d} \right] + \mathcal{O}(q^2),
$$

(5.43)

+ “coupling terms”.

The “coupling terms” contain only permutations with both at most 2 factors from the top left $d \times d$ block of $\mathbf{p} \mathbf{A}$ and at most $(B-1)d - 1$ factors from the bottom right $(B-1)d \times (B-1)d$ block. That these two conditions are equivalent is a consequence of the definition (5.42). It follows that the “coupling terms” in eq. (5.43) all contain terms from both $\mathbf{p} \mathbf{A}^{(1)}$ and $\mathbf{m} \mathbf{A}^{(1)}$. The vanishing of their $\mathcal{O}(q^0)$ terms follows from application of the LMBW eq. (5.38). Equation (5.29c) is already in the right form, for eq. (5.29b) use

$$
\sum_s \mathbf{A}^{(sb)} = \left( \frac{1}{\theta_0^{(b)}} \sum_s \mathbf{A}^{(bs)} \theta_0^{(e)} \right)^1.
$$

With this, eq. (5.43) becomes

$$
\det \left[ \mathbf{p} \mathbf{A}(q) - \lambda \mathbf{I}_{Bd} \right] = \det \left[ \mathbf{p} \mathbf{A}^{(\text{tot})}(q) - \lambda \mathbf{I}_d \right] \det \left[ \mathbf{p} \mathbf{A}(q) - \lambda \mathbf{I}_{Bd-d} \right] + \mathcal{O}(q^2),
$$

(5.44)

the necessary form for the existence of acoustic phonons.\(^7\) The existence of $d$ eigenvalues $\lambda^{\text{acoustic}}(q)$ of $\mathbf{p} \mathbf{A}$ with $\lambda^{\text{acoustic}}(q) = \gamma(q) q^2 + \mathcal{O}(q^3)$ is ensured. These however match the eigenvalues $\lambda^{\text{tot}}(q)$ of $\mathbf{p} \mathbf{A}^{(\text{tot})}(q)$ only up to (the vanishing) $\mathcal{O}(q)$. In other terms, provided identical ordering of the indices according to $\lambda_1(q) \leq \lambda_2(q) \leq \ldots \leq \lambda_d(q)$,

$$
\lambda^{\text{tot}}(q) - \lambda^{\text{acoustic}}(q) = \mathcal{O}(q^2), \quad \sigma = 1,2,\ldots,d.
$$

(5.45)

In systems with a center of inversion, $\mathbf{p} \mathbf{A}^{(1)}(q)$ and $\mathbf{m} \mathbf{A}^{(1)}(q)$ are of leading order $\mathcal{O}(q^2)$ and the contributions of the “coupling terms” consequently of $\mathcal{O}(q^4)$. They are then negligible versus the first line of eq. (5.43) in the limit of small $|q|$,\(^8\) and $\lambda^{\text{tot}}(q) - \lambda^{\text{acoustic}}(q) = \mathcal{O}(q^4)$. Beyond this system-specific symmetry, appendix C will give an explicit block-diagonalization of $\mathbf{A}$ up to $\mathcal{O}(q^3)$ for the binary case.

\(^7\)Implicit use is made of the continuity of the characteristic polynomial (5.43) in $\lambda(q)$ with its coefficients (cf. [Zed65]).

\(^8\)The generic physical case is $\lim_{q \to 0} \lambda(0)/q^2 > 0$ for reasons of mechanical stability. The non-generic case — so-called “soft modes” — can be understood from the theory of displacive phase transitions [Dov03, chapter 12].
6. Thermodynamic DFT approach

Here, the complementary static approach to crystal elasticity is presented. A condition of thermodynamic equilibrium is derived with equilibrated internal strains. For comparison with the role of optical modes in chapter 5, the corresponding internal strain is then studied in an example.

In this thesis, elastic constants were defined in eq. (3.52b) from the phenomenological free energy expansions (3.51). They stepped in at the coarse-grained level, whereas an exact microscopical starting point is provided by classical DFT from the density functional introduced in chapter 4:

\[ \delta F\{\delta \rho^{(s)}\} = \delta F_{\text{lin}} + \sum_{a,b=1}^{B} \int d^{d}r \, d^{d}r' \, \delta \rho^{(a)} (r) \, C^{(ab)} (r, r') \, \delta \rho^{(b)} (r') + \mathcal{O} (\delta \rho^2) \] (6.1)

\[ \delta F_{\text{lin}} = \sum_{s=1}^{B} \int d^{d}r \, C^{(s)} (r) \, \delta \rho^{(s)} (r) , \]

where

\[ = \sum_{s=1}^{B} \mu^{(s)} \int d^{d}r \, \delta \rho^{(s)} (r) = V \sum_{s=1}^{B} \mu^{(s)} \delta n_{0}^{(s)} . \]

\( \delta F_{\text{lin}} \) vanishes as the average particle densities \( n_{0}^{(s)} \) are constant, viz \( \delta n_{0}^{(s)} = 0 \) by assumption. The following section illustrates a general approach of obtaining a priori exact microscopic expressions for the elastic constants by relating \( \delta \rho^{(b)} \) in the expansion (6.1) back to the fields of elasticity theory stated in paragraph 3.3.2. The derivation is based on the outline of [CL10, section 6.4.9] and is followed by a simple calculation example for binary crystals.

Assume an equilibrium particle density \( n \) given by

\[ n (r) = \sum_{g} n_{g} e^{i g \cdot r} \quad \text{with} \quad n_{g} = \sum_{s=1}^{B} n_{g}^{(s)} , \]

\[ n_{g}^{(s)} = \frac{1}{V} \left\langle \sum_{i=1}^{N} e^{-i g \cdot r_i} \right\rangle . \]

The most general density fluctuation \( \delta \rho^{(s)} \) is given in terms of fluctuations \( \delta \epsilon^{(s)} \) (or
δn^(s)(r), u and \( \left\{ \delta n_{g}^{(s)} \mid g \in G \setminus \{0\} =: G_{0} \right\} \) by

\[
\delta \rho^{(s)}(r) = -u(r) \cdot \nabla n^{(s)}(r) + \frac{n^{(s)}(r)}{n_{0}^{(s)}} \delta n^{(s)}(r) + \sum_{g \in G_{0}} e^{ig \cdot r} \delta n_{g}^{(s)} \bigg|_{u,\{\delta n^{(s)}\}} \tag{6.2a}
\]

\[
\left(3.45\right) - \nabla \cdot n^{(s)}(r) u(r) - \frac{n^{(s)}(r)}{n_{0}^{(s)}} \delta c^{(s)}(r) + \sum_{g \in G_{0}} e^{ig \cdot r} \delta n_{g}^{(s)} \bigg|_{u,\{\delta c^{(s)}\}} \cdot \tag{6.2b}
\]

\( \delta n_{g}^{(s)} \bigg|_{u,\{\delta n^{(c)}\}} \) signifies the microscopic contribution to the density fluctuation in reaction to at fixed strain and density/defect \(^1\) fluctuation. Before further commenting on this contribution, it will be useful to derive the expressions (6.2) in reciprocal space. Use

\[
n^{(s)}(r) f(r) = \sum_{g \in G} e^{ig \cdot r} n_{g}^{(s)} \int \frac{d^{2}k}{(2\pi)^{2}} \delta^{(g+k) \cdot r} f(k)
\]

\[
= \sum_{g \in G} n_{g}^{(s)} \int \frac{d^{2}k}{(2\pi)^{2}} \delta^{(g+k \cdot r)} f(k)
\]

where \( f \) stands for \( u \) and \( \delta c^{(s)}/\delta n_{0}^{(s)} \), respectively. Further bear in mind that contributions of the spatially slowly varying fields \( f(k) \) can be restricted to the first Brillouin zone, and consequently \( k \notin 1^{st} \text{BZ} \Rightarrow f(k) = 0 \). With this

\[
\delta \rho^{(s)}(k) = - \int d^{d}r e^{-ik \cdot r} \nabla \cdot \left[ n^{(s)}(r) u(r) + \frac{n^{(s)}(r)}{n_{0}^{(s)}} \delta c^{(s)}(r) \right] + \sum_{g \in G_{0}} \delta (g - k) \delta n_{g}^{(s)} \bigg|_{u,\{\delta c^{(s)}\}}
\]

\[ - \frac{1}{2\pi} \sum_{g' \in G} \int d^{d}q' \left[ i (g' + q') \cdot u(q') + \delta c^{(s)}(q')/n_{0}^{(s)} \right] \delta (g' + q' - k) + \]

\[ + \sum_{g' \in G_{0}} \delta n_{g'}^{(s)} \bigg|_{u,\{\delta c^{(s)}\}} \delta (g' - k). \tag{6.3} \]

To evaluate the \( \delta \)-peaks in eq. (6.3), it is useful to decompose \( k = g + q \) into a reciprocal lattice vector \( g \) and a vector \( q \in 1^{st} \text{BZ} \) from the first Brillouin zone. Recalling \( \delta \rho^{(s)}(k = g + q) = \delta \rho_{g}^{(s)}(q) \), we find

\[ \delta \rho_{g}^{(s)}(q) = -n_{g}^{(s)} \left[ ig \cdot u(q) - \delta n^{(s)}(q)/n_{0}^{(s)} \right] + \delta (q) \delta n_{g}^{(s)} \tag{6.4a} \]

\[
= -n_{g}^{(s)} \left[ ig \cdot u(q) + \delta c^{(s)}(q)/n_{0}^{(s)} \right] + \delta (q) \delta n_{g}^{(s)}. \tag{6.4b} \]

The first two contributions in eq. (6.4a) reduce to [Härt13, eq. 5] in the single species case and the first two contributions of eq. (6.4b) can be identified by [Härt13, eq. 6]. The last term in the equations (6.4) however is not present in those previous results. The contributions present in [Härt13] have been related to an affine transformation — due to \( u \) — and a rescaling — due to \( \delta c \) — of the equilibrium density \( n \) in [Wal09, paragraph 4.2.1]. To give a visual idea of the physical meaning of the additional
Figure 6.1: Strain in a linear periodic chain interacting by soft (red) and hard (blue) harmonic springs. Top: Unstrained equilibrium configuration with lattice constant $a$. Center: Each unit cell and spring compressed by the same factor with the leftmost particle fixed (affine transformation). Bottom shows the relaxation from the constraint of identical compression for both springs. It is indicated by black arrows.

contribution, figure 6.1 considers a defect-free linear chain of alternating soft and hard springs. It seems intuitively clear that the middle configuration, where every spring segment has been compressed by the same distance, will not be stable. The non-affine relaxation is indicated by arrows halfway between the center and the bottom row. A keyword for this effect is “internal strain” [MA67]. It will certainly occur in a similar manner for infinitesimal deformations and within a statistical physics description to which we now return.

Apparently, the $\delta n^{(s)}|_{u,\{\delta \rho^{(s)}\}}$ are no independent variational parameters within elasticity theory. They have to be reexpressed in terms of $u$ and $\{\delta c^{(s)}\}$ (or $\{\delta n^{(s)}\}$) in order to obtain expressions for the elastic constants $K^{(s)}$ from paragraph 3.3.3. The relations $\delta n^{(s)}|_{u,\{\delta \rho^{(s)}\}}$ can be found from the condition that the $\delta n^{(s)}|_{u,\{\delta \rho^{(s)}\}}$ assume their equilibrium value which generically varies linearly with strain and defect fluctuations also in the deformed crystal. The condition is the same as in the unstrained equilibrium case and reads

$$\frac{\partial}{\partial \delta n^{(a)}|_{u,\{\delta \rho^{(a)}\}}} \mathcal{F} \left[ \{n^{(s)} + \delta \rho^{(s)}\} \right] = 0 \quad \forall a \in \{1,\ldots,B\} \quad g \in \mathbb{G}.$$  (6.5)

To simplify notation, we henceforth omit the constraint in $\delta n^{(s)}|_{u,\{\delta \rho^{(s)}\}} = \delta n^{(s)}$ (not to be confused with $\delta n^{(s)}(q)$ which has an extra wave-vector argument). The condition (6.5) can be rewritten with a functional expansion of $\mathcal{F}$ about the unstrained equilibrium state.

$$\mathcal{F} \left[ \{n^{(s)} + \delta \rho^{(s)}\} \right] = \mathcal{F} \left[ \{n^{(s)}\} \right] + \sum_b \int d^d r \, C^{(b)} \left[ \{n^{(s)}\} \right] (r) \, \delta \rho^{(b)} (r) +$$  (6.6)

$$+ \frac{1}{2} \sum_{a,b} \int d^d r \, d^d r' \, \delta \rho^{(a)} (r) \, C^{(ab)} \left[ \{n^{(s)}\} \right] (r, r') \, \delta \rho^{(b)} (r') + \mathcal{O} \left( \delta \rho^{(s)} \right).$$

At fixed strain, it is equivalent to additionally fix the density or the defect fluctuations.\footnote{At fixed strain, it is equivalent to additionally fix the density or the defect fluctuations.}
If we insert this expansion into (6.5) the first term vanishes by the equilibrium condition
\[
\frac{\partial}{\partial \delta n_{k}^{(s)}} \mathcal{F} \left[ \left\{ n^{(s)} \right\} \right] = 0.
\]

The second term also vanishes,
\[
\int d^d r C^{(b)} \left[ \left\{ n^{(s)} \right\} \right] (r) \frac{\partial}{\partial \delta n_{k}^{(b)}} \delta \rho^{(b)} (r) = \int d^d r C^{(b)} \left[ \left\{ n^{(s)} \right\} \right] (r) e^{i \mathbf{g} \cdot \mathbf{r}} = \mu^{(b)} (g) =: \mu_{k}^{(b)} = 0,
\]
because the chemical potential has no short-range variations. The nonvanishing contribution from the third order term is obtained with \( \partial / \partial \delta n_{k}^{(a)} \delta \rho^{(a)} (r) = \delta_{ab} e^{i \mathbf{g} \cdot \mathbf{r}} \)
and can be written into a single integral by interchanging the integration variables and making use of the symmetry \( C^{(ab)} (\mathbf{r}, \mathbf{r}') = C^{(ba)} (\mathbf{r}', \mathbf{r}) \).

With these steps, the condition (6.5) is modified to
\[
0 = \frac{1}{\partial \delta n_{k}^{(a)}} \left[ \left\{ n^{(s)} + \delta \rho^{(s)} \right\} \right] \quad (6.7)
\]
\[
\iff \sum_{b} \int d^d r \int d^d r' e^{-i \mathbf{g} \cdot \mathbf{r}} C^{(ab)} (\mathbf{r}, \mathbf{r}') \left[ \mathbf{u} \cdot \nabla' n^{(b)} - n^{(b)} \frac{\delta n^{(b)} (r)}{\delta n_{k}^{(b)}} (r') \right] (r') + \mathcal{O} (\delta \rho^2) = \sum_{b} \int d^d r \int d^d r' e^{-i \mathbf{g} \cdot \mathbf{r}} C^{(ab)} (\mathbf{r}, \mathbf{r}') \sum_{g' \in G_0} \delta n_{k}^{(b) *} e^{-i \mathbf{g'} \cdot \mathbf{r}'} = \sum_{b, g' \in G_0} C^{(ab)} (g, g') \delta n_{k}^{(b) *}.
\]

Ansatz (6.2b) was used and the conjugate complex taken to obtain eq. (6.7). Following the approach in [Har+15], the slowly varying field \( \mathbf{u} (\mathbf{r}') \) therein will now be expanded about \( \mathbf{r} \).

\[
\mathbf{u} (\mathbf{r}') = \mathbf{u} (\mathbf{r}) + (\mathbf{r}' - \mathbf{r}) \cdot \nabla \mathbf{u} (\mathbf{r}) + \mathcal{O} (\nabla \nabla \mathbf{u}) = \mathbf{u} (\mathbf{r}) + (\mathbf{r}' - \mathbf{r}) \cdot \nabla' \mathbf{u} (\mathbf{r}') + \mathcal{O} (\nabla \nabla \mathbf{u}) .
\]

The second equality above will be useful for a more consistent notation in what follows. The zeroth order term \( \propto \mathbf{u} (\mathbf{r}) \) in eq. (6.7) can be eliminated with the translational LMBW equation,
\[
\sum_{b} \int d^d r' \mathbf{u} (\mathbf{r}) \left[ \delta_{ab} \frac{\delta}{\delta n_{k}^{(a)}} (\mathbf{r}) - c^{(ab)} (\mathbf{r}, \mathbf{r}') \right] \mathbf{\nabla}' n^{(b)} (\mathbf{r}') = \mathbf{u} (\mathbf{r}) \left[ \frac{\nabla n_{k}^{(a)} (\mathbf{r})}{n_{k}^{(a)} (\mathbf{r})} - \sum_{b} \int d^d r' c^{(ab)} (\mathbf{r}, \mathbf{r}') \mathbf{\nabla}' n^{(b)} (\mathbf{r}') \right] (5.33) = 0.
\]
The middle line of eq. (6.7) can now be rewritten as follows:

\[
\text{“LHS”} := \sum_b \iiint d^3r \, d^3r' \, e^{-i\mathbf{g} \cdot \mathbf{r}} C^{(ab)}(\mathbf{r}, \mathbf{r}') \left[ \mathbf{u} \cdot \nabla' n_0^{(b)} + n_0^{(b)} \frac{\delta n_0^{(b)}}{n_0^{(b)}} \right](\mathbf{r}') = \\
= \sum_b \iiint d^3r \, d^3r' \, e^{-i\mathbf{g} \cdot \mathbf{r}} C^{(ab)}(\mathbf{r}, \mathbf{r}') \left\{ \left[ (r' - r) \alpha \nabla' n_0^{(b)}(\mathbf{r}') \right] \nabla'_\alpha u_\beta(\mathbf{r}') + \\
+ n_0^{(b)}(\mathbf{r}') \frac{\delta n_0^{(b)}}{n_0^{(b)}} \right\} \}
\]

\[
= \sum_b \iiint d^3r \, d^3r' \, e^{-i\mathbf{g} \cdot \mathbf{r}} C^{(ab)}(\mathbf{r}, \mathbf{r}') \left\{ \left[ (r' - r) \alpha \nabla' n_0^{(b)}(\mathbf{r}') \right] \nabla'_\alpha u_\beta(\mathbf{r}') - \\
\right. \\
\left. n_0^{(b)}(\mathbf{r}') \left[ \nabla'_\gamma u_\gamma(\mathbf{r}') + \frac{\delta \chi^{(b)}}{n_0^{(b)}}(\mathbf{r}') \right] \right\}.
\]

Similarly to [Här+15, eq. (22)], “LHS” contains both terms slowly and rapidly varying in space. The leading order terms in the slow fields \( \mathbf{u} \) and \( \{ \delta n^{(s)} \} \) will be more easily recognized with the following coefficients

\[
\zeta^{(ab)}_{\alpha\beta; g} := \frac{1}{V} \iiint d^3r \, d^3r' \, e^{-i\mathbf{g} \cdot \mathbf{r}} C^{(ab)}(\mathbf{r}, \mathbf{r}') \left( r' - r \right) \alpha \nabla' n_0^{(b)}(\mathbf{r}') ,
\]

\[
\Delta \zeta^{(ab)}_{\alpha\beta; g}(\mathbf{r}') := \frac{1}{V} \iiint d^3r \, d^3r' \, e^{-i\mathbf{g} \cdot \mathbf{r}} C^{(ab)}(\mathbf{r}, \mathbf{r}') \left( r' - r \right) \alpha \nabla' n_0^{(b)}(\mathbf{r}') - \zeta^{(ab)}_{\alpha\beta; g},
\]

\[
\zeta^{(ab)}_g := \frac{1}{V} \iiint d^3r \, d^3r' \, e^{-i\mathbf{g} \cdot \mathbf{r}} C^{(ab)}(\mathbf{r}, \mathbf{r}') n_0^{(b)}(\mathbf{r}') ,
\]

\[
\Delta \zeta^{(ab)}_g(\mathbf{r}') := \frac{1}{V} \iiint d^3r \, d^3r' \, e^{-i\mathbf{g} \cdot \mathbf{r}} C^{(ab)}(\mathbf{r}, \mathbf{r}') n_0^{(b)}(\mathbf{r}') - \zeta^{(ab)}_g.
\]

With these, we can rewrite

\[
\text{“LHS”} = \sum_b \int d^3r \left\{ \zeta^{(ab)}_{\alpha\beta; g} \nabla_\alpha u_\beta(\mathbf{r}) + \zeta^{(ab)}_g \frac{\delta n_0^{(b)}}{n_0^{(b)}}(\mathbf{r}) \right\} + \mathcal{O} \left( \nabla^2 u + \nabla \delta n \right). \tag{6.9}
\]

To see this, the intuitive argument of length scale separation given in [Här+15] can be backed up by consideration of the mean value theorem. We use it to state that both \( \nabla_\alpha u_\beta(\mathbf{r}) \) and \( \delta n^{(s)}(\mathbf{r}) \) assume their volume average \( \bar{\mathbf{r}} \) with

\[
\bar{\mathbf{r}} = \frac{1}{V} \int_V d^3r \mathbf{f}(\mathbf{r}) , \quad \mathbf{f} \in \{ \nabla_\alpha u_\beta, \delta n^{(s)}, \delta c^{(s)} \}
\]

for at least one (not necessarily unique) point \( \mathbf{r}_r \) inside the sample volume \( V \). With \( \mathbf{f}(\mathbf{r}) - \bar{\mathbf{r}} = \Delta \mathbf{r}(\mathbf{r}) \), split off the average values in “LHS”:

\[
\text{“LHS”} = \sum_b \int d^3r' \left\{ \left[ \zeta^{(ab)}_{\alpha\beta; g} + \Delta \zeta^{(ab)}_{\alpha\beta; g}(\mathbf{r}') \right] \left[ \nabla_\alpha u_\beta + \Delta \nabla_\alpha u_\beta(\mathbf{r}') \right] + \\
\right. \\
\left. + \left[ \zeta^{(ab)}_g + \Delta \zeta^{(ab)}_g(\mathbf{r}') \right] \frac{1}{n_0^{(b)}} \left[ \delta n_0^{(b)} + \Delta \delta n_0^{(b)}(\mathbf{r}') \right] \right\}.
\]

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The cross terms in eq. (6.10) vanish by construction. For the $\Delta\Delta$-term we note that

$$
\Delta\nabla_\alpha u_\beta (r') = \nabla_\alpha u_\beta (r' - r_{\nabla_\alpha u_\beta}) \cdot \nabla \nabla_\alpha u_\beta (r_{\nabla_\alpha u_\beta})
$$

$$
\Delta\delta_n^{(s)} (r') = (r' - r_{\delta_n^{(s)}}) \cdot \nabla \delta_n^{(s)} (r_{\delta_n^{(s)}})
$$

In the limit of slowly varying elasticity fields these contributions can be neglected versus the leading order terms. To summarize, this yields eq. (6.9) and turns the condition (6.7) into

$$
\sum_b \sum_{g \in G_0} C_{\mathbf{g} \mathbf{g'}}^{(ab)} \delta n_{\mathbf{g}}^{(b)} = \sum_b \int \mathrm{d}^d r \left\{ \zeta_{\mathbf{g} \mathbf{g'}}^{(ab)} \nabla u_\beta (r) + \zeta_{\mathbf{g} \mathbf{g'}}^{(ab)} \frac{\delta n_{\mathbf{r}_0}^{(b)}}{\eta_{\mathbf{r}_0}^{(b)}} (r) \right\} + \text{h.o.t.} \quad (6.11)
$$

where $C_{\mathbf{g} \mathbf{g'}}^{(ab)} = C^{(ab)} (\mathbf{g}, \mathbf{g'})$.

The higher order terms here consist in both terms of $\mathcal{O} (\delta \rho^2)$ and $\mathcal{O} (\nabla^2 u + \nabla \delta n)$ which become negligible in the limit of small fluctuations (linear response) and spatially slowly varying fields, respectively. Equation (6.11) can be read as an $(B \times \infty) \times (B \times \infty)$-dimensional set of inhomogeneous linear equations. Multiplying it with the inverse of the matrix formed by $C_{\mathbf{g} \mathbf{g'}}^{(ab)}$ will yield $\{\delta n_{\mathbf{g}}^{(s)}\}$ in terms of $\nabla u$ and $\{\delta n_{\mathbf{g}}^{(s)}\}$. A caveat in the above discussion is $\delta n_{\mathbf{g}}^{(s)} = 0$ if the number of particles in the volume $V$ is fixed like in the canonical ensemble. On the other hand, the average particle density inside the sample will clearly be increased by compression (cf. [Här+15, section IV.C.]). Further discussion should include consideration of the grand canonical ensemble and a reformulation of eq. (6.11) with defect densities $\delta c$ rather than particle densities.

Before turning back to the implications of condition (6.11) for elasticity theory we indicate that it can also be formulated fully in reciprocal space. Reconsider eq. (6.7),

$$
0 = \frac{1}{\partial \delta n_{\mathbf{g}}^{(s)}} \left[ \{n_{\mathbf{g}}^{(s)} + \delta \rho^{(s)}\} \right]
$$

$$
= \sum_b \int \mathrm{d}^d r' C^{(ab)} (-\mathbf{g}, r') \delta \rho^{(b)} (r')
$$

$$
= \sum_b \sum_{\mathbf{g}} \int_{BZ} \frac{\mathrm{d}^d q}{(2\pi)^d} C^{(ab)} (-\mathbf{g}, -\mathbf{g}' - \mathbf{q}) \delta \rho^{(b)} (\mathbf{q}) \quad (6.12)
$$
The Fourier transform of $C^{(ab)}$ in a periodic crystal can be written as

$$
C^{(ab)}(\mathbf{k}, \mathbf{k}') = \frac{1}{V} \int d^3r \int d^3r' e^{-i\mathbf{k}\cdot\mathbf{r}} e^{-i\mathbf{k}'\cdot\mathbf{r}'} C(\mathbf{r}, \mathbf{r}')
$$

$$
= \frac{1}{V} \int d^3r e^{i\mathbf{R}\cdot(\mathbf{g}-\mathbf{k})} C^{(ab)}(\mathbf{g}) \left( \frac{\mathbf{k}' - \mathbf{k}}{2} \right)
$$

$$
= \sum_g \delta(\mathbf{g} - \mathbf{k}') C^{(ab)}(\mathbf{g}) \left( \frac{\mathbf{k}' - \mathbf{k}}{2} \right).
$$

With this, rewrite eq. (6.12) as

$$
0 = \sum_b \sum_{g',g''} \int_{BZ} \frac{d^3q}{(2\pi)^3} \int V \delta g''_0 + g + q \phi_{g''_0}^{(ab)} \left( \frac{g' - g + q}{2} \right)
$$

$$
\times \left\{ -n_s^a \mathbf{g}' \cdot \mathbf{u}(q) - 2\delta n_s(q) \right\} + \delta \delta n_s^a(q) \right\}.
$$

The integral over $\mathbf{R}$ in the upper line of eq. (6.14) yields a $\delta$-peak in the thermodynamic limit which will eliminate all contributions for $\mathbf{q} \neq 0$. Beforehand, the leading order contributions need to be identified from the lower line by expanding $\mathbf{u}(\mathbf{q})$ and applying the equation

$$
0 = \sum_{b,g'} J^{(ab)}_{bg'}(\mathbf{q} = 0) n_{g'} \mathbf{g}'.
$$

This is the translational LMBW equation in reciprocal, obtained from a Fourier transform of eq. (5.33). The computations sketched here to rewrite eq. 6.11 fully in reciprocal space are left for future work.

Equations (3.52) in paragraph 3.3.2 introduced elastic constants as second thermodynamic derivatives, based on the principle that the increase in the thermodynamic potential must be quadratic in infinitesimal fluctuations of $u_{\alpha\beta}$ and $\{\delta n_{(s)}\}$. Insertion of the ansatz (6.2b) into the expansion (6.1) with a solution for eq. (6.11) will yield a quadratic form in the fields $\nabla \mathbf{u}$ and $\{\delta n_{(s)}\}$ again. This is not to be confused with an expansion of $\mathbf{F}$ about a non-equilibrium configuration, i.e. at finite $\nabla \mathbf{u}$ and/or $\{\delta n_{(s)}\}$ and thus nonvanishing initial stress $\sigma_0 \neq 0$ (cf. the definition (3.49)). The expansions (6.1) and (3.51a) can indeed be generalized to finite initial stresses $\sigma_0$. How to obtain the resulting generalized elastic constants $B^n_{\alpha\beta\gamma\delta}$ is discussed for the defect-free, one-component, isothermal case in [Wal98, section 4.4] and [Wal67]. These so-called “Birch coefficients” [Bir47] are given in [Kim+07, eq. (2)] for isotropic external (hydrostatic) pressure $\sigma_0 = p_0 \delta_{\alpha\beta}$,

$$
B^n_{\alpha\beta\gamma\delta} = C^n_{\alpha\beta\gamma\delta} + p_0 \left( \delta_{\alpha\beta} \delta_{\gamma\delta} - \delta_{\alpha\gamma} \delta_{\beta\delta} - \delta_{\alpha\delta} \delta_{\beta\gamma} \right).
$$

This reflects the situation in experiments and simulations when external pressure cannot be ignored (also that of the applications in chapter 7).
The ansatz (6.2) together with eq. (6.11) in principle gives the exact linear response of the average particle densities \( \{ n^s(\mathbf{r}) \} \) to the fields \( \nabla \mathbf{u} \) and \( \{ \delta n^s(\mathbf{r}) \} \) in the limit of linear elasticity theory. Its evaluation however is generally not feasible - just like the exact global minimum \( \{ n^s(\mathbf{r}) \} \) of the density functional \( \mathcal{F}[\{ \rho^s(\mathbf{r}) \}] \) normally has to be approximated in an infinite-dimensional function space. In practice, only a limited number of parameters \( \eta_1, \eta_2, \ldots, \eta_L \) can be employed to parametrize the infinite set \( \{ n^s(\mathbf{g}) \} \subseteq G_\mathbf{g}, s \in 1, 2, \ldots, B \}. \) Minimization of \( \mathcal{F}[\{ \rho^s(\mathbf{r}) \}] \) over the set of parameters \( \{ \eta_L \} \) then yields an approximation \( \{ \tilde{n}^s(\mathbf{r}) \} \) to the actual equilibrium densities \( \{ n^s(\mathbf{r}) \} \). In a subsequent step, the condition (6.7) is formulated for each element in \( \{ \eta_L \} \) instead of \( G_\mathbf{g} \). The \( \eta_L \) will be referred to as “relaxation parameters”.

**Example for single sublattice displacement**

We now give an example of the proceeding for a one-parameter relaxation in a binary crystal, assuming \( \{ \delta n^s(\mathbf{r}) \equiv 0 \} \) for a simplified treatment. We parametrize the equilibrium density \( n \) as (cf. eq. (2.13))

\[
n(\mathbf{r}) = \sum_{\mathbf{g} \in G} \left( n_g^{(1)} + n_g^{(2)} \right) e^{i \mathbf{g} \cdot \mathbf{r}} = \sum_{\mathbf{g} \in G} \left( \delta n_{\mathbf{g}}(1) + \delta n_{\mathbf{g}}(2) e^{-i \mathbf{g} \cdot \mathbf{b}} \right) e^{i \mathbf{g} \cdot \mathbf{r}}.
\]

(6.17)

The constant vector \( \mathbf{b} \) determines the relative equilibrium position of the two particles in a unit cell. The phase factor \( e^{i \mathbf{g} \cdot \mathbf{b}} \) is made explicit here as \( \mathbf{b} \) is the single relaxation parameter to be considered.\(^2\) Note that even for the simplest parametrizations of \( n \), determining the equilibrium densities \( n^s(\mathbf{r}) \) involves a minimization over more parameters than \( \mathbf{b} \), e.g. Gaussian widths \( \alpha^s(\mathbf{r}) \) (represented by matrices \( \alpha^s(\mathbf{g}) \) in the anisotropic case). Relaxation of the Gaussian width in a strained primitive lattice has been considered in [JM88], [Kir+90] and [MKR91]. A DFT approach to elastic constants in binary crystals is presented in [TT94, §4], restricted however to crystals with inversion symmetry. Here, no such symmetry assumption is made. The limitation to the basis vector \( \mathbf{b} \) as a relaxation parameter corresponds to the thermodynamic constraint that the \( \{ \delta n_{\mathbf{g}} \} \) remain fixed.

With the given approximations and the chain rule

\[
\delta n_{\mathbf{g}}^s = \frac{\partial n_{\mathbf{g}}^s}{\partial \delta \mathbf{b}} \delta \mathbf{b},
\]

the general equilibrium density fluctuation eq. (6.2a) is now confined to

\[
\delta \rho^s(\mathbf{r}) = -\mathbf{u}(\mathbf{r}) \cdot \nabla n^s(\mathbf{r}) - i \delta s_2 \delta \mathbf{b} \cdot \sum_{\mathbf{g} \in G} \mathbf{g} \delta n_{\mathbf{g}}^s e^{i \mathbf{g} \cdot (\mathbf{r} - \mathbf{b})} \]

\[
= -\mathbf{u}(\mathbf{r}) \cdot \nabla n^s(\mathbf{r}) - \delta s_2 \delta \mathbf{b} \cdot \nabla n^s(\mathbf{r}).
\]

\(^2\)We choose as convention that the first species be centered about the coordinate origin with a basis vector confined to \( \mathbf{0} \).
With this, the expansion eq. (6.6) can be rewritten in a form specific to the given parametrization. The equilibrium condition for $b$

$$\frac{\partial F}{\partial b_{\alpha}} \{ n^{(s)} + \delta \rho^{(s)} \} = 0, \quad \alpha = 1, \ldots, d,$$

then yields the analogue of eq. (6.7) as

$$\sum_{b} \int d^{d}r d^{d}r' \nabla n^{(2)} (r) C^{(2b)} (r, r') \left[ \Delta r_{c} \nabla_{\beta} n^{(b)} (r') \right] \nabla_{\alpha} u_{\beta} (r') + \text{ h.o.t.} \quad \Rightarrow \int d^{d}r d^{d}r' \nabla n^{(2)} (r) C^{(22)} (r, r') \nabla n^{(2)} (r') \cdot \delta b.$$  

Provided that $\mathbf{Y}$ is invertible, this can be solved for $\delta \mathbf{b}$ to

$$\delta b_{\alpha} = Y^{-1}_{\alpha \beta} \int d^{d}r d^{d}r' \sum_{b} \nabla_{\beta} n^{(2)} (r) C^{(2b)} (r, r') \left[ \Delta r_{c} \nabla_{\gamma} n^{(b)} (r') \right] \nabla_{\gamma} u_{\delta} (r') + \text{ h.o.t.},$$

with the coupling tensor $\chi$ defined as

$$\chi_{\alpha \gamma \delta} := \frac{1}{V} Y^{-1}_{\alpha \beta} \int d^{d}r d^{d}r' \sum_{b} \nabla_{\beta} n^{(2)} (r) C^{(2b)} (r, r') \left[ \Delta r_{c} \nabla_{\gamma} n^{(b)} (r') \right].$$  

Equation (6.19a) is obtained with the same mean-value argument as eq. (6.11). In crystals with a center of inversion, coordinates can be chosen such that

$$\nabla_{\delta} n^{(b)} (r') = -\nabla_{\delta} n^{(b)} (-r') \quad \text{and} \quad C^{(ab)} (r, r') = C^{(ab)} (-r, -r').$$

Then

$$\chi_{\alpha \gamma \delta} = \frac{1}{V} Y^{-1}_{\alpha \beta} \int d^{d}r d^{d}r' \nabla_{\beta} n^{(2)} (r) C^{(2b)} (r, r') \left[ \Delta r_{c} \nabla_{\gamma} n^{(b)} (r') \right] \quad \Rightarrow \quad \int d^{d}r d^{d}r' \nabla_{\beta} n^{(2)} (r) C^{(2b)} (-r, -r') \left[ \Delta r_{c} \nabla_{\gamma} n^{(b)} (-r') \right] \quad \Rightarrow \quad -\int d^{d}r d^{d}r' \nabla_{\beta} n^{(2)} (r) C^{(2b)} (r, r') \left[ \Delta r_{c} \nabla_{\gamma} n^{(b)} (r') \right] = 0 \quad (6.20)$$

shows the independence of $\delta \mathbf{b}$ from linear strain for such systems. We will come back to $\chi$ for a comparison with [Wal98, section 2.7] in section 8.2.
7. Application to binary hard sphere crystals

This chapter is dedicated to the determination of the phonon eigenmodes for various binary hard sphere (HS) crystals. The discontinuity of the interaction potential renders these systems inaccessible to potential expansion approaches, making them an appealing application example. The first section 7.1 will consider a simple DFT approach to determine both the crystalline equilibrium densities \( n^{(1)}, n^{(2)} \) at the freezing point and from that the dispersion relations. It is based on the work of Haymet and Rick presented in [RH89; RH90]. The second section 7.2 will determine dispersion relations from particle-position snapshots obtained within a Molecular Dynamics (MD) simulation of a binary HS crystal. The homogeneous liquid state in both cases is characterized by the following parameters:

\[
\begin{align*}
\sigma^{(s)} : & \text{ sphere diameter of species } s = 1, 2, \\
m^{(s)} : & \text{ particle mass of species } s, \\
n^{(s)}_{\text{liq}} = \frac{N^{(s)}}{V} : & \text{ particle density of species } s.
\end{align*}
\]

We assume \( \sigma^{(1)} \leq \sigma^{(2)} \) w.l.o.g. Firstly, the qualitative behavior of the system is invariant under simultaneous rescaling of both the spheres \( \sigma^{(s)} \rightarrow \alpha \sigma^{(s)}, s = 1, 2 \) and the system volume \( V \rightarrow \alpha V \). Secondly, for the structures studied in the following the close packing limit will be determined by \( \sigma^{(2)} \). Consequently all lengths will be given in units of \( \sigma^{(2)} \). Using a diameter ratio \( \sigma^{(1)} / \sigma^{(2)} = : \varsigma \). Particle masses will similarly be given in units of \( m^{(2)} =: m \).

7.1. DFT approach

As sketched in chapter 4 DFT reduces the question of thermodynamic stability to the minimization of an — a priori unknown — density functional \( \mathcal{F}^{\text{ex}} \left[ n^{(1)}, n^{(2)} \right] \) (cf. [CL10, eq. (3.1.45)]). Assuming this functional is known at reference densities \( \{ n^{(1)}_0, n^{(2)}_0 \} \), it can be expanded in a functional power series (cf. [DA91, section II A]),

\[
\begin{align*}
\beta \left( \mathcal{F}^{\text{ex}} \left[ n^{(1)}, n^{(2)} \right] - \mathcal{F}^{\text{ex}} \left[ n^{(1)}_0, n^{(2)}_0 \right] \right) = & \\
= - \sum_{m=1}^{\infty} \frac{1}{m!} \prod_{n=1}^{m} \int d^n r_n \sum_{s_n=1}^{2} c^{(s_1...s_m)} (r_1, \ldots, r_m; n^{(1)}_0, n^{(2)}_0) \Delta n^{(s_1)} (r_1) \ldots \Delta n^{(s_m)} (r_m)
\end{align*}
\]

[71]
with the direct correlation functions $c^{(s_1...s_m)}$ obtained from eq. (4.6) and $\Delta n^{(s)} = n^{(s)} - n^{(s)}_0$. The theory of homogeneous liquids provides various expressions for $c^{(ab)}$ out of which we will employ the HS result found for the Percus–Yevick integral equation [PY58] by Wertheim [Wer63] and generalized to binary systems by Lebowitz [Leb64]. An approach to the freezing of a HS liquid is obtained from truncating the expansion (7.1) after $m = 2$ with $n^{(s)}_0 \equiv n^{(s)}_\ell$ the homogeneous fluid and $n^{(s)}$ the solid particle densities. This is the so-called “Ramakrishnan–Yousuf approximation” [RY79] which was first applied to the freezing of binary HS mixtures in [SH87; Hay87].

Liquids and solids normally coexist at different densities. This is accounted for by comparing the grand potential difference between solid and liquid phase $\Delta \Omega = \Omega_s\{\mu^{(s)}_s\}, V, T - \Omega_l\{\mu^{(s)}_l\}, V, T$ at pairwise equal chemical potentials $\mu^{(s)}_s = \mu^{(s)}_l$. Stability of the liquid/solid phase, is indicated by a positive/negative $\Delta \Omega$, phase coexistence by $\Delta \Omega = 0$. The first term of the expansion (7.1) can be rewritten as

$$\int d^d r \sum_{s=1}^2 c^{(s)}(r; n^{(1)}_0, n^{(2)}_0) \Delta n^{(s)}(r) = - \int d^d r \sum_{s=1}^2 \left\{ \beta \mu^{(s)} - \ln \left[ n^{(s)}_0(r) \lambda^{(s)}_f^2 \right] \right\} \Delta n^{(s)}(r)$$

where we employed eqs. (4.3) and (4.5). $\Delta \Omega(\mu, V, T)$ is now obtained from

$$\Delta \Omega = \mathcal{F} \left[ n^{(1)}_0, n^{(2)}_0 \right] - \mathcal{F} \left[ n^{(1)}_0, n^{(2)}_0 \right] - \sum_{s=1}^2 \mu^{(s)} \int d^d r \Delta n^{(s)}(r)$$

$$= k_B T \sum_{s=1}^2 \int d^d r \left\{ n^{(s)}(r) \ln \left[ n^{(s)}_0(r) \right] - \Delta n^{(s)}(r) \right\} + \sum_{s=1}^2 \mu^{(s)} \int d^d r \Delta n^{(s)}(r)$$

$$= k_B T \sum_{a,b=1}^2 \int d^d r \int d^d r' c^{(ab)}(r,r') \Delta n^{(a)}(r) \Delta n^{(b)}(r') + \mathcal{O}\left(\Delta n^{(3)}\right).$$

$c^{(ab)}(r,r') = c^{(ab)}(|r-r'|; n^{(1)}_\ell, n^{(2)}_\ell)$ is taken to be the Percus–Yevick (second-order) direct correlation function, evaluated at the homogeneous liquid densities $n^{(1)}_\ell, n^{(2)}_\ell$. Isotropy and translational invariance of $c^{(ab)}$ are absent in a crystal. The formally exact expression (7.1) accounts for this by the lattice-periodic expansion arguments $\Delta n^{(s)}$. The lack of knowledge about $c^{(s_1...s_m)}$ of arbitrary order $m$ is considered a limit to the reliability of this approach [DA91]. Haymet and Rick include part of the third order terms $\Delta \Omega^{ex}_3$ based on the reciprocal-space relation

$$c^{(abc)}(k=0,k'=0) = \frac{\delta c^{(ab)}(k=0)}{\delta n^{(c)}_\ell}.$$

Their approximation $\Delta \Omega_{\text{HR}}$ in total reads

$$\Delta \Omega_{\text{HR}} = \Delta \Omega^{\text{id}} + \Delta \Omega^{\text{ex}}_2 - \frac{k_B T}{6} \sum_{a,b,c=1}^2 c^{(ab)}(k=0,k'=0) \Delta n^{(a)}_0 \Delta n^{(b)}_0 \Delta n^{(c)}_0.$$
where $\Delta n_0^{(s)} = n_s^{(s)} - n^{(s)}$ and $n_s^{(s)} = N_s^{(s)} / V$ are the average particle densities in the solid phase. We will henceforth set $\beta \Delta \Omega = \Delta \Omega$ as for HS systems the thermodynamic potentials scale linearly with temperature, leaving the coexistence densities invariant.

Explicit discussion of the contributions $\Delta \Omega^{id}$ and $\Delta \Omega^{ex}_2$ requires a parametrization of the crystal equilibrium densities $\{n^{(s)}\}$. The most transparent choice is a truncation of the Fourier series (3.55) to subsets $G^{(s)} \subset G$ of the reciprocal lattice, yielding the order parameters $\eta^{(s)}_g$ themselves as parameters. It recovers the exact equilibrium density in the limit of infinitely many parameters. Simpler but still physically-motivated is the Gaussian parametrization first proposed in [Jac83],

$$n^{(s)}(r) = \eta^{(s)} \left( \frac{\alpha^{(s)}}{\pi} \right)^{3/2} \sum_{\mathbf{R} \in \mathbf{L}} e^{-\alpha^{(s)} \left( r - \mathbf{R} - \mathbf{b}^{(s)} \right)^2}, \quad s = 1, \ldots, B \quad (7.2)$$

with the following parameters for the solid phase at equilibrium

- $\eta^{(s)}$: occupancy of sublattice $s$,
- $\alpha^{(s)} = 1 / \varepsilon^{(s)}$: Gaussian localization on sublattice $s$,
- $\mathbf{R} \in \mathbf{L}$: Bravais lattice vectors,
- $\mathbf{b}^{(s)}$: basis vector of sublattice $s$,
- $n_s^{(s)}$: particle density of species $s$.

Now for some comments on these parameters: The occupancies $\eta^{(s)}$ account for the presence of point defects which in monodisperse HS crystals occur with a low concentration of approx. $10^{-4}$ per particle and occur almost exclusively as vacancies ($\eta \lesssim 1$, cf. [PF01]). A subsequent study for polydisperse HS crystals is presented in [PF04] and shows an increase in the concentration of interstitials up to the percent range with polydispersity. For the present case of bidisperse HS crystals we will initially follow the quoted works of Haymet et al. in neglecting point defects entirely ($\eta^{(s)} = 1$). The general crystal case actually requires the ansatz of anisotropic Gaussian density peaks. This corresponds to a symmetric, positive definite "localization" matrix $\alpha^{(s)}$ as employed in [JM88, eq. (4.2)]. However, as further stated in eq. (C16) therein, these matrices become proportional to the unity matrix in the cubic crystal system. This special case applies to all examples studied in the following. We also introduced the rewriting $\varepsilon^{(s)} = 1 / \sqrt{\alpha^{(s)}}$ with the physical unit of a length for easier interpretation. Finally note that the Bravais lattice $\mathbf{L}$ of the considered crystal phase is implicitly assumed in the sum in eq. (7.2). The ansatz will be evaluated for two different crystal structures to be specified below. In both of these cases, the volume of the primitive unit cell $V_c = 1 / n_c = n^{(s)} / n_s^{(s)}$ is the inverse of the unit cell density. The ideal gas part $\Delta \Omega^{id} = \Delta \Omega^{id,(1)} + \Delta \Omega^{id,(2)}$

---

1The extension of that statement from a single matrix $\alpha$ to $\alpha^{(s)}$ for several species follows from the fact that each $\alpha^{(s)}$ has to be separately invariant under the point group of the given crystal.
can be written as a sum of single-species contributions. Nontrivial is the integration
\[
\mathcal{I}_{\text{id}}^{(s)} = \frac{1}{V} \int d^d r \sum_{R \in \mathbb{L}} e^{-\left(\frac{r-R}{\gamma(s)}\right)^2} \ln \left[ \sum_{R' \in \mathbb{L}} e^{-\left(\frac{r-R'}{\gamma(s)}\right)^2} \right],
\]
notably for the regime \( \varepsilon(s) \geq 0.2 \) occurring for the small species at sufficiently high size disparity \( \varsigma \).\(^2\) As long as the localization of the particles \( \varepsilon(1) < 0.2 \), overlap of the density peaks from different lattice sites can be neglected and the integral (7.3) can be approximated by a sum of “single-site contributions”,
\[
\mathcal{I}_{\text{id,joint}}^{(s)} \approx \frac{1}{V} \int d^d r \sum_{R \in \mathbb{L}} e^{-\left(\frac{r-R}{\gamma(s)}\right)^2} \ln \left[ e^{-\left(\frac{r-R}{\gamma(s)}\right)^2} \right] = -\frac{3}{2} \eta(s) \frac{\pi^{3/2}}{2} \varepsilon(s)^3.
\]
For \( \varepsilon(s) \geq 0.2 \), lattice sites adjacent to \( R \) contribute to the logarithm in eq. (7.3). With a suitable set of lattice points \( \mathbb{A} \subset \mathbb{L} \) in the vicinity of \( R \) (usually \( 10 \) to \( 100 \) nearest neighbor shells), \( \mathcal{I}_{\text{id}}^{(s)} \) is generalized to
\[
\mathcal{I}_{\text{id,olap}}^{(s)} \approx \frac{1}{V} \int d^d r \sum_{R \in \mathbb{L}} e^{-\left(\frac{r-R}{\gamma(s)}\right)^2} \ln \left[ \sum_{\Delta R \in \mathbb{A}} e^{-\left(\frac{r-(R+\Delta R)}{\gamma(s)}\right)^2} \right]
\]
which has to be integrated numerically. Exploiting the symmetry of the fcc lattice, the integration area can be restricted to \( 1/48 \) of the Wigner-Seitz cell, i.e. \( 1/192 \) of the conventional unit cell. The integral (7.5) corresponds to [RH89, eq. (A4)]. Compared to this previous work, the second approximation eq. (7.5) was evaluated for larger sets \( \mathbb{A} \) and found to become relevant already for smaller values of \( \varepsilon \) than the stated 0.3. In combination, \( \Delta \Omega^{\text{id},(s)} \) was evaluated as
\[
\Delta \Omega^{\text{id},(s)} / V = \begin{cases} 
\frac{n_{\ell}^{(s)} - n_{s}^{(s)}}{\ell} \left[ \ln \left( n_{\ell}^{(s)} \right) + 3 \ln \left( \frac{\pi^{1/2}}{\gamma(s)} \right) + 5 \right] - \ln \eta(s), & \varepsilon(s) < 0.2, \\
\frac{n_{\ell}^{(s)} - n_{s}^{(s)}}{\ell} \left[ \ln \left( n_{\ell}^{(s)} \right) + 3 \ln \left( \frac{\pi^{1/2}}{\gamma(s)} \right) + 1 + \frac{\eta(s)}{\gamma(s)} \mathcal{I}_{\text{id,olap}}^{(s)} \right] - \ln \eta(s). & \varepsilon(s) \geq 0.2.
\end{cases}
\]
Rather than evaluating \( \Delta \Omega^{\text{id},(s)}_2 \) with the above mentioned approximations for \( c^{(ab)} \) and \( n^{(s)} \), we will take a step back to the general expression for \( \Delta \Omega^{\text{id},(s)}_2 \). It can be transformed to reciprocal space by application of Plancherel’s theorem. The following auxiliary function will prove to be useful\(^3\)
\[
h^{(ab)}_{\mathbf{q};\alpha_1,\ldots,\alpha_l}(\mathbf{r}) := \int d^d r' c^{(ab)}(\mathbf{r},\mathbf{r}') e^{-i\mathbf{q} \cdot (\mathbf{r}-\mathbf{r}')} \nabla'_{\alpha_1} \cdots \nabla'_{\alpha_l} n^{(b)}(\mathbf{r}'),
\]
\(^2\)While the nearest-neighbor distance in the HS crystals studied below is always greater than \( \sigma \) it never exceeds the value of \( \sigma \) by far.
\(^3\)The parameters \( \mathbf{q} \) and \( \alpha_1,\ldots,\alpha_l \) are obsolete in the present context but will be needed below for a similar rewriting of the dynamical matrix \( \mathbf{A} \). For the cases \( \mathbf{q} = 0 \) and \( i = 0 \), we will omit the respective parameters in the subscript.
which is transformed after inserting the Fourier series expansion \((5.21)\) for \(c^{(ab)} \equiv c^{(ab)} \left(\cdot, \cdot ; n_0^{(1)}, n_0^{(2)} \right)\),

\[
\begin{align*}
  & h^{(ab)}_{\mathbf{q}; \alpha_1,\ldots,\alpha_l} (\mathbf{q}') = \\
  & = \int d^d r e^{-i \mathbf{q}' \cdot \mathbf{r}} \int d^d r' c^{(ab)} (\mathbf{r}, \mathbf{r}') e^{-i \mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')} \nabla'_{\alpha_1} \ldots \nabla'_{\alpha_l} n^{(b)} (\mathbf{r}') \\
  & = \int d^d r e^{-i \mathbf{q}' \cdot \mathbf{r}} \int d^d r' \sum_G e^{i \mathbf{G} \cdot \mathbf{q}'} c^{(ab)}_G (\mathbf{r} - \mathbf{r}') e^{-i \mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')} \nabla'_{\alpha_1} \ldots \nabla'_{\alpha_l} n^{(b)} (\mathbf{r}') \\
  & = \int d^d R \int d^d \Delta r e^{-i \mathbf{q}' \cdot (\mathbf{R} + \Delta \mathbf{r} / 2)} \sum_G e^{i \mathbf{G} \cdot \mathbf{R}} c^{(ab)}_G (\Delta \mathbf{r}) e^{-i \mathbf{q} \cdot \Delta \mathbf{r}} \sum_g i^g (g_{\alpha_1} \ldots g_{\alpha_l}) n^{(b)}_g e^{i \mathbf{G} \cdot (\mathbf{R} - \Delta \mathbf{r} / 2)} \\
  & = \sum_{G,g} (2\pi)^3 \delta (\mathbf{q}' - \mathbf{G} - \mathbf{g}) c^{(ab)}_G \left( \mathbf{q} + \frac{\mathbf{q}' + \mathbf{g}}{2} \right) i^g (g_{\alpha_1} \ldots g_{\alpha_l}) n^{(b)}_g. \tag{7.8}
\end{align*}
\]

To compute \(\Delta \Omega_2^{ex}\), we first apply eq. \((7.8)\) to

\[
\begin{align*}
  & \sum_{a,b=1}^2 \int d^d r d^d r' n^{(a)} (\mathbf{r}) c^{(ab)} (\mathbf{r}, \mathbf{r}') n^{(b)} (\mathbf{r}') = \\
  & = \sum_{a,b=1}^2 \int d^d r n^{(a)} (\mathbf{r}) h^{(ab)} (\mathbf{r}) = \frac{1}{(2\pi)^d} \sum_{a,b=1}^2 \int d^d \mathbf{q}' n^{(a) \ast} (\mathbf{q}') h^{(ab)} (\mathbf{q}') \\
  & = \frac{1}{(2\pi)^d} \sum_{a,b=1}^2 \int d^d \mathbf{q}' \sum_{G} n^{(a) \ast}_G \int d^d \mathbf{r} e^{i (\mathbf{q}' - \mathbf{G}) \cdot \mathbf{r}} h^{(ab)} (\mathbf{q}') \\
  & = V \sum_{a,b=1}^2 \sum_{G} n^{(a) \ast}_G c^{(ab)}_G (\mathbf{g} + \frac{\mathbf{G}}{2}) n^{(b)}_G. \tag{7.9}
\end{align*}
\]

The direct correlation function \(c^{(ab)}\) employed in the above expressions has as arguments not necessarily \(\{n^{(s)}\}\). As stated above, we approximate it here by a binary homogeneous liquid result \(c^{(ab)} \left( |\Delta \mathbf{r}|; n_0^{(1)}, n_0^{(2)} \right)\) whose Fourier components \(c_G\) vanish except \(c_{G=0}^{(ab)}\) because of translational invariance. The fluid term in \(\Delta n^{(s)}\) contributes to eq. \((7.9)\) only at \(\mathbf{g} = \mathbf{0}\) such that

\[
\Delta \Omega_2^{ex} = -\frac{1}{2} \sum_{a,b=1}^2 \sum_{G} \Delta n^{(a) \ast}_G c^{(ab)}_G (\mathbf{g}) \Delta n^{(b)}_G \tag{7.10}
\]

with \(\Delta n^{(s)}_G = \begin{cases} \Delta n^{(s)}_0, & \mathbf{g} = \mathbf{0}, \\ n^{(s)}_G, & \text{else}. \end{cases} \)
To summarize,

\[
\frac{\beta}{V} \Delta \Omega_{HR} = \sum_{s=1}^{2} \Delta \Omega_{d,(s)}^{(d)} \cdots \sum_{a,b=1}^{2} \sum_{g \in G} c^{(ab)}(g) \Delta n_{g}^{(a)} \Delta n_{g}^{(b)} + \frac{1}{6} \sum_{a,b,c=1}^{2} c^{(abc)}(k = 0, k' = 0) \Delta n_{0}^{(a)} \Delta n_{0}^{(b)} \Delta n_{0}^{(c)}. \tag{7.11}
\]

The \( c^{(ab)}(g) \) are obtained from a Fourier transform of [Leb64, eq. (37)], facilitated by use of the general expression for spherosymmetric functions \( f(r) = f(k) = \int_{0}^{\infty} dr r \sin(kr) f(r). \) (7.12)

The expansion of \( c^{(ab)}(k) \) at \( k = 0 \) can be obtained by evaluating eq. (7.12) with the power series of \( \sin(kr)/k \). This is helpful to avoid numerical artifacts in the limit \( \lim_{k \to 0} c^{(ab)}(k) \).

For the ansatz (7.2) the order parameters can be split up into three parts with distinct physical meaning,

\[
n^{(s)}_{g} = n^{(s)} \times e^{-ig \cdot b^{(s)}} \times e^{-g^{2} \varepsilon^{2}(s)/4}. \tag{7.13}
\]

The Debye-Waller factor ensures that the reciprocal lattice sum in eq. (7.10) converges and that it is usually dominated by a small number of nearest neighbor shells to the origin in the reciprocal lattice.\(^4\)\(^5\) The freezing-transition is obtained by the following procedure:

0. Choose equilibrium crystal candidate and liquid stoichiometry \( n_{l}^{(1)} / n_{l}^{(2)} = \chi. \) (This determines the exact form of \( \Delta \Omega_{HR} \). The approach can of course be generalized to a set of potential crystal structures.)

1. Choose estimated liquid freezing density \( n_{l}^{(2)}. \)

2. Determine \( \min_{(n^{(s)}_{s}), \{\varepsilon(s)\}} \frac{\beta}{V} \Delta \Omega_{HR} \left(n_{l}^{(2)}\right). \)

3. Go back to 2. until root \( \Delta \Omega_{HR} \left(n_{l}^{(2)} = n_{l}^{(2),\text{crit}}\right) \) is found to the desired accuracy.

4. Return minimum \( n_{l}^{(2)} \) as crystal melting parameters.

\(^4\)The triplet term \( \Delta \Omega_{ex}^{(3)} \) will show two Debye-Waller factors. Thus contributions other than the \((0,0,0)\)-term in eq. (7.11) decay more strongly.

\(^5\)Note that specifically for this parametrization it is not necessary to resort to the Fourier representation by \( n_{g}^{(s)}. \) The integration in eq. (7.9) can be rewritten as a product of two Gaussian integrals and subsequently be evaluated along the lines of the single-species real-space approach in [DE06].
7.1 DFT approach

It is important to bear in mind that the above ansatz to describe the freezing-transition of HS mixtures is only an expedient to obtain expressions for the crystal equilibrium densities \( \{ n^{(s)} \} \). Any other approach to obtain \( \{ n^{(s)} \} \) of thermodynamically stable crystals (at given solid densities \( \{ n^{(s)} \} \) and temperature \( T \)) can be used as well. With the solid equilibrium densities at hand the next step will be to determine the dispersion relations/eigenmodes \( \omega(a) (\mathbf{q}) \) from the dynamical matrix \( \Lambda (\mathbf{q}) \) eq. (5.14).

### 7.1.1. Evaluation of the dispersion relations

Before moving on to the discussion of specific crystal structures we give the general expression for \( \Lambda \) in reciprocal space. Recall the expanded form of \( \Lambda \) eq. (5.37) which can be rewritten with the auxiliary function eq. (7.7), written in reciprocal space in eq. (7.8)

\[
\Lambda^{(ab)} (\mathbf{q}) = \frac{N^{(a)} \theta_0}{\beta V \theta_0^{(a)}} q q \delta_{ab} + \frac{\theta_0}{\beta V} \int d^d r \left\{ \sum_s \frac{\delta_{ab}}{2 \theta_0^{(a)}} \left[ -2qqn^{(a)}_s (\mathbf{r}) h^{(as)}_s (\mathbf{r}) + \right. \right.
\]
\[
\left. \left. + (i \nabla + q) n^{(a)}_s (\mathbf{r}) \left( -i h^{(as)}_s (\mathbf{r}) + q h^{(as)}_s (\mathbf{r}) \right) \right] + \right. \right.
\]
\[
\left. \left. + \left[ (i \nabla + q) n^{(a)}_s (\mathbf{r}) \left( -i h^{(as)}_s (\mathbf{r}) + q h^{(as)}_s (\mathbf{r}) \right) \right]^\dagger \right] + \right. \right.
\]
\[
- \frac{1}{\theta_0^{(b)}} (i \nabla + q) n^{(a)}_s (\mathbf{r}) \left( -i h^{(ab)}_{\mathbf{q}} (\mathbf{r}) + q h^{(ab)}_{\mathbf{q}} (\mathbf{r}) \right) \right\}.
\]

Note the second and third line are mutually adjoint. With Plancherel’s theorem,

\[
\Lambda^{(ab)} (\mathbf{q}) = \frac{N^{(a)} \theta_0}{\beta V \theta_0^{(a)}} q q \delta_{ab} + \frac{\theta_0}{\beta V} \frac{1}{(2\pi)^d} \int d^d q' \left\{ \sum_s \frac{1}{2 \theta_0^{(a)}} \left[ -2qqn^{(a)*}_s (\mathbf{q}') h^{(as)}_s (\mathbf{q}') + \right. \right.
\]
\[
\left. \left. + (i \mathbf{q}' + q) n^{(a)*}_s (\mathbf{q}') \left( -i h^{(as)}_s (\mathbf{q}') + q h^{(as)}_s (\mathbf{q}') \right) \right] + [\ldots]^\dagger \right] + \right. \right.
\]
\[
- \frac{1}{\theta_0^{(b)}} (i \mathbf{q}' + q) n^{(a)*}_s (\mathbf{q}') \left( -i h^{(ab)}_{\mathbf{q}} (\mathbf{q}') + q h^{(ab)}_{\mathbf{q}} (\mathbf{q}') \right) \right\}
\]

which, inserting eq. (7.8), gives

\[
\Lambda^{(ab)} (\mathbf{q}) = \frac{N^{(a)} \theta_0}{\beta V \theta_0^{(a)}} q q \delta_{ab} + \frac{\theta_0}{\beta} \sum_{G,g} \left\{ \sum_s \frac{\delta_{ab}}{2 \theta_0^{(a)}} \left[ -2qqn^{(a)*}_g + G c^{(as)}_G (g + \frac{G}{2}) n^{(s)}_g + \right. \right.
\]
\[
\left. \left. + (g + G + q) n^{(a)*}_g c^{(as)}_G (g + \frac{G}{2}) (g + q) n^{(s)}_g + [\ldots]^\dagger \right] + \right. \right.
\]
\[
- \frac{\theta_0}{\theta_0^{(b)}} (g + G + q) n^{(a)*}_g c^{(ab)}_G (g + \frac{G}{2} + q) (g + q) n^{(b)}_g \right\}. \quad (7.14)
\]
(a) Conventional unit cell of the sodium chloride (NaCl) structure

(b) Schematic illustration of the random fcc structure

Figure 7.1.: Illustrations of the two crystal structures employed. (a) shows the conventional unit cell of the sodium chloride (NaCl) structure with the small/large ("sodium/chloride") spheres in red/blue. For the random fcc structure, the particle positions in the primitive unit cell are obtained from the blue spheres in (a) alone. Their statistical occupation with large/small spheres of a given size ratio is schematically illustrated by azimuthal angles in (b).

With the Percus–Yevick ansatz for $c^{(ab)}$, i.e. that of a translationally invariant liquid, the sum over $G$ in eq. (7.14) vanishes like in eq. (7.10), yielding

$$\Lambda^{(ab)}(q) = \frac{c^{(ab)}}{\beta V} \sum_{g} \delta(q - q_g) n^{(s)}(g) + \sum_{s} \left[ -2 q q n^{(s)}(g) n^{(s)}(g) + (g + q) n^{(s)}(g) (g + q) n^{(s)}(g) + \left( (g + q) n^{(as)}(g) (g + q) n^{(s)}(g) \right) \right] +$$

$$- \left( \frac{\rho_0}{\rho} \right) (g + q) n^{(as)}(g) (g + q) n^{(s)}(g) \right) \right]. \quad (7.15)$$

From the HS crystal structures described in [SH87, section II] the "ordered sodium chloride (NaCl) structure" (3) and the "substitutionally disordered (random) fcc crystal" (1) will be now reconsidered, generalizing the latter to a non-equimolar fluid phase in paragraph 7.1.4. Schematic illustrations of these two structures are shown in figure 7.1 as conventional unit cells. These are not to be misread as unique microscopic pictures which by the nature of the thermodynamic equilibrium approach cannot be given (nor are required). Figure 7.1(b) in particular depicts the proportion to which the underlying fcc lattice is occupied by small/large spheres through an azimuthal angle.
7.1 DFT approach

Figure 7.2.: Parameters of the HS NaCl structure equilibrium density at solid-liquid coexistence. (a) compares the present results with those of [RH90, figure 3]. The lower/upper curves show the liquid/solid densities \( n_{s,1}^{\text{crit}} \) of both single species at coexistence. (b) shows the coexistence widths \( \varepsilon_{(s)} \) of both Gaussians. For comparison also the width \( \varepsilon_{\text{crit}} \) is shown, obtained from \( n_s^{\text{crit}} \) and the Lindemann-criterion of melting.

7.1.2. NaCl structure

Figure 7.2 compares the results of Haymet et al. [RH90, figure 3] with own ones for the defect-free NaCl crystal. For this specific example both liquid and solid phase are taken to be equimolar and consequently characterized by a single particle density \( n_{s,1/2} \). Finally both species are confined to separate sublattices. These assumptions correspond to \( \eta_{(1)} = \eta_{(2)} = 1 \) and \( b_{(1)} \neq b_{(2)} \) in eq. (7.2). The coexistence densities \( n_{s,1}^{\text{crit}} \) in figure 7.2(a) show good agreement for diameter ratios \( 0.25 \leq \zeta < 0.445 \geq \sqrt{2} - 1 \). The upper discrepancy starts slightly above the size of the octahedral gap which contains the smaller species. If \( \sigma_{(1)} \) exceeds the size of that gap to a certain extent the smaller hard spheres impose a lower bound to the lattice constant. This effect does not show exactly at \( \zeta = \sqrt{2} - 1 \) because the larger spheres are not exactly at close packing. A possible explanation for the lower critical densities of the reproduced results compared to those of Haymet are inaccuracies in the numerical integration of the ideal gas contribution \( \Delta H_{id} \) at higher \( \varepsilon_{(2)} \) for which the approximation (7.6) of \( \Delta H_{id} \) does not hold. This would require a more detailed study of [RH89, eqs. (A2) to (A14)]. A further physical check to the present results is shown in figure 7.2(b) as a critical Lindemann-length \( \varepsilon_{\text{crit}} \). The Lindemann-criterion of melting states for the mean square displacement \( \langle r^2 \rangle \) of a particle bound to a

\footnote{The parameters of all plots shown in this section are listed in table 7.1}
Chapter 7  Application to binary hard sphere crystals

lattice site of a melting crystal [BZR14],

$$\frac{\sqrt{\langle r^2 \rangle}}{a_0} \approx 0.07$$

with \( a_0 \) : primitive lattice constant/nearest neighbor distance. \( \text{(7.16)} \)

which is applied here with the given critical density \( n_{\text{crit}} \) (rather than a melting temperature). “Nearest neighbor” refers to a site of the same sublattice. It is easy to see from figure 7.1 that in fcc lattices \( a_0 \) is related to the edge length \( a \) of the conventional unit cell cube by a factor of \( \sqrt{2} \). \( a = \sqrt{2}a_0 \) is obtained from the conventional unit cell as \( a = (4/n_{\text{crit}})^{1/3} \) and will be referred to as the (conventional) lattice constant. Evaluating eq. (7.2) for a single lattice site yields \( \langle r^2 \rangle (\varepsilon(s)) = 3/2\varepsilon(s)^2 \). Equation (7.16) can then be solved for \( \varepsilon \) to obtain

$$\varepsilon_{\text{crit}} \approx \frac{0.07}{\sqrt{3}} \left( \frac{4}{n_{\text{crit}}} \right)^{1/3} .$$

\( \text{(7.17)} \)

Figure 7.2(b) shows a qualitative agreement of \( \varepsilon^{(2)} \) and \( \varepsilon_{\text{crit}} \) evaluated with \( n_{\text{crit}} \). The variations of the latter are too small to be visible on the \( \varepsilon \)-range of the plot.

An example of the dispersion relation for \( \zeta = 0.445 \) is shown in figure 7.3(a). Equal particle masses \( m^{(1)} = m^{(2)} \) were assumed for simplicity. The set of wave-vectors \( q \) for which the symmetrized dynamical matrix \( \tilde{\mathbf{A}}(q) \) (cf. eq. (5.25)) has been numerically diagonalized is visualized in figure 7.3(b). It includes the 2-, 3- and 4-fold symmetry axes of the NaCl structure inside the first Brillouin zone and two segments on the BZ boundary. The cartesian axes are chosen along the 4-fold axes which point along the edges of the primitive unit cells of figure 7.1 in real space. The numerical values of actual wave vectors follow from the size of the Brillouin zone whose extension is proportional to the inverse lattice constant. For every example of this chapter, e.g. the segment \( \Gamma X = \Delta \) has a length of \( 4\pi/a \). The reciprocal lattice sums involved in the calculation of \( \mathbf{A} \) were cut at a sphere of radius roughly 40 times the nearest neighbor distance in reciprocal space. Note from eq. (5.15) that the eigenvalues \( \lambda \) of \( \mathbf{A} \) are related to the physical eigenfrequencies by \( \lambda = \hbar^2 \omega^2 \). The physical eigenvectors \( \mathbf{j} \) are related to those of \( \tilde{\mathbf{A}} \) by eq. (5.24). The principal purpose of the plot figure 7.3(a) is to demonstrate that the ansatz (5.14) leads to a series of important physical features in the dispersion relations:

**Long wavelength limit:** In the limit \( q \to 0 \), near the origin \( \Gamma \) of the Brillouin zone, the \( B \times d = 2 \times 3 = 6 \) modes group into 3 acoustic and 3 optical modes. The linear dispersion of the former which has been expressed analytically in eq. (C.4a) is clearly visible. The degeneracy of the latter to a single finite value at \( q = 0 \) is a consequence of the isotropic Gaussian localization \( \alpha \) and as such of the cubic symmetry of the NaCl structure. By assumption, crystals in this section coexist with a liquid at nonvanishing isotropic pressure \( p_0 \). Consequently the slopes of the acoustic branches will yield linear combinations of the Birch coefficients eq. (6.16) as presented for cubic crystals in [Wal09, table 4.2].
7.1 DFT approach

\[ L \approx X W K \approx \frac{\hbar}{m^\omega} \]

\[ \omega = \sqrt{\frac{k_B T}{m^\omega}} \]

Degeneracies along X- and L-path The vertical arrows in the \( \Delta \) segment of figure 7.3(a) highlight pairwise degeneracies of the dispersion relations which continue in the \( \Lambda \) segment. They agree with those predicted by group theory for the transverse modes with \( q \) parallel to an at least 3-fold symmetry axis (cf. [Lax91, chapter 12.2]). Hence, the present modes are marked as L/T and O/A for longitudinal/transversal and optical/acoustic.

Level repulsion The inset shows an occurrence of level repulsion [Fra94] in the \( W-X \) segment, i.e. on the BZ boundary with \( q \) pointing along a low-symmetry direction. Apparently, level crossings do occur between the highest-frequency modes e.g. in the \( K-W \) and the \( \Delta \) segment. The latter however does not lie in the BZ boundary. The former lies on the \( xy \)-mirror plane at the intersection of 2 BZ planes. Despite the necessity of a detailed analysis in this case it seems plausible that an interaction between the crossing levels is forbidden by symmetry.

To summarize, the dispersion relations found for the NaCl structure of hard spheres seem in qualitative agreement with physical expectations. They are to be taken with a grain of salt in view of the discrepancies to Haymet’s results at low \( \zeta \) in figure 7.2(a).
We tried to minimize the potential impact of these discrepancies by choosing for $\zeta$ a value far inside the range of best agreement. Dispersion relations for an ionic NaCl crystal have been measured by neutron scattering in [RAS69]; figure 1 therein shows the segments $\Delta$, $\Sigma$ and $\Lambda$ respectively together with 3 different theoretical models. A remarkable difference to figure 7.3(a) is the existence of two different optical frequencies around the $\Gamma$ point. This lifted degeneracy for the ionic solids — the so-called “LO-TO splitting” — can be understood from the long range of the Coulomb interaction in polarizable media (cf. [LST41] and [MS66, chapter 27]). For the finite-range HS interaction the cubic degeneracy is fully obeyed. Moreover, the accessibility of optical modes through the e.o.m. (5.11) has hereby been demonstrated.

It still seems desirable to get a feeling of the orders of magnitude involved in the present result. We consider the example of $\sigma = 10^{-6}$ m, $m = 10^{-15}$ kg and $T = 300$ K which yields $\omega$ in units of approximately 2 kHz. The optical eigenfrequencies at the $\Gamma$-point follow as approx. 135 kHz (low radio frequencies). The speed of sound $c_{q,\pi}$ for the various directions of propagation $\hat{q}$ and polarizations $\pi$ is obtained from the group velocity in the infinite-wavelength limit,

$$c_{q,\pi} = \frac{\partial \omega}{\partial q} (q = 0) .$$

As both $\omega$ and $q$ are measured in units proportional to $\sigma^{-1}$, the particle diameter scales out of the result. The (reciprocal) length of the $\Sigma$ segment in terms of the inverse of the lattice constant $a$ is $3\pi/(\sqrt{2}a)$. With this scaling of the $q$-axis in figure 7.3(a) follows for the sound velocities parallel to the $\Sigma$ segment

$$c_{\Sigma,\pi} = \sqrt{\frac{\hbar T}{\gamma\pi m}} \quad \text{with} \quad \gamma\pi \approx \begin{cases} 
150, & \pi = z\text{transversal} , \\
419, & \pi = (xy)\text{transversal} , \\
807, & \pi = (xy)\text{longitudinal} .
\end{cases} \quad (7.18)$$

The dimensionless coefficient $\gamma\pi$ can be compared with the adiabatic index $\gamma_{\text{adiabatic}}$ of gases where one has (longitudinal sound only)

$$c_{\text{ideal gas}} = \sqrt{\frac{\hbar T}{\gamma_{\text{adiabatic}} m}} .$$

Typical values of $\gamma_{\text{adiabatic}}$ range around 1.4, thus $c_{K,\pi}$ lie above ideal gas results by a factor of 10 to 24. The polarizations $\pi$ in that specific direction can be decomposed into a $z$-transversal mode and a transversal plus a longitudinal mode in the $xy$ plane. This matches the prediction for $q$ in a mirror plane illustrated for cubic crystals in [Bor71]. Here, mirror planes are both the $xy$-plane and the plane spanned by $\{\hat{e}_x + \hat{e}_y, \hat{e}_z\}$. With the temperature and mass specified above (guided by colloidal orders of magnitude) $c_{K,\pi}$ ranges from approximately 2 cm/s to 6 cm/s with the highest speed of sound for the longitudinal wave. When inserting atomic masses for $m$ into eq. (7.18), more familiar crystal results in the range of km/s are obtained.
7.1 DFT approach

Figure 7.4: The same as figure 7.2 for the random fcc structure with its different $\zeta$-range. Data was reobtained down to $\zeta = 0.2886$. (a) shows the coexistence densities $n_{f/c}^{\text{crit}}$ of the large species (left axis) and the crystal stoichiometry Na$_x$Cl$_{1-x}$ (right axis) on the same scale. In (b) $\xi_{\text{crit}}$ is computed from the total melting density.

### 7.1.3. Random fcc structure

The statistical approach to the microscopic crystal structure offers a straightforward approach to substitutional disorder as in the random fcc structure. The equilibrium densities $n^{(s)}$ at freezing were again determined following [RH90]. The evaluation of eq. (7.11) differs from the previous NaCl case in two respects: Firstly both species occupy the same fcc lattice such that $b^{(s)} = 0$ in eq. (7.13). Secondly, as a consequence, the occupancies $\eta^{(s)} < 1$ are shared among the two species. In the defect-free case still holds $\eta^{(1)} + \eta^{(2)} = 1$, with phase separation $\eta^{(1)} \neq \eta^{(2)}$ allowed (compared to the equimolar reference liquid). The terms in $\eta^{(s)}$ in eq. (7.6) signify a mixing entropy contribution. The results for the freezing transition are shown in figure 7.4. The minimization of $\Delta \Omega_{\text{HR}}$ is performed over $\xi^{(1)}, \xi^{(2)}$ and also both solid densities $n^{(s)}$. The plot in [RH90] is for the large sphere densities, and figure 7.4(a) shows excellent agreement. The additional parameter $\chi^{\text{crit}}$ for the solid stoichiometry Na$_x$Cl$_{1-x}$ (used synonymous with “Small$_x$Large$_{1-x}$-NaCl structure”) is shown on the right-hand axis. $\zeta = 1$ corresponds to the one-component HS crystal and yields an equimolar crystal phase $\chi^{\text{crit}} (\zeta = 1) = 1$ as one would expect from mixing entropy. For $\zeta < 1$ the large species quickly prevails in the crystal. It seems plausible to think of a lattice site occupied by the small species as a “partial vacancy”: The space available in each unit cell is bounded from below by the large species and is not filled to the same extent by the small. This makes it energetically favorable for the large species to enter the crystal while mixing entropy still favors equimolarity.

Not the entire range in $\zeta$ was recomputed: In figure 7.4(b) $\xi^{(1)}$ increases more and more strongly for $\zeta \lesssim 0.33$. To treat larger values of $\xi^{(1)}$, a third approximation for
the integral \((7.3)\) would be needed which remains to be implemented. Interestingly, also in figure 7.2(b) a jump in \(\varepsilon_{(1)}\) begins near \(\zeta = 0.33\). A potential physical mechanism behind this drop in the localization of the small particles could be hopping across tetrahedral gaps. At close packing, the tetrahedral gap has a diameter of 0.225\(\sigma\). With the lattice constants at \(\zeta = 0.3\), the tetrahedral gap has diameters of approximately 0.244\(\sigma\) and 0.233\(\sigma\) in the NaCl respectively the random fcc crystal. This is about 4/5 of the small sphere diameter. In [Fil+11] hopping processes of the small species in an Na\(_x\)Cl\(_{1-x}\) structure through tetrahedral gaps were analyzed by molecular dynamics (MD) simulations. It was found that, while keeping a constant diameter ratio \(\zeta = 0.3\), an increase in the occupancy \(\eta(s)\) of the small sphere sublattice facilitated the hopping processes. While a direct study of this effect requires the consideration of irreversible dynamics the so-called Na\(_x\)Cl\(_{1-x}\) “interstitial solid” offers a system where finally point defects are expected to play a major role. The following paragraph 7.1.4 generalizes the DFT approach from paragraph 7.1.2 to a partly occupied Na sublattice which will be compared to the evaluation of Monte Carlo (MC) simulation data in section 7.2.

The dispersion relations for the random fcc crystal are shown in figure 7.5 at (a) \(\zeta = 0.9\) and (b) \(\zeta = 0.3\). Unlike in the NaCl evaluation, small and large particles

\[
\text{Polarization within } \Sigma
\]

LO --- LA

TO\(_x\) --- TA\(_x\)

TO\(_{xy}\) --- TA\(_{xy}\)

Figure 7.5.: Dispersion relations for the random fcc structure at (a) \(\zeta = 0.9\) and (b) \(\zeta = 0.3\). The wave vectors are again from the path shown in figure 7.3(b). The polarizations of the corresponding eigenvectors along the \(\Sigma\) segment are given in the key of (a) for both plots. The inset in (b) magnifies the crossover region between acoustic and optical modes. For the full set of equilibrium density parameters cf. table 7.1.
Table 7.1.: Equilibrium structure parameters for the dispersion relations shown in this chapter

<table>
<thead>
<tr>
<th>Structure</th>
<th>Parameter</th>
<th>( \varsigma )</th>
<th>( m^{(1)} ) ([m])</th>
<th>( \chi_{\ell} ) ([\sigma^{-3}])</th>
<th>( n_{\ell}^{\text{crit},(2)} ) ([\sigma^{-3}])</th>
<th>( \chi_{s} ) ([\sigma^{-3}])</th>
<th>( n_{s}^{\text{crit},(2)} ) ([\sigma^{-3}])</th>
<th>( \varepsilon^{(1)} ) ([10^{-2}\sigma])</th>
<th>( \varepsilon^{(2)} ) ([10^{-2}\sigma])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(<em>{1})Cl(</em>{1}) fig. 7.3(a)</td>
<td>0.445</td>
<td>1</td>
<td>1</td>
<td>1.00692</td>
<td>1</td>
<td>1.13285</td>
<td>3.9943</td>
<td>4.3804</td>
<td></td>
</tr>
<tr>
<td>rand. fcc 7.5(a)</td>
<td>0.9 (\varsigma^3)</td>
<td>1</td>
<td>0.56783</td>
<td>0.56852</td>
<td>0.78768</td>
<td>7.8255</td>
<td>3.0350</td>
<td></td>
<td></td>
</tr>
<tr>
<td>rand. fcc 7.5(b)</td>
<td>0.3 (\varsigma^3)</td>
<td>1</td>
<td>0.97073</td>
<td>0.14276</td>
<td>1.11065</td>
<td>39.371</td>
<td>2.1111</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na(<em>{5})Cl(</em>{1}) – DFT and sim. fig. 7.9</td>
<td>0.3</td>
<td>1</td>
<td>3.6</td>
<td>0.91533</td>
<td>0.66880</td>
<td>1.24844</td>
<td>7.4643</td>
<td>2.4853</td>
<td></td>
</tr>
</tbody>
</table>

were not given identical masses but identical mass densities, i.e. \( m^{(1)}/m^{(2)} = \varsigma^3 \). This better represents an experimental setup where both species consist of the same material. While for the NaCl dispersion relations figure 7.3(a) all of the 6 six eigenmodes showed significant variations in their frequency throughout the BZ, the frequency scale is clearly split in figure 7.5. For easier reference, the 6 curves will be associated with the polarization of the corresponding eigenvector along the \( \Sigma \) path which are the same in figures 7.5(a) and (b). Only close to the \( \Gamma \) point do the 3 acoustic curves show the expected linear slope and then quickly saturate to a more or less constant plateau value. A way to understand this feature seems to be via the weaker localization of the small spheres: The dispersion relations can be seen as the result of probing the linear response of a sample to a plane-wave deformation of various wave length and direction. The weaker the localization to the lattice sites, the more a species will appear as a liquid on short length scales. This seems clearly connected to the observation that there is roughly a factor of 5 between \( \varepsilon^{(1)} \approx 0.078 \) in figure 7.5(a) and \( \varepsilon^{(1)} \approx 0.394 \) in figure 7.5(b). Further note that two of the three acoustic modes decay more strongly from figure 7.5(a) to (b). These were identified as transversal modes (along \( \Sigma, \Delta \) and \( \Gamma \) which will be absent in a homogeneous liquid. The remaining longitudinal acoustic mode is the one affected by the ideal-gas contribution \( \Lambda_{\text{id}} \) in \( \Lambda \). It is obtained from setting \( c^{(ab)} \equiv 0 \) in eq. (7.14). Diagonalization of \( \Lambda_{\text{id}}^{(11)}/\varrho_0 \) yields a linear dispersion relation \( \omega_{\text{id}} \) along \( \Sigma \). With the values provided in table 7.1 follows \( \omega_{\text{id}}(\mathbf{q} = \mathbf{K}) \approx 3.46[k_B T/(m\sigma^2)]^{1/2} \) which is slightly above the LA frequency in figure 7.5(b). This seems counterintuitive as one would expect interaction to increase the eigenfrequencies compared to the ideal gas limit. A role in that might play the coupling to the heavier large spheres: Figure 7.6 shows the eigenvector components of the modes polarized in the \( xy \) plane for both species. While the large species asymptotically decouples from the \( \text{TA}_{xy} \) mode (cf. figure 7.6(a)) and the \( \text{TA}_z \) mode (not shown) shows qualitatively the same behavior (also for \( \mathbf{q} \) up to the \( \mathbf{K} \) point), a sign change of the eigenvector
component of the large species occurs for the LA\textsubscript{xy} mode (inset of figure 7.6(a)). The limit \( \lim_{q \to 0} \) of a complete small sphere delocalization remains to be studied. It corresponds to the “fast sphere” structure (5) introduced in [SH87]. More generally, figure 7.6 shows the crossover of acoustic and optical modes visible in the inset of figure 7.5(b) in terms of the eigenvectors of \( \mathbf{S}^\Lambda \). Each mode is associated with two graphs for the normalized amplitude of the small and the large species. Towards the \( \Gamma \) point, i.e. \( q = 0 \), the optical mode shows antiparallel movement of both species. Reassuringly, the ratio of amplitude between small and large species is found to be determined by

\[
\frac{\mathbf{S}_{\text{optical}}}{\mathbf{S}_{\text{optical}}} (q = 0) = \frac{\mathbf{n}_{\text{crit.}}(2) \mathbf{M}(2)}{\mathbf{n}_{\text{crit.}}(1) \mathbf{M}(1)}.
\]

With eq. (5.24), this matches the physical requirement of a resting center of mass for the optical modes at \( q = 0 \),

\[
\mathbf{q} = 0 \mathbf{j} + \mathbf{q} = 0 \mathbf{j} = 0 \text{ (as a statistical average)}.
\]

For the acoustic modes at \( q = 0 \), both species move parallel and contribute to the total momentum also according to \( \mathbf{q} = 0 \mathbf{j} \). After the crossover, the dominant contributions of small and large species to optical and acoustic mode have exchanged their roles. The originally optical mode with largely moving small spheres is now mainly defined by a movement of the large species and vice versa. This coincides with the observation that the original optical modes in figure 7.5 resemble in shape the acoustic modes in a one-component fcc crystal (cf. e.g. [NL11, figure 5]). In that sense, the small-\( q \) optical modes take the role of the acoustic modes in most of the Brillouin zone, especially for weakly localized small spheres.
7.1 DFT approach

Figure 7.7.: Coexistence parameters for the Na\textsubscript{x}Cl\textsubscript{1} structure plotted versus the liquid stoichiometry $\chi_\ell$ at constant diameter ratio $\varsigma = 0.3$. (a) and (b) show the same as figures 7.2 and 7.4 where however $\varsigma$ was varied at constant $\chi_\ell$. (c) shows the stoichiometry of the solid phase $\chi_s$. It can here alternatively be read as the Na-sublattice occupancy $\eta_{(1)}$. The freezing parameters at $\chi_s = 2/3$ will be used for a comparison to simulation in section 7.2.

7.1.4. NaCl interstitial solid

With the approach to the defect-free Na\textsubscript{1}Cl\textsubscript{1} structure established in paragraph 7.1.2, the generalization to the Na\textsubscript{x}Cl\textsubscript{1} “interstitial solid” case is straightforward. The sublattice of the large “Cl” hard spheres is again assumed defect free. For the incompletely occupied Na sublattice holds $\eta_{(1)} = \chi$ yielding an extra entropic contribution compared to Na\textsubscript{1}Cl\textsubscript{1} (cf. eq. (7.6)). Study of a crystal at the desired occupancy can be achieved within a broad range by adapting the stoichiometry $\chi_s$ of the coexisting liquid. As a function of $\chi_s$ at constant $\varsigma = 0.3$, figure 7.7 shows the equilibrium parameters of the Na\textsubscript{x}Cl\textsubscript{1} crystal at melting. With Lebowitz’s above-quoted liquid solution for $c^{(ab)}$, crystallization is promoted by the addition of small spheres to the liquid below $\chi_s \neq 1$. This is reflected in a decrease of $n_s^{\text{crit.}(2)}$ in the lowest $\chi_\ell$ range (cf. figure 7.7(a)). At the same time the Gaussian widths (figure 7.7(b)) take their maximum near $\chi_\ell = 0.5$. As mentioned above, the initial increase in $\varepsilon_{(s)}$ might be related to the increase in small-sphere diffusion with increasing interstitial (i.e. small-sphere sublattice) concentration observed by [Fil+11]. The occupancy/solid stoichiometry of $\chi_s = 2/3$ studied therein is reached at $\chi_\ell \approx 3.6$ in the present DFT approach (figure 7.7(c)). The corresponding dispersion relations will be compared to some obtained by MC simulations following [Fil+11] in figure 7.9.

In the absence of the small species $\chi_s (\chi_\ell = 0) = 0$ as expected. Moreover, comparison with figure 7.4 at $\varsigma = 1$ shows that the single HS crystal freezing
parameters are reproduced (note the factor of 2 between both plots for \( n_{s/2}^{\text{crit}} \) due to the different reference crystal structures).

### 7.2. Dispersion relations from position measurements

For the single-component periodic crystal, Walz and Fuchs solved the \( \infty + 3 \) dissipationless and isothermal Zwanzig–Mori e.o.m. — [WF10, eq. (25)] respectively eqs. (5.11) for \( B = 1 \) — by the following ansatz [Wal09; WF10]

\[
\delta n_g (q, t) = -i (g + q)_\alpha n_g \delta u_\alpha (q, t) - \frac{n_g}{n_0} \delta c (q, t). \tag{[WF10, eq. 34]}
\]

It allows to relate the solution of each e.o.m. to a simple hydrodynamic relation whose validity is ensured. With the caveat in mind that the equilibrium fluctuations treated in eqs. (5.11) for \( B \geq 2 \) decay on different time scales in the hydrodynamic limit, we generalize eq. ([WF10, eq. 34]) to that case, restricting ourselves to \( B = 2 \) for simplicity.

The vector components \( v_{\alpha g}^{(s)} (q) = i (g + q)_\alpha n_g^{(s)} \) are easily generalized from [WF10, eq. (28a)] to rewrite the e.o.m. as

\[
\partial_t \delta n_g^{(s)} (q, t) = -\frac{v_{\alpha g}^{(s)} (q)}{\theta_0^{(s)}} \epsilon_{\alpha}^{(s)} (q) \delta j_\alpha^{(s)} (q, t), \tag{5.11a}
\]

\[
\partial_t \delta j_\alpha^{(a)} (q, t) = \sum_{b=1}^{B} \left( \sum_{g, g'} v_{\alpha g'}^{(a)*} (q) J_{g, g'}^{(ab)*} (q) \delta n_g^{(b)} (q, t) \right). \tag{5.11b}
\]

The ansatz

\[
\delta n_g^{(s)} (q, t) = -v_{\alpha g}^{(s)} (q) u_\alpha^{(s)} (q, t) - \frac{n_g^{(s)}}{n_0} \delta c^{(s)} (q, t) \tag{7.20a}
\]

\[
\overset{(3.45)}{=} -v_{\alpha g}^{(s)} (0) u_\alpha^{(s)} (q, t) + \frac{n_g^{(s)}}{n_0} \delta n_g^{(s)} (q, t) \tag{7.20b}
\]

turns the equations of motion (5.11a) into

\[
v_{\alpha g}^{(s)} (q = 0) \left[ \partial_t u_\alpha^{(s)} (q, t) - \frac{1}{\theta_0^{(s)}} \delta j_\alpha^{(s)} (q, t) \right] =
\]

\[
= n_g^{(s)} \left[ \frac{i}{\theta_0^{(s)}} q_\alpha \delta j_\alpha^{(s)} (q, t) - \partial_t \left( iq_\alpha \delta u_\alpha^{(s)} (q, t) - \frac{1}{n_0} \delta c^{(s)} (q, t) \right) \right] \forall g. \tag{7.21}
\]

The left hand side vanishes with eq. (3.56), the r.h.s. with both eq. (3.45) and the continuity equation for \( \delta n_g^{(s)} \) eq. (3.40). Concerning eq. (5.11b) we can follow [WF10, eq. (36) et seqq.]:

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\[ \partial_t \delta j^{(a)}_{\alpha}(\mathbf{q}, t) = - \sum_{b, g} v_{\alpha g}^{(a)*}(\mathbf{q}) J_{g g}^{(ab)*}(\mathbf{q}) \left[ v_{\beta g}^{(b)}(\mathbf{q}) u_{\beta}^{(b)}(\mathbf{q}, t) + \frac{n_{\alpha g}^{(b)}}{n_0^{(b)}} \delta \epsilon_{(b)}(\mathbf{q}, t) \right] \]

\[ = - \frac{1}{\varrho_0} \sum_{b} \left[ A^{(ab)}_{\alpha \beta}(\mathbf{q}) \varrho_0^{(b)} u_{\beta}^{(b)}(\mathbf{q}, t) - V^{(ab)}_{\alpha}(\mathbf{q}) \delta \epsilon_{(b)}(\mathbf{q}, t) \right] \]

where \( V^{(ab)}_{\alpha}(\mathbf{q}) = \sum_{g', g} v_{\alpha g'}^{(a)*}(\mathbf{q}) \tilde{J}_{g' g}^{(ab)*}(\mathbf{q}) \frac{n_{\alpha g'}^{(b)}}{n_0^{(b)}}. \)

With the assumption of species-wise constant defect densities, \( \partial_t \delta \epsilon^{(s)} \equiv 0 \) and again eq. (3.56), eq. (7.22) becomes the wave equation (5.12),

\[ \partial_t^2 \delta j^{(a)}_{\alpha}(\mathbf{q}, t) = - \frac{1}{\varrho_0} \sum_{b} A^{(ab)}_{\alpha \beta} \delta j_{\beta}^{(b)}(\mathbf{q}, t). \]

Consequently, the eqs. (7.19) can be rewritten as known physical relations with the ansatz (7.20a). Bear in mind that this requires Working hypothesis 1 to hold.

Because the ansatz (7.20a) is a species-wise generalization of [WF10, eq. (34)] it is straightforward to solve it for \( \delta u^{(s)} \) and \( \delta n^{(s)} \) in the same species-wise manner:

\[ \delta u^{(s)}(\mathbf{q}, t) = i \mathcal{N}^{(s)-1} \cdot \sum_{g \in \mathcal{G}} n_{\mathbf{g}}^{(s)*} g \delta n_{\mathbf{g}}^{(s)}(\mathbf{q}, t) \]

\[ \text{with } \mathcal{N}_{\alpha \beta}^{(s)} = \sum_{g} \left| n_{\mathbf{g}}^{(s)} \right|^2 g_{\alpha} g_{\beta}, \]

cf. [WF10, eq. (41)]. Equation (42) therein on the other hand generalizes to

\[ \delta n^{(s)}(\mathbf{q}, t) = \frac{n_0}{\mathcal{N}_0^{(s)}} \sum_{g} n_{\mathbf{g}}^{(s)*} \delta n_{\mathbf{g}}^{(s)}(\mathbf{q}, t) \]

\[ \text{with } \mathcal{N}_0^{(s)} = \sum_{g} \left| n_{\mathbf{g}}^{(s)} \right|^2. \]

With eq. (3.45) and following [WF10, eq. 43], eq. (7.23b) is equivalent to

\[ \delta \epsilon^{(s)}(\mathbf{q}, t) = -n_0 \sum_{g} n_{\mathbf{g}}^{(s)*} \left( \frac{1}{\mathcal{N}_0^{(s)}} - \frac{1}{\mathcal{N}^{(s)} \cdot \mathcal{N}_0^{(s)}} \right) \delta n_{\mathbf{g}}^{(s)}(\mathbf{q}, t). \]

It is insightful to compare eq. (7.23a) as as definition of \( u \) with that employed in the potential expansion method: The ideal, defect-free lattice referred to by the latter has been replaced by average particle densities \( n^{(s)} \) which in eq. (7.23) occur explicitly and via

\[ \delta n_{\mathbf{g}}^{(s)}(\mathbf{q}, t) = \rho^{(s)}(\mathbf{g} + \mathbf{q}, t) - \delta(\mathbf{q}) n_{\mathbf{g}}^{(s)}. \]
Figure 7.8.: Schematic illustration of the pre-processing step of particle position data in order to evaluate eq. (7.23). The curly brackets indicate a set of statistically independent measurements of the particle positions taken at fixed times (“snapshots”). The rightmost frame shows the average particle densities derived from that set.

With a suitable experimental or simulation method of obtaining statistically independent positional measurements $\rho_i^{(s)}(r, t_i)$ at fixed times $t_i$, a set of “snapshots” can be extracted.\footnote{One needs to ensure that these measurements are taken from an equilibrated crystal.} Averaging over this ensemble then yields the equilibrium densities $n^{(s)}$ as

$$n^{(s)}(r) = \lim_{I \to \infty} \frac{1}{I} \sum_{i=1}^{I} \rho_i^{(s)}(r, t_i) =: \langle \rho_i^{(s)}(r) \rangle_{\mathcal{M}} .$$

The subscript “$\mathcal{M}$” indicates an average over a set of measurements whose size $I$ needs to provide sufficient statistics of a system’s phase space. The procedure is schematically illustrated for a hypothetical 2d interstitial solid in figure 7.8. Subsequently, the snapshots can be processed to measurements of $\delta n^{(s)}$ (or $\delta c^{(s)}$) with eqs. (7.23). The displacement field correlations $\langle \delta u^{(a)} \delta u^{(b)} \rangle(q)$ obey

$$\langle \delta u^{(a)} \delta u^{(b)} \rangle(q) = \frac{V k_B T}{\xi_0} D_{\alpha\beta}^{(ab)} \langle q \rangle$$

where $D \sim \frac{1}{\xi_0} \Lambda$ is the physical dynamical (block) matrix whose eigenvalues give the physical eigenfrequencies $\omega_\sigma$ of the phonon modes (cf. [Här13, eq. (66)]).

A set of positional snapshots was obtained with a Molecular Dynamics simulation in the $NVT$ ensemble as described in [Fil+11] and references therein. The cubic simulation box contained an equilibrated Na$_x$Cl$_{1-x}$ hard sphere crystal with $N^{(2)} = 2048$ large particles at a particle density of $n^{(2)}_0 = 1.35$ and $N^{(1)} = 1366$ small particles, matching an occupancy of approximately $\chi_s \approx 2/3$. Effects of the box walls were eliminated by periodic boundary conditions. This setup was used to evaluate the dynamical matrix $D$ from eq. (7.24) with $\langle \cdot \rangle \equiv \langle \cdot \rangle_{\mathcal{M}}$ and $I = 500$ equilibrium configurations and assuming equal particle masses $m^{(1)} = m^{(2)}$. The eigenvalues of $D(q)$ are plotted as crosses in figure 7.9 for the three high-symmetry BZ paths $\Sigma, \Delta$ and $\Lambda$ shown in the previous dispersion relations and continuously beyond the first Brillouin zone in the same directions. The lines in that figure were obtained for approximately the same occupancy $\chi_s$ from the DFT approach outlined...
7.2 Measurement data processing

Figure 7.9.: Dispersion relations for the Na$_{2/3}$Cl$_1$ system described in paragraph 7.1.4 obtained from MC simulations through eq. (7.24) (symbols) and the DFT approach (lines). Shown are plots along the three high symmetry paths $\Sigma$, $\Delta$ and $\Lambda$, going beyond the first Brillouin zone. For the full set of equilibrium density parameters cf. table 7.1.

in paragraph 7.1.4. Table 7.1 shows the equilibrium density parameters employed in both approaches. Note that the match in $\chi_s$ between simulation and theory required different solid particle densities $n_s^{\text{crit,(2)}}$. The resulting different lattice constants mean that the $q$-axis in figure 7.9 needs to be read in terms of 2 differently–sized Brillouin zones. Furthermore, the DFT results were rescaled to eye to match the optical/upper MC modes, bringing these curves to a quantitative match within no more than 10%. The degeneracies of the transversal modes along the (100)- and the (111)-direction are well caught by the simulation results, too. The degeneracy at $X'$ in the leftmost part occurs where the wave vector $q$ reaches another axis of 4-fold symmetry of the reciprocal lattice.\(^8\) The actual (unscaled) acoustic/lower DFT eigenfrequencies lie about 10% above the simulation results. Both approaches compare very well qualitatively and well for the lower modes quantitatively while the upper modes are underestimated in the DFT approach by a factor of 1.4. Even better agreement could probably be obtained with more advanced DFT approaches to crystals which desirably will reproduce a given sublattice occupancy at the same lattice constant as the simulation. Study of the small-$q$ limit within the simulation approach is restricted by the size of the (cuboid) simulation box: The cartesian wave-vector components $q_\alpha$ of $q = q_\alpha \hat{e}_\alpha$ for which eq. (7.24) is evaluated need to be integer multiples of $2\pi/L_\alpha$ where $L_\alpha$ is the length of the $\alpha^{th}$ box edge. In other words, $q$ can be chosen from a cubic lattice determined by the 3 edge lengths of the

\(^8\) $X'$ is equivalent to $X$ if the first BZ is constructed about the reciprocal lattice point at $2\Gamma$. 

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simulation box. A further comparison proposed by A. Zippelius\textsuperscript{9} would be to extract the direct correlation function from the simulation statistics and evaluate eq. (7.14) with this input. In particular, this promises insight into the influence of isotropy and translational invariance in the analytical approximation made for $c^{(ab)}$.

\textsuperscript{9}personal communication, summer 2016.
8. Comparison of results

This chapter concludes part II by an overview of its findings in section 8.1. Section 8.2 then confronts them with results of the perfect-lattice potential expansion approach from [Wal98, chap. 2.7] and presents a simple test case in the honeycomb lattice.

8.1. Dynamic and static approach

The dynamical matrix $P_\gamma(q)$ from paragraph 5.3.2 could be shown to yield the desired $d$ acoustic eigenvalue branches $\lambda^{\text{acoustic}}(q)$ with $\lambda^{\text{acoustic}}(q) = \gamma(q) q^2 + O(q^3)$. However, it remains open whether — for systems lacking inversion symmetry — the $\gamma^{\text{tot}}(q)$ obtained from exclusive consideration of $PA^{(\text{tot})}(q)$ are identical to the $\gamma^{\text{tot}}(q)$ (cf. eq. (5.45)). This might not be the case if the blocks $PA^{(s)}(q)$ and $PA^{(s)}(q)$ contain terms of $O(q)$. The block $PA^{(\text{tot})}(q)$ gives the couplings of the total momentum-variable to itself and corresponds to [Wal09, eq. (27)] in the single-species case. At the same time, even for a single-species system, the ansatz [WF10, eq. (34b)] does not contain all terms present in eq. (6.4b). In the latter, the additional terms were attributed to internal (non-affine) strain. Note that [Wal09, eq. (2.34)] starts off with a relation similar to eq. (6.4b) before arguing against contributions at Bragg peaks other than $g = 0$. Indeed, internal strain cannot be seen as an independent thermodynamic variable like e.g. temperature. Elastic constants can be defined at constant temperature or entropy whereas internal strain inevitably assumes its equilibrium value at given external strains.

For internal strain in the form of sublattice displacements, the connection to optical modes is discussed in [MA67] by expanding the sublattice displacements in optical-mode eigenvectors. To get a better feeling for the role of the blocks $PA^{(s)}$ and $PA^{(s)}$ in systems lacking inversion symmetry, the dispersion relations were calculated for the diamond structure distinguishing two sublattices from the Gaussian parametrization (7.2)\(^2\). Albeit this ansatz suffers from conceptual problems, it seems

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\(^1\)For later discussion, the usage of generalized point defect densities rather than $\delta n_{1\gamma} \mid_{\delta \varepsilon} \delta \varepsilon\gamma$ seems preferable because it is less redundant and more intuitive. The $\delta \varepsilon\gamma$ will give the counterpart to the generalized currents $\delta j_{\gamma}$ from eqs. (5.9).

\(^2\)A metastable diamond structure was obtained from appropriate superposition of the GEM4 potential described in [Här13, and references therein].
worthwhile mentioning that $0 < \gamma_{\sigma} (\mathbf{q}) < \gamma_{\sigma}^{\text{tot}} (\mathbf{q})$ was found which corresponds to a lowering of the elastic constants from the coupling to optical modes. A first suggestion for future work is to calculate dispersion relations for a zincblende structure, obtained from diamond by decoration of one sublattice with a different species. This promises more decisive insights: On the one hand, phenomenological hydrodynamics of binary mixtures [Das11, sec. 5.1.5] also predicts a wave equation for the total momentum density $\mathbf{j}$. On the other hand, $0 < \gamma_{\sigma} (\mathbf{q}) < \gamma_{\sigma}^{\text{tot}} (\mathbf{q})$ is expected to persist to zincblende (or equivalent). From that, one could conclude that either Working hypothesis 2 or Working hypothesis 1, at least in binary systems, does not hold.

The mentioned conceptual problems in the treatment of diamond restrict the finding of optical modes from chapter 5 to systems of several species. Diamond, while forming a non-primitive lattice, consists only of a single species. But as there is no correspondence between particle and lattice site by the nature of the approach, the total momentum density $\mathbf{j}$ cannot be decomposed into single species contributions and relative currents are hard to define. Yet, non-hydrodynamic currents occurred in the general e.o.m. (5.9) in the form of the $\{\delta \mathbf{j}_g (\mathbf{q}, t)\}$. Based on the parametrization

$$n_g = \sum_{s=1}^{B} e^{-i \mathbf{g} \cdot \mathbf{b}^{(s)}} n_g^{(s,0)}$$

with $n_g^{(s,0)}$ characterizing the density peaks on sublattice $s$, M. Fuchs proposed the following ansatz:

$$\delta \mathbf{j}_g (\mathbf{q}, t) = \frac{1}{n_0} \sum_{s=1}^{B} e^{-i \mathbf{g} \cdot \mathbf{b}^{(s)}} n_g^{(s,0)} \delta \mathbf{j}_g^{(s)} (\mathbf{q}, t). \quad (8.1)$$

It aims to identify currents $\delta \mathbf{j}_g^{(s)}$ associated with the different basis positions. An inversion of the relation (8.1) in the style of eq. (7.23) would recover a set $\{\delta \mathbf{j}_g^{(s)}\}$, defined in terms of quantities that are microscopically well-defined for any number of species. Inserting a relation $\delta \mathbf{j}_g^{(s)} (\{\delta \mathbf{j}_g\})$ into the e.o.m. (5.9) is expected to recover a dynamical matrix of the form (5.13).

Note that this problem is not encountered in the perfect-lattice regime which we identified with the classical, defect-free low temperature limit in section 2.3. Sublattices can be clearly identified which motivates a final stretch back to the potential-expansion method and eq. (1.2). Provided that the classical low temperature limit for a given equilibrium density $n$ is well-defined and leads to a defect-free structure, one would expect to recover the same dispersion relations from $\Lambda$ as from $\mathbf{D}$.

### 8.2. Potential expansion method

A central objective of this thesis is the description of phonons in crystals with an arbitrary amount of point defects at any temperature $T$ below melting and compatible
8.2 Potential expansion method

Figure 8.1: Honeycomb lattice. Equilibrium particle positions are marked by dots, nearest-neighbor interactions by lines. Coordinate axes are shown for later reference.

with eq. (2.1). In a classical treatment, this should still include systems without point defects in the perfect-lattice regime (introduced on page 16) for which the mechanical equilibrium densities $n^{(s)}$ are described by,

$$ n^{(s)}(\mathbf{r}) = \sum_{\mathbf{R} \in \mathbf{L}} \delta(\mathbf{r} - \mathbf{R} - \mathbf{b}^{(s)}) $$

with $\mathbf{b}^{(s)}$ the basis vector of the $s$th species (cf. eq. (2.14)). The equilibrium density (8.2) is nothing else than the reference configuration of the potential-expansion method. The absence of point defects restores the one-to-one mapping of particles to lattice-sites in equilibrium. In a crystal with a basis occupied by only one species, we can hence still refer to each sublattice separately. From the result (6.20) we conclude the necessity to consider a crystal without a center of inversion. A well-known binary example of that kind is the “honeycomb structure” shown in figure 8.1. We will use it as a test case to compare the results of [Wal09] to those of chapter 5 within the perfect lattice regime below. With the same example in mind, we first draw a more formal comparison to Wallace’s presentation of a static potential approach [Wal98, section 2.7]. Crucially, the paragraph on “nonprimitive lattices” therein must hold as the honeycomb structure features more than one particle per unit cell. A generalization of [Wal98, section 2.7] is presented in [Kan95] which overcomes a limitation of the “Wallace approach”: The mechanical equilibrium condition used by Wallace to determine “internal strains” at a given external strain has to be replaced by a thermodynamic one at finite temperature. Yet, in the perfect-lattice regime — where thermal fluctuations are neglected — both approaches become equivalent.

The connection of the potential expansion (1.1) to the dynamical matrix $\mathbf{A}(\mathbf{q})$ from [WF10, eq. (27)] is discussed in section V.C. therein and in more detail in [Wal09, sections 3.3 and 3.4]. We quote the Zwanzig–Mori wave equation at vanishing defect...
fluctuations $\delta c = 0$ from [Wal09, sec. 3.3]

$$m n_0 \delta \ddot{u}_\alpha = -A_{\alpha\gamma}(q) \delta u_\gamma$$

$$= \ldots = A^{(2)}_{\alpha\beta\gamma\delta} \delta \dot{q}_\beta \delta \dot{q}_\delta u_\gamma$$

[Wal09, eq. (2.42)]

where the "wave propagation tensor" $A^{(2)}_{\alpha\beta\gamma\delta}$ can be obtained from $A$ by [Wal09, eq. (3.43)]. The discussion in [Wal09, sec. 3.4] then shows that in the (classical) low-temperature limit and with the mean-spherical approximation for the direct correlation function,

$$c(r, r') = -\beta \Phi(r, r')$$

[MA97],

$$A^{(2)}_{\alpha\beta\gamma\delta} = \frac{1}{2V} \sum_{ij \in L} \frac{\partial^2 \Phi}{\partial u^{(i)}_{\alpha} \partial u^{(j)}_{\gamma}} \left( R^{(i)}_\beta - R^{(j)}_\beta \right) \delta \left( R^{(i)}_\gamma - R^{(j)}_\gamma \right)$$

[Wal09, eq. (3.56)]

where $\hat{A}^{(\text{primitive})}_{\alpha\gamma\delta}$ is the wave propagation tensor defined for primitive lattices in [Wal98, eq. (7.20)] and employed in [Wal98, eq. (12.11)]. The case of nonprimitive lattices is also considered in [Wal98, section 2.7] and the generalization to $\hat{A}$ is introduced in [Wal98, eq. (7.60)]:

$$\hat{A}_{\alpha\gamma\delta} = -\frac{1}{2V} \sum_{i\nu,\mu} \Phi_{\alpha\gamma} (0\mu, i\nu) [R_\beta (i\nu) - R_\beta (0\mu)] [R_\delta (i\nu) - R_\delta (0\mu)] +$$

$$+ \frac{1}{2V} \sum_{i\nu,\mu} \sum_{\kappa} \Phi_{\kappa\gamma} (0\mu, i\nu) [R_\delta (i\nu) X_{\kappa,\alpha\beta} (\mu) + R_\beta (i\nu) X_{\kappa,\alpha\delta} (\mu)]$$

(8.3)

with $\Phi_{\alpha\beta} (i\nu, j\mu) = \frac{\partial^2 \Phi}{\partial u^{(i\nu)}_{\alpha} \partial u^{(j\mu)}_{\beta}} (\{ R (k\rho) \})$

and $R (k\rho) = R^{(k\rho)}$ the equilibrium positions.

The coupling tensor $X$ is defined in [Wal98, eqs. (7.50) and (7.51)] by the mechanical equilibrium condition

$$S_\alpha (\mu) = \sum_{\beta\gamma} X_{\alpha,\beta\gamma} (\mu) u_{\beta\gamma}$$

(8.4)

where the constant vector $S (\mu)$ is the sublattice displacement of the $\mu^{th}$ sublattice. In a binary system $S$ (2) can be identified with $\delta b$ from chapter 6. Equation (8.4) corresponds to eq. (6.19a) and $X$ to $\chi$. Further, Wallace discusses the vanishing of $X$ [Wal98, p. 85] — also found for $X$ in eq. (6.20) — in crystals with a center of inversion. On that condition, the simpler form $\hat{A}_{\alpha\beta\gamma\delta}^{(\text{primitive})}$ identified by [Wal09, eq. (3.56)] is recovered. However, this simplification does not hold for lattices such as honeycomb or diamond as will be seen in the following model calculation:

\[\text{The uniqueness of that solution is ensured by fixing the w.l.o.g. first sublattice in space, } S (1) := 0.\]
8.2 Potential expansion method

**Honeycomb model calculation**

An exemplary dispersion relation will be derived in the harmonic potential approximation [BH88; LW70] already mentioned in chapter 1. The displacement $u_{(ia)}^{(i)}(q,t)$ of the $a^{th}$ basis particle in the $i^{th}$ unit cell w.r.t. its equilibrium position obeys the e.o.m.

$$ m^{(s)} \frac{\partial^2}{\partial t^2} u_{(ia)}^{(i)}(q,t) = - \sum_{m,b} \Phi_{\alpha \beta}^{(ia,jb)} u_{(jb)}^{(jb)}(q,t) \quad (8.5a) $$

$$ \Leftrightarrow \frac{\partial^2}{\partial t^2} \sqrt{\frac{m^{(s)}}{m}} u_{(ia)}^{(i)}(q,t) = - \sum_{j,b} \Phi_{\alpha \beta}^{(ia,jb)} \sqrt{\frac{m^{(b)}}{m}} u_{(jb)}^{(jb)}(q,t) \quad (8.5b) $$

with $m^{(s)}$ the particle mass of species $s$, $m = \sum_s m^{(s)}$ and

$$ \Phi_{\alpha \beta}^{(ia,jb)} = \frac{\partial^2 \Phi}{\partial u_{(ia)}^{(ia)} \partial u_{(jb)}^{(jb)}} \left( \left\{ R_{(ia)}^{(ia)} \right\} \right) \quad (8.6) $$

the second equilibrium derivative of the pair interaction potential $\Phi \left\{ R_{(ia)}^{(ia)} \right\}$ w.r.t. displacements of the $i^{th}$ and the $j^{th}$ particle (cf. eq. (1.1)). A plane-wave ansatz

$$ u_{(is)}^{(i)}(q,t) = \sqrt{\frac{m^{(s)}}{m}} u_{(s)}^{(s)}(q) e^{i q \cdot R_{(ia)}^{(ia)} - \omega t} \quad (8.7) $$

— with $q$ restricted to a set $B \subset 1^{st}$ BZ compatible with periodic boundary conditions — recovers from eq. (8.5b) the e.o.m. (1.2)

$$ \omega^2 u_{(ia)}^{(i)}(q) = \sum_b D_{\alpha \beta}^{(ab)}(q) u_{(jb)}^{(jb)}(q) \quad (8.8) $$

with the dynamical matrix

$$ D_{\alpha \beta}^{(ab)}(q) = \frac{1}{\sqrt{m^{(s)} m^{(b)}}} \sum_{i,a,j,b} \Phi_{\alpha \beta}^{(ia,jb)} e^{-i q \cdot \left( R_{(ia)}^{(ia)} - R_{(jab)}^{(jb)} \right)} \quad (8.9) $$

The reformulation of the e.o.m. (8.5b) resembles the transform eq. (5.24) in that it allows to formulate the eigenvalue problem with a self-adjoint and $q$-antisymmetric dynamical block matrix

$$ D(q) = D^\dagger(q) = D^T(-q) \quad \text{cf. eq. (5.26)} \quad . $$

Under the assumption of centrosymmetric nearest-neighbor interactions, the harmonic potential energy $\Phi_h \left( \left\{ u^{(i)} \right\} \right)$ can be written as

$$ \Phi_h \left( \left\{ u^{(i)} \right\} \right) = \frac{f}{2 a^2} \sum_{k_{\text{n.n.}}} \left[ \left( R_{(k_e)}^{(k_e)} - R_{(k_d)}^{(k_d)} \right) \cdot \left( u_{(k_e)}^{(k_e)} - u_{(k_d)}^{(k_d)} \right) \right]^2 $$

with $f$: spring constant, $a$: lattice constant.

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4 Prof. R. Schilling, personal communication (lecture notes on “Quantentheorie makroskopischer Systeme”), summer term 2009.
The symmetric sum \( \sum_{(n.n.)} \) goes over all pairs of lattice vectors that belong to nearest neighbors. Inserting this expression for \( \Phi \) into eq. (8.6) yields

\[
\frac{\partial^2 \Phi_h}{\partial u_{\alpha i}^{(l_a)} \partial u_{\beta j}^{(l_b)}} \left( \{ u^{(j)} \} \right) = \frac{f}{a^2} \sum_{k_c, l_d (n.n.)} \left( R^{(k_c)} - R^{(l_d)} \right)_\alpha \left( R^{(k_c)} - R^{(l_d)} \right)_\beta \times \\
\times \left[ \delta_{i,c} k_c \delta_{j,k_c} + \delta_{i,l_c} \delta_{j,k_d} - (\delta_{i,k_c} \delta_{j,k_d} + \delta_{i,l_c} \delta_{j,k_d}) \right] \\
= 2 \frac{f}{a^2} \delta_{ab} \sum_{i}^{(l_a) (n.n.)} R^{(i_a)} R^{(i_b)} - 1 \delta_{i_{ab} (n.n.)} \left[ \left( R^{(i_a)} - R^{(i_b)} \right)_\alpha \left( R^{(i_a)} - R^{(i_b)} \right)_\beta \right] \right \} \tag{8.10}
\]

where \( 1 \delta_{i_{ab} (n.n.)} = \begin{cases} 1 & \text{if } i_a, i_b \text{ belong to nearest neighbors,} \\ 0 & \text{else.} \end{cases} \tag{8.11} \)

Note that the first term in the expression (8.10) is zero if \( a \neq b \) whereas the second term vanishes, because of the definition (8.11) if \( a = b \). Here we tacitly assumed a bipartite lattice where nearest neighbors to a given sublattice must belong to another sublattice. In the case of two sublattices, we can identify diagonal and off-diagonal blocks of the dynamical matrix as follows:

\[
D^{(ss)}_{\alpha \beta} (q) = \frac{2}{m^{(s)}} \frac{f}{a^2} \sum_{\delta^{(s)}} \delta^{(s)}_{\alpha} \delta^{(s)}_{\beta}, \quad s = 1, 2, \tag{8.12a}
\]

\[
D^{(12)}_{\alpha \beta} (q) = -\frac{2}{\sqrt{m^{(1)} m^{(2)}}} \frac{f}{a^2} \sum_{\delta^{(1)}} \delta^{(1)}_{\alpha} \delta^{(1)}_{\beta} e^{-i q \delta^{(1)}}, \tag{8.12b}
\]

\[
D^{(21)}_{\alpha \beta} (q) = -\frac{2}{\sqrt{m^{(2)} m^{(1)}}} \frac{f}{a^2} \sum_{\delta^{(2)}} \delta^{(2)}_{\alpha} \delta^{(2)}_{\beta} e^{-i q \delta^{(2)}}. \tag{8.12c}
\]

Here the \( \delta^{(s)}_{\alpha} \) are nearest neighbors of a particle on sublattice \( s \). For the honeycomb lattice we have identical species \( m^{(1)} = m^{(2)} \), and the set \( \delta^{(s)} \) takes the cartesian form

\[
\{ \delta^{(s)} \} = \left\{ a \begin{pmatrix} \cos \left( \frac{\ell 2 \pi}{3} + \varphi^{(s)} \right) \\ \sin \left( \frac{\ell 2 \pi}{3} + \varphi^{(s)} \right) \end{pmatrix} \right\} \left| \ell = 0, 1, 2 \right\}
\]

with \( \varphi^{(2)} - \varphi^{(1)} = \pi \) in addition. Without loss of generality, we choose the coordinate system shown in figure 8.1 and call “sublattice 1” the one centered at the origin \( 0 \) with \( \varphi^{(1)} = 0 \). For our purpose, we choose specifically \( \hat{e}_z \) as the direction of wave propagation, i.e. \( q = g \hat{e}_z \). This puts us in a position to evaluate the entries (8.12) of
the dynamical matrix for the given honeycomb model:

\[
\frac{1}{a^2} \sum_{\delta^{(1)}} \delta^{(s)}_x \delta^{(s)}_x = \frac{1}{a^2} \sum_{\delta^{(1)}} \delta^{(s)}_y \delta^{(s)}_y = 2 \sum_{\ell=0}^2 \cos^2 \left( \frac{2\pi}{3} \right) = \frac{3}{2},
\]

\[
\frac{1}{a^2} \sum_{\delta^{(1)}} \delta^{(s)}_x \delta^{(s)}_y = \frac{1}{a^2} \sum_{\delta^{(1)}} \delta^{(s)}_y \delta^{(s)}_x = 2 \sum_{\ell=0}^2 \sin^2 \left( \frac{2\pi}{3} \right) \cos \left( \frac{2\pi}{3} \right) = 0,
\]

which holds for \( b = 1, 2 \), irrespective of \( \mathbf{q} \). For the off-diagonal blocks we obtain

\[
\frac{1}{a^2} \sum_{\delta^{(1)}} \delta^{(1)}_x \delta^{(1)}_x e^{-i\mathbf{q} \cdot \mathbf{d}} = 2 \sum_{\ell=0}^2 \cos \left( \frac{2\pi}{3} \right) e^{-iaq \cos(\ell 2\pi/3)} = \frac{1}{2} e^{iaq/2} + e^{-iaq},
\]

\[
\frac{1}{a^2} \sum_{\delta^{(1)}} \delta^{(1)}_y \delta^{(1)}_y e^{-i\mathbf{q} \cdot \mathbf{d}} = 2 \sum_{\ell=0}^2 \sin \left( \frac{2\pi}{3} \right) e^{-iaq \cos(\ell 2\pi/3)} = \frac{3}{2} e^{iaq/2},
\]

\[
\frac{1}{a^2} \sum_{\delta^{(1)}} \delta^{(1)}_x \delta^{(1)}_y e^{-i\mathbf{q} \cdot \mathbf{d}} = \frac{1}{2} \sum_{\ell=0}^2 \sin \left( \frac{4\pi}{3} \right) e^{-iaq \cos(\ell 2\pi/3)} = 0.
\]

The \( s = 2 \) elements are the corresponding complex conjugates. In summary, we obtain for the Dynamical matrix

\[
D \left( q_0 \right) = \frac{f}{m} \begin{pmatrix}
3 & 0 & -e^{iaq/2} - 2e^{-iaq} & 0 \\
0 & 3 & 0 & -3e^{iaq/2} \\
-e^{-iaq/2} - 2e^{iaq} & 0 & 3 & 0 \\
0 & -3e^{-iaq/2} & 0 & 3
\end{pmatrix}. \quad (8.13)
\]

As each of the 4 blocks in eq. (8.13) has diagonal form \( x \)- and \( y \)-direction decouple, and we can immediately identify a longitudinal and a transversal subspace along \( \hat{e}_x/y \). We consider the longitudinal eigenmodes and obtain as criterion for the dimensionless eigenfrequencies \( \tilde{\omega} := \left( \frac{m}{f} \right)^{1/2} \omega \)

\[
0 \equiv \det \begin{pmatrix}
3 - \tilde{\omega}^2 & -e^{iaq/2} - 2e^{-iaq} \\
e^{-iaq/2} - 2e^{iaq} & 3 - \tilde{\omega}^2
\end{pmatrix}
\]

\[
= \left[ 3 - \tilde{\omega}^2 \right]^2 - \left[ \cos \left( \frac{aq}{2} \right) + 2 \cos (aq) \right]^2 - \left[ \sin \left( \frac{aq}{2} \right) - 2 \sin (aq) \right]^2.
\]

This gives

\[
\tilde{\omega}^2_\pm = 3 \pm \sqrt{\left[ \cos \left( \frac{aq}{2} \right) + 2 \cos (aq) \right]^2 + \left[ \sin \left( \frac{aq}{2} \right) - 2 \sin (aq) \right]^2}
\]

\[
= 3 \pm \sqrt{\left[ 3 - \frac{9}{8} (aq)^2 \right]^2 + \frac{9}{4} (aq)^2} + O \left( q^4 \right)
\]

\[
= 3 \left[ 1 \pm \sqrt{1 - \frac{1}{2} (aq)^2} \right] + O \left( q^4 \right),
\]

\[
\tilde{\omega}^2_\mp = \frac{3}{4} (aq)^2 + O \left( q^4 \right). \quad (8.14)
\]

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Now how is this to be compared with the result from [Wal09] in the perfect-lattice limit? The wave propagation tensor from eq. ([Wal09, eq. (3.56)]) is obtained by summing over all lattice vectors without distinction of sublattices. But dropping that distinction is equivalent to summing over all 4 blocks $D^{(ab)}$ of the dynamical matrix from eq. (8.9). Before obtaining a low $q$ limit for the acoustic mode from that sum, we give a second argument for that approach by working back from the microscopic to the field-theoretical approach: The plane-wave ansatz (8.7) made for the displacement vectors $u^{(s)}(r,t)$ from paragraph 3.3.3 in the perfect-lattice regime. First we assume that the $u^{(s)}(R)$ can be expressed as a normalized superposition of the ansatz (8.7) for every $q \in B$, $B \subset 1^{st}$ BZ being the set of wave vectors compatible with the periodic boundary conditions,

$$ u^{(i_s)}(t) = \sum_{q \in B} u^{(i_s)}(q,t) \left/ \sum_{q \in B} 1 \text{TD limit} \frac{1}{V_{BZ}} \int_{BZ} d^d q u^{(i_s)}(q,t) = \frac{1}{(2\pi)^d n_0^{(s)}} \sqrt{\frac{m}{m^{(s)}}} \int_{BZ} d^d q u^{(s)}(q) e^{i(q R_{i_s} - \omega t)}. \right. \tag{8.15} $$

Now we insert this into the microscopic particle density,

$$ \rho^{(s)}(r,t) = \sum_{i=1}^{N^{(s)}} \delta \left[ r - r^{(i_s)}(t) \right] = \sum_{i=1}^{N^{(s)}} \delta \left[ r - (R^{(i_s)} + u^{(i_s)}(t)) \right] $$

$$ = \sum_{i=1}^{N^{(s)}} \delta \left[ r - R^{(i_s)} - \frac{1}{(2\pi)^d n_0^{(s)}} \sqrt{\frac{m}{m^{(s)}}} \int_{BZ} d^d q u^{(s)}(q) e^{i(q r - \omega t)} + O(u^{(s)^2}) \right], $$

making use of the small-displacement limit and the argument of $\delta(\ldots)$ to approximate $R^{(i_s)}$ by $r$. This recovers a continuous displacement field

$$ \rho^{(s)}(r,t) = \sum_{i=1}^{N^{(s)}} \delta \left[ r - R^{(i_s)} - \frac{1}{(2\pi)^d n_0^{(s)}} \sqrt{\frac{m}{m^{(s)}}} \int_{BZ} d^d q u^{(s)}(q,t) + O(u^{(s)^2}) \right] $$

for which we assume the equations from paragraph 3.3.3 to hold within the perfect-lattice regime. Under this assumption we can draw a comparison with the wave equation (3.54b). Having $\varrho_0^{(1)} = \varrho_0^{(2)} = \varrho_0/2$ for the honeycomb lattice

$$ \frac{\partial^2}{\partial t^2} u(q,t) \overset{(3.57)}{=} \frac{\partial^2}{\partial t^2} \sum_{a=1}^{2} \varrho_0^{(a)} \mathbf{u}^{(a)}(q,t) \overset{(8.8)}{=} -\frac{1}{2} \sum_{a,b} D^{(ab)}(q) \cdot \mathbf{u}^{(b)}(q,t) \overset{(3.56)}{=} -\sum_{a,b} D^{(ab)}(q) \cdot \mathbf{j}^{(b)}(q,t) \quad (in\ the\ perfect\ lattice\ regime). \tag{8.16} $$

With the relation (3.41) for the reversible components of $\mathbf{j}^{(s)}$ follows

$$ \frac{\partial^2}{\partial t^2} \mathbf{j}^{(s)}(q,t) = -\sum_{a,b} D^{(ab)}(q) \cdot \mathbf{j}^{(b)}(q,t). \tag{8.17} $$
8.2 Potential expansion method

The sum $\sum_{a,b} D^{(ab)}(q)$ over the 4 blocks from eq. (8.13) yields for $q = q \hat{e}_x$ the low $q$ eigenfrequency limit

$$\tilde{\omega}^2 = 6 - 2 \left[ \cos \left( \frac{aq}{2} \right) + 2 \cos (aq) \right] = \frac{5}{2} (aq)^2 + \mathcal{O} \left( q^4 \right) \quad (8.17)$$

which lies above the result $\tilde{\omega}^2$ from eq. (8.14). Provided that the identification of this second result with $A^{(2)}_{xxx} q^2$ is valid\(^5\), $A^{(2)}$ cannot be the correct wave propagation matrix in the perfect-lattice limit. Possibly, the classical low-temperature limit was not performed correctly in [Wal09, sec. 3.4]. It seems then natural to ask which other limit could be obtained for $A^{(2)}$ that matches Wallace’s $\tilde{A}$\(^{\text{(primitive)}}\) in primitive lattices but contains additional terms in non-primitive ones.

More insight into the discrepancy to the binary result eq. (8.14) can be obtained from an approximate calculation of the corresponding eigenvector.

$$\left( \begin{array}{cc} 3 - \frac{3}{4} (aq)^2 & -e^{iaq/2} - 2e^{-iaq} \\ -e^{-iaq/2} - 2e^{iaq} & 3 - \frac{3}{4} (aq)^2 \end{array} \right) \left( \begin{array}{c} u_x^{(1)}(q) \\ u_x^{(2)}(q) \end{array} \right) = \left( \begin{array}{c} \mathcal{O}(q^3) \\ \mathcal{O}(q^3) \end{array} \right) \quad \Leftrightarrow \quad \begin{array}{l}
\left[ 3 - \frac{3}{4} (aq)^2 \right] u_x^{(1)}(q) - \left[ 3 - i\frac{3}{2}aq - \frac{9}{8} (aq)^2 \right] u_x^{(2)}(q) = \mathcal{O}(q^3), \\
- \left[ 3 + i\frac{3}{2}aq - \frac{9}{8} (aq)^2 \right] u_x^{(1)}(q) + \left[ 3 - \frac{3}{4} (aq)^2 \right] u_x^{(2)}(q) = \mathcal{O}(q^3). \quad (8.18)
\end{array}$$

We are looking for leading order corrections in the eigenvector $(u_x^{(1)}(q), u_x^{(2)}(q))$ and make the ansatz

$$u_x^{(s)}(q) = \gamma^{(s)} + \delta^{(s)}aq + \mathcal{O}(q^2).$$

Subsequently, we determine the parameters $\{\gamma^{(s)}, \delta^{(s)}\}$ by eliminating the leading orders in $q$ in the equations (8.18). The $q$-independent terms yield

$$3 \left( \gamma^{(1)} - \gamma^{(2)} \right) = 0 \quad \Leftrightarrow \quad \gamma^{(1)} = \gamma^{(2)}. \quad (8.19a)$$

For the linear order we obtain

$$3\delta^{(1)} - 3\delta^{(2)} + i\frac{3}{2} \gamma^{(1)} = 0 \quad \Leftrightarrow \quad \delta^{(1)} - \delta^{(2)} = -i\frac{1}{2} \gamma^{(1)} \quad (8.19b)$$

and finally, in the quadratic order

$$\frac{1}{2} \gamma^{(1)} - i2\delta^{(1)} - 4(\varepsilon^{(1)} - \varepsilon^{(2)}) = 0, \quad (8.19b)$$

$$-i2\gamma^{(1)} + 4(\varepsilon^{(1)} - \varepsilon^{(2)}) = 0. \quad (8.19c)$$

\(^5\)Note that this could be easily verified from an explicit evaluation of [Wal09, eq. (3.56)] given on page 96.
Within the 3 equations \((8.19a)\) to \((8.19c)\) occur 5 unknowns. The symmetric choice \(\varepsilon^{(1)} = \varepsilon^{(2)}\) simplifies the \(\mathcal{O}(q^2)\) equations and yields

\[
\delta^{(1)} = -\frac{1}{4} \gamma^{(1)}.
\]

Combining this with equation \((8.19a)\) implies

\[
\delta^{(1/2)} = \mp i \frac{1}{4} \gamma^{(1)}.
\]

For the normalization we choose

\[
\gamma^{(1)} = \frac{1}{\sqrt{1 + (1/4aq)^2}}
\]

and obtain, up to linear order in \(q\), the normalized longitudinal eigenvectors within our approximation

\[
\begin{aligned}
\mathbf{u}_x^{(1/2)}(q) &= \frac{1}{\sqrt{1 + (1/4aq)^2}} \left( 1 \mp i \frac{1}{4} aq \right).
\end{aligned}
\] (8.20)

For finite \(q\), a \(q\)-dependent phase shift occurs between the displacement fields at the two basis positions apparently. This is plausible as e.g. an in-phase oscillation would imply zero strain for the spring connecting the two basis atoms. A treatment of the system with a single displacement field however assumes fixed \(q\)-independent phase shifts among the basis positions. This is also visible from the summation over \(u^{(a)}\) in eq. \((8.16)\) where the \(\mathcal{O}(q)\) terms from eq. \((8.20)\) cancel out. A final comment to these findings will be given in the conclusions on pp. 123.
Part III.

Aspects of Quasiperiodic crystals
9. Extensions to chapter 5

Due to the characteristic structure of their reciprocal lattice, the generalization of the Zwanzig–Mori approach from chapter 5 to quasicrystals is a nontrivial task. This chapter points out major challenges of that endeavor and marks some strategies to deal with them.

9.1. Reciprocal lattice and Bogoliubov inequality

The restriction to periodic crystals in section 2.2 was obtained by requiring the set \{G_1, \ldots, G_I\} in eq. (2.7) to consist of linearly independent vectors. In the following, we will examine the consequences of relaxing this restriction, allowing for quasiperiodic crystals with indexing dimension \(D > d\). More precisely, a basis \{G_1, \ldots, G_D\} of \(G\) now has to be \textit{integrally} independent,

\[
(z_1, \ldots, z_D) \in \mathbb{Z}^D : \sum_{i=1}^{D} z_i G_i = 0 \iff z_1 = z_2 = \ldots = z_D = 0. \tag{9.1}
\]

Now, the case \(D > d\) becomes possible if incommensurate length scales occur in the system, a well-known example being the Fibonacci chain [Sen95; SD09]. Strictly speaking, the set \(G[\{G_1, \ldots, G_D\}]\) of integer linear combinations now forms a “Fourier module” rather than a lattice. This goes along with a dense distribution of points in the physical reciprocal space,

\[
\forall g \in G, \forall \varepsilon > 0 \exists g' \in G \setminus \{g\} : g' \in B_{\varepsilon, g} := \left\{ k \in \mathbb{R}^d \middle| \|k - g\| < \varepsilon \right\}.
\]

This implies that every neighborhood \(B_{\varepsilon, g}\) — defined as the open \(d\)-dimensional ball of radius \(\varepsilon\) around \(g \in G\) — contains an infinite subset \(G_{\varepsilon, g} := G \cap B_{\varepsilon, g} \setminus \{g\}\). With this in mind, the diffraction pattern figure 2.1 from a quasicrystal might confuse at first glance, showing only a finite number of diffraction spots. So before moving further, some elementary considerations are intended to give a better understanding of the structure of reciprocal space in quasicrystals. All considerations will be restricted to a single species system such that the species superscript \((s)\) can be dropped in the remaining chapters. First of all we give a physical argument that for each \(g \in G\), \(|n_g|\) (as defined in eq. (5.1)) can be seen as a local maximum by an arbitrary order of magnitude,

\[
\forall g \in G, \zeta > 0 \exists \varepsilon > 0 : \forall g' \in G_{\varepsilon, g} : |n_{g'}| < \zeta. \tag{9.2}
\]
The proof by contradiction assumes
\[ \exists \mathbf{g}_0 \in \mathbf{G}, \zeta > 0 \forall \varepsilon > 0 : \exists \mathbf{g} \in \mathbf{G}_{\varepsilon, \mathbf{g}_0} : |n_{\mathbf{g}}| \geq \zeta. \]

But from this an infinite set of Bragg peaks with scattering intensity bounded from below by \( \alpha \zeta^2 \) (with \( \alpha > 0 \) a physical constant) can be constructed — in violation of energy conservation. Thus statement (9.2) must be true and the number of Bragg peaks visible in scattering experiments be limited by measuring sensitivity. A more explicit estimate can be given with a reference point \( \mathbf{k} \equiv \tilde{R}d\mathbf{G}/\mathbf{G} = \mathbf{G}_1 \) and the (single-species) Bogoliubov inequality (5.6),
\[ \left\langle |\delta \rho_{\mathbf{G}}(\mathbf{k})|^2 \right\rangle \geq \frac{(\mathbf{G} + \mathbf{k})^2(Vk_B T)^2|n_{\mathbf{G}}|^2}{Rk^2}. \quad (5.6) \]

For any \( \mathbf{g} \in \mathbf{G} \) we will have \( \mathbf{k} - \mathbf{g} \in \tilde{R}d \) and
\[ \left\langle |\delta \rho(\mathbf{k})|^2 \right\rangle = \left\langle |\delta \rho(\mathbf{g} + \mathbf{k} - \mathbf{g})|^2 \right\rangle \geq \frac{k^2(Vk_B T)^2|n_{\mathbf{G}}|^2 V^2}{R||\mathbf{k} - \mathbf{g}||^2} \]
\[ \Rightarrow |n_{\mathbf{g}}|^2 \leq \frac{R||\mathbf{k} - \mathbf{g}||^2}{k^2(Vk_B T)^2 V^2} \left\langle |\delta \rho(\mathbf{k})|^2 \right\rangle \forall \mathbf{g} \in \mathbf{G}, \mathbf{k} \in \tilde{R}d. \]

This implies that a sequence \( \left( |n_{\mathbf{g}_n}| \right)_{n \in \mathbb{N}} \) with \( \lim_{n \to \infty} \mathbf{g}_n = \mathbf{k} \) will decay to 0 at least like \( ||\mathbf{k} - \mathbf{g}_n|| \).

After these initial considerations we will stick to the outline set in part I and consider new aspects arising for firstly the Zwanzig–Mori e.o.m. from section 5.2 and secondly the DFT elastic constants from chapter 6.

### 9.2. Zwanzig–Mori projection formalism in Quasicrystals

The first step in deriving the linear, dissipationless and isothermal e.o.m. within the projection-operator approach was the identification of hydrodynamic variables in section 5.1. While momentum conservation remains the same in every system, a new aspect arises for the broken symmetry variables \( \delta n_{\mathbf{g}} \). With the Bogoliubov inequality long-range autocorrelations of \( \delta \rho(\mathbf{k}, t) \) at every Bragg peak \( \mathbf{g} \in \mathbf{G} \) had been identified. For periodic crystals the values of \( \mathbf{k} \) in eq. (5.6) could be restricted such that at a given \( \mathbf{g} \in \mathbf{G} \) that equation represents a unique and isolated singularity. Because the underlying definition of the first Brillouin zone cannot be used in a

\(^1\)We assume the set \( \tilde{R}d \) to be nonempty. For the reciprocal lattice of the Fibonacci chain this is easily understood from the irrational (golden) ratio \( \tau \) of both basis vectors \( G_2 = \tau G_1 \): For example \( G_1/2 \notin \mathbf{G} \).
9.2 Projection formalism in Quasicrystals

dense reciprocal lattice, the singular points identified by eq. (5.6) will be equal to the dense set \( G \). A hierarchy of the lower bounds can nonetheless be established from that obtainable through (9.2) for the \( n_g \). We will assume that a priori \( \delta n_g(q, t) \) for every \( g \in G \) needs to be included into the set of projected variables, like for periodic crystals. Comparison with [Här+15, eq. (2)] raises the question whether the argument \( q \) might need a restriction to \( \tilde{R}^d \) (which would certainly be problematic in one dimension). Further bear in mind the \( n_g(q) \) are ill-defined in the sense that \( g \notin G \) can always be found such that \( \delta n_g(q) = n_g(q + \tilde{g}) \) does not violate upper bounds to the magnitude of the wave vector argument. In other words, the clear separation between \( g \) as a variable index and \( q \) as a wave vector argument is lost.

Having identified all relevant variables, chapter 5 proceeded by deriving eqs. (5.9). The closed form eqs. (5.11) was obtained from these by restricting the projectors to the first BZ. For eq. (5.9a), M. Fuchs proposed the following ansatz for the slow components of the generalized momentum densities,

\[
\delta j_g(q, t) = \frac{n_g}{n_0} \delta j(q, t) .
\]  

(9.3)

If we ignore the ambiguous definition of \( \delta j \) as previously for the \( \delta n_g \), we arrive at eq. (5.11a) without restricting the projection integrals. On the same basis, eq. (5.9b) formally yields eq. (5.11b) if considered at \( g = 0 \). However, the definition (5.10) leads to another ambiguity,

\[
V k_B \delta_{gg''} = V k_B \delta_{g - \tilde{g}, g'' - \tilde{g}} = \sum_{g'} \langle \delta \rho_{g - \tilde{g}} \rangle (q) \delta \rho_{g'} (q) \rangle J_{g', g'' - \tilde{g}} (q) \\
= \sum_{g'} \langle \delta \rho_{g + \tilde{g}} \rangle (q + \tilde{g}) \delta \rho_{g'} (q) \rangle J_{g + \tilde{g}, g'' - \tilde{g}} (q) \\
= \sum_{g'} \langle \delta \rho_{g + \tilde{g}} \rangle (q) \delta \rho_{g'} (q + \tilde{g}) \rangle J_{g + \tilde{g}, g'' - \tilde{g}} (q) .
\]

Index shifts in both arguments and the summation over \( g' \) were used together with argument shifts in \( \delta \rho_{g'} \). Consistency with the original implicit definition of \( J_{gg'} \) is achieved by assuming

\[
J_{g - \tilde{g}, g'' - \tilde{g}} (q) = J_{gg''} (q + \tilde{g}) \forall \tilde{g} \in G .
\]

Further, each reciprocal-lattice sum now goes over a dense set which raises the question how to properly approximate them by sums over a finite subset of \( G \) in explicit calculations. In section 7.1 the cutoff of reciprocal lattice sums was made beyond all significant nearest-neighbor generations. It seems legitimate to say that the lack of a Brillouin zone remains ubiquitous in the reciprocal-space treatment of quasicrystals. The following paragraph is hence dedicated to a well-known approach to reestablishing a Brillouin zone: The introduction of higher-dimensional periodic structures from which the observed physical structures are obtained by geometric projection.
9.3. Superspace approach

As indicated above, the appeal of the superspace approach comes from the underlying $D$-dimensional periodic lattices which allow point symmetries incompatible with translational order in physical space. Historically [AP13], inspiration for this step was taken from the mathematical works of N. G. de Bruijn [Bru81a; Bru81b] on the construction of Penrose tilings through the cut-and-project method [DK85]: Physical space $\mathbb{R}^d \subset \mathbb{R}^D$ forms a subspace whose decoration with point particles is obtained from a $D$-dimensional superlattice through a projection window/strip $\mathcal{W} \subset \mathbb{R}^{D \perp} =: \mathbb{R}^p$. Membership of a lattice point from $\mathbb{R}^D$ in the physical structure is determined by an indicator function,

$$\chi : \mathbb{R}^p \to \{0, 1\},$$

$$r^\perp \mapsto \begin{cases} 1 & \text{if } r^\perp \in \mathcal{W}, \\ 0 & \text{else.} \end{cases}$$

Here we introduced the superscript “$\perp$” for the projected components of a $D$-dimensional vector $r$. Similarly, the physical components will be indicated by a superscript “$\parallel$”. A translation of the window $\mathcal{W}$ in $\mathbb{R}^p$ — the so-called “internal/complementary space” — will alter the projected structure only by a local isomorphism. This means that any bounded region which appears before the internal translation will also appear afterwards [Lev85; LS86]. This implies that the diffraction pattern/static structure factor will remain indistinguishable in that process. The realization of this property shows interesting connections to number theory: Apparently, a given $(\lambda_1, \lambda_2, \ldots, \lambda_D) \in \mathbb{R}^D \setminus \{0\}$ such that $\sum_i \lambda_i \mathbf{G}_i^\parallel = 0$ has to involve at least one irrational coefficient $\lambda_i$ so as not to violate the condition (9.1). Consequently, $\mathbf{G}_i^\parallel \backslash \mathbf{G}_j^\parallel$ has to be an irrational number for a least one pair $i \neq j$ and $\alpha \in \{1, \ldots, d\}$.

In superspace, these irrational length ratios are reflected by irrational angles between the lattice basis vectors $\mathbf{L}_i$ respectively $\mathbf{G}_i$ and the cartesian coordinate axes. In the Fibonacci chain the projection occurs from a 2-dimensional superspace to a line and can therefore conveniently be visualized — cf. e.g. [Eng04, figure 2.2]³. Figure 2.1 therein shows a decorated superlattice as one of several equivalent approaches to constructing quasicrystal structures. The simplest projections to a plane tiling from $D = 3$ are shown in [Eng08]⁴.

For real structures, the cut-and-project approach can be easily generalized beyond point lattices to more complex structures in superspace. For the equilibrium density

\[\text{108}\]

\[\text{2}\] Algebraic irrational length ratios such as $\tau$ are required in constructing quasicrystals whose orientational symmetry corresponds to a regular polygon/polyhedron in two/three dimensions [LS86].

\[\text{3}\] A limitation to this example is that there are only two space groups in one dimension (characterized by inversion symmetry). Rotation symmetries cannot be considered.

\[\text{4}\] Physically relevant systems require $D \geq 2d$. The case $D = 2d$ is called “minimal embedding”.

9.3 Superspace approach

\[ n \left( r^\parallel \right) = \int d^p r^\perp \chi \left( r^\perp \right) n \left( \frac{r^\parallel}{r^\perp} \right) \]

with \( \left( \frac{r^\parallel}{r^\perp} \right) := r^\parallel + r^\perp \in \mathbb{R}^D \).

Doing the Fourier transform for \( n \left( r^\parallel \right) \) we obtain with the help of Plancherel’s theorem,

\[ n \left( k^\parallel \right) = \int d^d r^\parallel e^{-i k^\parallel \cdot r^\parallel} n \left( r^\parallel \right) = \int d^p r^\perp \chi \left( r^\perp \right) n \left( \frac{k^\parallel}{k^\perp} \right) \]

\[ = \frac{1}{(2\pi)^p} \int d^p k^\perp \chi \left( -k^\perp \right) n \left( \frac{k^\parallel}{k^\perp} \right) \]

\[ = \sum_{g \in G} \chi \left( g^\perp \right) n_g \delta \left( k^\parallel - g^\parallel \right). \quad (9.4) \]

Bear in mind that the \( n_g \) in eq. (9.4) are defined in \( D \) dimensions. A simple example for the set \( W \) is a \( p \)-dimensional, half-open cube with edges of length \( 2\zeta \) such that

\[ \chi \left( k^\perp \right) = \int_{w_{d+1} \pm \zeta} \int_{w_{d+1} \pm \zeta} \cdots \int_{w_D \pm \zeta} dr_{d+1} e^{-i k_{d+1} r_{d+1}} \cdots e^{-i k_D r_D} \]

\[ = \prod_{i=d+1}^D e^{-i k_i \cdot w_i^\parallel} \frac{2 \sin \left( k_i \parallel \zeta \right)}{k_i \parallel}. \quad (9.5) \]

This gives a better understanding of the hierarchy of the physical order parameters \( \chi \left( g^\perp \right) n_g \) found in eq. (9.4) which decay with increasing \( \|g^\parallel\| \). Figure 9.2 gives an illustration of the resulting physical intensities for a specific subset of \( G \).

Even if formally possible, a rewriting of the e.o.m. to superspace was not found expedient. This is because dynamics needs to remain bound to the physical space.

### 9.3.1. Symmetry classification from superspace

Like the point groups, the space groups defined in eq. (2.12) can be generalized to \( D > 3 \) dimensions. Unlike for periodic crystals, symmetry transforms in superspace will generally not leave the physical structure invariant but only locally isomorphic. Driven by this observation and the ambition to circumvent the mathematical workaround of superspace N. D. Mermin and coworkers developed an alternative universal
classification of space groups in quasiperiodic crystals [Mer92; DM96; AN00]. It is based on the notion of indistinguishability of two equilibrium densities, $n \sim n' : \Leftrightarrow \frac{1}{V} \int d^d r \prod_{j=1}^{i} n (r_j - r) = \frac{1}{V} \int d^d r \prod_{j=1}^{i} n' (r_j - r) \ \forall \ i \geq 2, r_j \in \mathbb{R}^d$

which can be shown to be equivalent to the existence of a linear “gauge function” $\chi$ such that

$$n' (g) = e^{2\pi i \chi (g)} n (g) \ \forall \ g \in G .$$

The gauge functions $\Phi_P$ associated with point transforms $P \in \mathbb{P}$ are called “phase functions” (describing symmetry in the space of phases) and obey

$$\Phi_{PQ} (g) = \Phi_P (Q \cdot g) + \Phi_Q (g) \ \mod \mathbb{Z} \ \forall \ P, Q \in \mathbb{P}, \ g \in G .$$

As clarified by T. Janssen in a correspondence with Mermin [Jans01], an explicit form for such phase space functions had been worked out previously: Building upon the Fourier-space classification of space groups for periodic crystals by A. Bienenstock and P. P. Ewald [BE62], an element $(T, P) \in S$ of a superspace group with

$$n \left( \begin{array}{c} r^\parallel \\ r^\perp \end{array} \right) = n \left( \begin{array}{c} P^\parallel \cdot r^\parallel + T^\parallel \\ P^\perp \cdot r^\perp + T^\perp \end{array} \right)$$

(9.6)

can be characterized on the physical reciprocal space by

$$n \left( g^\parallel \right) = e^{-2\pi i g^\perp \cdot T^\perp} e^{-2\pi i g^\parallel \cdot T^\parallel} n \left( P^\parallel \cdot g^\parallel \right) .$$

The phase factor $e^{-2\pi i g^\perp \cdot T^\perp}$ not present in periodic crystals generalizes the notion of symmetry and gives a non-unique form $\Phi_P (g^\parallel) = -g^\perp \cdot T^\perp$ for Mermin’s phase function (for details see [JCB07, sec. 2.6]).

Here we started by assuming the superspace approach and reviewed in what sense it is equivalent to Fourier space crystallography. T. C. Lubensky illustrates the opposite reasoning from irreducible representations of phase space symmetries (viz Fourier-space crystallography) to superspace in [Lub88, sec. 6.1].

### 9.4. Self-consistent approximation

The original aim of this thesis was understood as the retrieval of well-defined acoustic phonon modes for quasicrystals. Their existence is suggested by inelastic scattering
experiments of e.g. de Boissieu et al. [De +07]⁶. This was believed to involve a wave equation like eq. (5.12) with a somehow reinterpreted dynamical matrix \( A \). [JCB07, paragraph 6.4.1] states that such an exact form — given there in eq. (6.9) for periodic crystals — does not exist in quasicrystals. Considering the potential-expansion ansatz, the authors point out the impossibility to reduce the number of coupled equations to \( Bd \) at given BZ wave vector \( q \) like in periodic crystals. A connection to experimental observations can be drawn by their subsequent discussion: They make a continuum approximation in the long-wavelength limit to obtain an e.o.m. (\( d = p = 1 \) w.l.o.g.)

\[
\frac{\partial^2}{\partial r^2} u(r,t) = T(r) \frac{\partial^2}{\partial r^2} u(r,t) \tag{9.7}
\]

with a space-dependent force constant per mass density \( T \). The physical quantities can be embedded in superspace (\( D = 2 \), arbitrary but fixed internal space component), and with

\[
u(r,t) = u\left(r^\parallel, r^\perp\right) e^{-i\omega t}, \quad T(r) = T\left(r^\parallel, r^\perp\right)
\]

eq. (9.7) becomes

\[
-\omega^2 u\left(r^\parallel, r^\perp\right) = T\left(r^\parallel, r^\perp\right) \frac{\partial^2}{\partial r^\parallel^2} u\left(r^\parallel, r^\perp\right). \tag{9.8}
\]

\( u\left(r^\parallel, r^\perp\right) \) is then written as a Bloch function [MS66] for a given, sufficiently small wave vector \( q \) and expanded in a Fourier series

\[
u\left(r^\parallel, r^\perp\right) = \sum_{g \in G} \gamma^q(g) e^{i\left[(g^\parallel + q)r^\parallel + g^\perp r^\perp\right]}
\]

and similarly

\[
T\left(r^\parallel, r^\perp\right) = \sum_{g \in G} S(g) e^{i\left[g^\parallel r^\parallel + g^\perp r^\perp\right]}
\]

Inserting this into eq. (9.8) finally leads to

\[
\omega^2 \gamma^q(g) = \sum_{\tilde{g}} S(\tilde{g}) \left(q + g^\parallel - \tilde{g}^\parallel\right)^2 \gamma^q(g - \tilde{g}) \tag{9.9}
\]

This eigenvalue problem has some similarity to the discussion of electron wave functions in an external potential [MS66, chap. 8 et seqq.]. There, as in eq. (9.9), strong coupling occurs between modes whose wave vectors differ by a reciprocal lattice vector \( g \). The coupling constants \( S(g) \) are strongest if \( g \) corresponds to a prominent Bragg peak. A “pseudo-Brillouin zone” is defined by considering just strongest Bragg peaks near the origin as reciprocal lattice points [Nii89]. [JCB07, Figure 6.2] shows how such a “pseudo-acoustic mode” reappears when the masses of a periodic diatomic harmonic chain are weakly modulated over a larger unit cell. Figure 9.1 tries to capture the same idea from the schematic dispersion relations of the linear chain
shown in figure 6.1 with identical particle masses $m$ and alternating spring constants $K_{1/2}$. For the calculation, those were chosen to $K_1 = 1$ and $K_2 = 1.5$ in units of an arbitrary spring constant $K$. The acoustic and optical mode are plotted up to the boundary of the second Brillouin zone. The dashed acoustic mode was obtained for a monoatomic linear chain with nearest neighbor interactions $\tilde{K} = (K_1 + K_2)/2$ and a lattice constant $a/2$. This can be understood as an average structure with a BZ twice as big as the original structure. One can of course work in the reverse direction and introduce larger and larger unit cells with weakly modulated spring constants. The resulting BZ will only be a fraction of the original. But a “pseudo-acoustic” mode — in the sense of the dashed line in figure 9.1 and [JCB07, Figure 6.2] — could certainly still be identified. Bearing in mind that a quasicrystal can be described as the limit of a series of “periodic approximants”\(^8\), this seems to give a qualitative explanation for the measurements from [De +07, fig. 3]. Their identification of the “acoustic character” of a mode by a normalized inelastic intensity is explained in the methods part of that publication (see also [De 11] for a detailed review).

Now what could be done if acoustic-like modes were indeed not obtainable from the Zwanzig–Mori eqs. (5.9) under consideration of all couplings? How subsets of the reciprocal lattice can be excluded in a systematic and easy way will require further studies. In some quasicrystals exhibiting scaling symmetry — including the Fibonacci chain — points in the reciprocal superlattice can be mapped onto each other by discrete hyperbolic rotations [Jan92]. This allows to restrict the reciprocal

\(\text{optical mode} \quad \text{average mode} \quad \text{acoustic mode}\)

Figure 9.1.: Dispersion relations for a linear chain. The solid lines show the acoustic and optical mode obtained from alternating spring constants $K_{1/2}$ up to the second BZ boundary. The dashed line shows the acoustic mode from the same linear chain with only one average spring constant $\tilde{K} = (K_1 + K_2)/2$. The resulting BZ will only be a fraction of the original. But a “pseudo-acoustic” mode — in the sense of the dashed line in figure 9.1 and [JCB07, Figure 6.2] — could certainly still be identified. Bearing in mind that a quasicrystal can be described as the limit of a series of “periodic approximants”\(^8\), this seems to give a qualitative explanation for the measurements from [De +07, fig. 3]. Their identification of the “acoustic character” of a mode by a normalized inelastic intensity is explained in the methods part of that publication (see also [De 11] for a detailed review).

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\(^6\)See [JCB07, paragraph 6.5.1] for the theory behind these measurements.

\(^7\)Note that this proceeding differs from the definition of a \textit{reduced} spring constant $K_1K_2/(K_1 + K_2)$ which would yield the correct long wavelength limit.

\(^8\)Term for a periodic structure created when approximating irrational length ratios in the construction of quasicrystals by rational numbers [JCB07].
lattice subset and the $q$-integrals in eq. (5.9) in a self-consistent way: Figure 9.2 shows part of the reciprocal lattice projection in the Fibonacci chain with a cutoff criterion $|g^\perp| \leq k^\perp_{\text{cut}}$ for lattice points in the subset $G_\Delta \subset G$. The hyperbolic envelope

![Figure 9.2: Construction of a subset $G_\Delta \subset G$ of the reciprocal lattice. The hyperbolic zone is shown for two different lattice points. The projection boundaries are marked by dotted horizontal and the projections by dashed vertical lines. The size of the projected points was obtained from eq. (9.5) with $\zeta = 5^{1/4}$ to illustrate the hierarchy in Bragg peaks.](image)

\[ |(k^\parallel - g^\parallel)(k^\perp - g^\perp)| = 1 \]

is drawn for two lattice points. We conjecture that the set

\[ \left\{ (k^\parallel, k^\perp) \in \tilde{\mathbb{R}}^2 \left| |(k^\parallel - g^\parallel)(k^\perp - g^\perp)| < 1 \right. \right\} \]

contains no other lattice points than $(g^\parallel, g^\perp)$ and can therefore be used at given $k^\perp_{\text{cut}}$ to restrict the projection in eqs. (5.9) by

\[ |q| < \frac{1}{2k^\perp_{\text{cut}}}. \quad (9.10) \]

Then eqs. (5.11) are recovered with the subset $G_\Delta$ of $G$ obtained from the cutoff. The case that $|q|$ is much smaller than the boundary set in eq. (9.10) can then be reestablished as the long-wavelength limit. Connections of this ansatz to the concepts of periodic average structures [SH99] and the average unit cell [SBW16] should be investigated.
Finally recall that the Bogoliubov argument (5.6) gives a lower bound to the
divergencies of the autocorrelations \( \lim_{q \to 0} \langle |\delta \rho_g(q)|^2 \rangle \) proportional to the scattering
intensities. This raises the question whether a hierarchy of the (in any case diverging)
decay times among the slow variables \( \delta n_g(q,t) \) might exist.

### 9.5. Coupling to phasons

By construction, constant phase factors as in the example eq. (9.5) will leave \( n \)
indistinguishable. In the absence of external fields, the local rearrangements of
particles will cost no energy in total. In addition to homogeneous spatial translations
\( u \) quasiperiodic crystals therefore show extra continuous symmetries \( w \) which are
spontaneously broken in the ground state. Following paragraph 3.2.2, this implies
the existence of additional long-lived “phason” modes. The phason displacement
\( w(r^\parallel, t) \) is a slowly varying hydrodynamic field defined in physical space. The
linear, isothermal, reversible e.o.m. for \( w \) has to be added to the phenomenological
e.o.m. (3.43) (see [LRT85] for a broader discussion). We quote it from [Wal03,
eq (3.31e)] for the generic case of purely dissipative phason currents \( X^w \).

\[
\frac{\partial}{\partial t} w(k, t) = - X^w(k, t) \frac{\text{ reversible \ dynamics}}{0} \].

[Wal03, eq. (3.31e)]

The remaining three e.o.m. remain formally unaltered. For the sake of the argument,
in paragraph 3.3.3 the stress tensor \( \sigma \) was extended by a non-hydrodynamic coupling
(to “optical strain \( b \)”, cf. eq. (3.59)). With \( w \) being a proper hydrodynamic field,
a coupling to linear phason strain \( \nabla_\alpha w_\beta (r,t) =: w_{\alpha\beta} (t) \) must be included into the
hydrodynamic description. We postpone discussion of the generalized free energy
expansion to chapter 10.

Coming back to the projection-operator treatment, the ansatz (6.4) now needs
to be extended by the contributions to \( \delta n_g(q,t) \) that are due to variations in \( w \).
Expanding the phase factor in eq. (9.5) for small \( |w^\parallel| \) and inserting into eq. (9.4)
motivates an ansatz proposed by C. Walz\( ^{10} \):

\[
\delta n_g(q,t) = \text{“previous terms”} - i n_g g^\perp_{\hat{\alpha}} w_{\hat{\alpha}}.
\]

Here \( \hat{\alpha} \in \{d+1, \ldots, D\} \) with a hat indicates the \( p \) internal components of \( g = g^\parallel + g^\perp \)
and \( q = q^\parallel + q^\perp \) is restricted to physical space. “previous terms” stands for the
contributions already found in periodic crystals and given in eq. (6.4b). We will omit
the non-affine contribution \( \delta n_g \) for ease of discussion and with the expectation that

\( ^9 \)In experiment, propagating, sound-like phason can be observed for certain structures [LRT86].
\( ^{10} \)unpublished notes available as PDF files “quasicrystal.pdf” and “excerptQC.pdf”, dated from
October 2010
— like for periodic crystals — important qualitative properties remain unchanged. Hence
\[
\delta n_g(q,t) = -i n_g \left[ (g^\parallel + q) \cdot u + g^\perp \cdot w \right](q,t) - \frac{n_g}{n_0} \delta c(q,t). \tag{9.11}
\]

C. Walz further considered a generalization of the projection (7.23a) to include the phason field\(^{10}\). With a block matrix
\[
N = \begin{pmatrix} \mathcal{N}^\parallel \parallel & \mathcal{N}^\parallel \perp \\ \mathcal{N}^\perp \parallel & \mathcal{N}^\perp \perp \end{pmatrix} = \sum_{g \in G} |n_g|^2 \begin{pmatrix} g^\parallel g^\parallel & g^\parallel g^\perp \\ g^\perp g^\parallel & g^\perp g^\perp \end{pmatrix}
\]
and its schematic inverse\(^{11}\)
\[
M = \begin{pmatrix} \mathcal{M}^\parallel \parallel & \mathcal{M}^\parallel \perp \\ \mathcal{M}^\perp \parallel & \mathcal{M}^\perp \perp \end{pmatrix} := N^{-1}
\]
we consider the ansatz
\[
\begin{pmatrix} u \\ w \end{pmatrix}(q,t) = iM \cdot \sum_g \begin{pmatrix} g^\parallel \\ g^\perp \end{pmatrix} n_g^* \delta n_g(q,t).
\]

Applying a time derivative yields with eqs. (9.11) and (5.11a)
\[
\frac{\partial}{\partial t} \begin{pmatrix} u \\ w \end{pmatrix}(q,t) = \frac{1}{\varrho_0} M \cdot \sum_g \begin{pmatrix} g^\parallel \\ g^\perp \end{pmatrix} |n_g|^2 \begin{pmatrix} g^\parallel & g^\perp \end{pmatrix} \cdot \begin{pmatrix} \delta j \\ 0 \end{pmatrix}(q,t)
\]
\[
= \frac{1}{\varrho_0} M \cdot N \cdot \begin{pmatrix} \delta j \\ 0 \end{pmatrix}(q,t)
\]
\[
= \frac{1}{\varrho_0} \begin{pmatrix} \delta j \\ 0 \end{pmatrix}(q,t).
\]

This is in accordance with the reversible phenomenological hydrodynamics including eq. ([Wal03, eq. (3.31e)])).

From a further analysis of the ansatz (9.11) two additional microscopic coupling constants follow. Taking the time derivative of eq. (5.11b) we obtain
\[
\frac{\partial^2}{\partial t^2} j(q,t) = -\frac{1}{\varrho_0} A(q) \cdot j(q,t) - \left[ \lambda^\parallel \perp (q) - i q \mu^\perp (q) \right] \cdot \frac{\partial}{\partial t} w(q,t) \tag{9.12}
\]
\[
\lambda^\parallel \perp (q) = \sum_{g' \neq g} g'^\parallel n_{g'}^* J_{g'g}^*(q) n_g g^\perp,
\]
with
\[
\mu^\perp (q) = \sum_{g' \neq g} n_{g'}^* J_{g'g}^*(q) n_g g^\perp.
\]

\(^{11}\)Note some peculiarities in inverting block matrices. For 2 by 2 blocks, a formula in terms of the single blocks can be found e.g. on [https://en.wikipedia.org/wiki/Block_matrix](https://en.wikipedia.org/wiki/Block_matrix)
These couplings do not enter reversible dynamics when $w$ has no reversible currents. They constitute relevant couplings in the elastic free energy which shall be reconsidered in the following chapter 10. In anticipation of that discussion, we consider the block matrix

$$\begin{pmatrix} \lambda_{\|,\|} & \lambda_{\|,\perp} \\ \lambda_{\perp,\|} & \lambda_{\perp,\perp} \end{pmatrix} (q) = \sum_{g' \rightarrow g} \left( g_{\perp}^* \right) n_{\perp}^* J_{g'g}^* (q) n_{g} (g_{\|}, g_{\perp}) = \left( \begin{pmatrix} \lambda_{\|,\|} & \lambda_{\|,\perp} \\ \lambda_{\perp,\|} & \lambda_{\perp,\perp} \end{pmatrix} \right) (q) = \left( \begin{pmatrix} \lambda_{\|,\|} & \lambda_{\|,\perp} \\ \lambda_{\perp,\|} & \lambda_{\perp,\perp} \end{pmatrix} \right)^T (-q) .$$

Its self-adjointness and antisymmetry in $q$ can be shown like that of $\Lambda (q)$ in paragraph 5.3.1 (cf. eq. (5.26)). Further inspiration can be drawn from paragraph 5.3.2 and appendix B to show that

$$\begin{pmatrix} \lambda_{\|,\|} & \lambda_{\|,\perp} \\ \lambda_{\perp,\|} & \lambda_{\perp,\perp} \end{pmatrix} (q) = O (q^2) . \quad (9.13)$$

In doing so, a "phason" LMBW equation (cf. eq. (5.33)) needs to be used. It can be easily derived by the same argument as in [WF10, sec. IV.B.1] with an infinitesimally small translation $s_{\perp}$ along complementary space. This transform resembles the physical translation $s_{\|}$ in that it costs no energy. In the absence of external potentials follows

$$\nabla_{\perp} \ln n (r) = \int d^dr' c (r, r') \nabla_{\perp'} n (r') . \quad (9.14)$$

As a consequence of eqs. (9.13) and (9.14), the couplings $\lambda_{\|,\|}, \lambda_{\|,\perp}$ and $\mu_{\perp}$ to $j$ respectively $w$ in eq. (9.12) match phenomenological hydrodynamics in their leading order in $q$. 

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10. Thermodynamic approach to elasticity

A potential application to a common model system for a quasicrystal concludes the last part of this thesis. The approach suggested in section 9.4 gives reason to expect that in the limit of infinite-wavelength deformations $q \to 0$ the Zwanzig–Mori equations (9.4) can be recovered in exact form\(^\text{1}\); on the one hand because of perfect time-scale separation, on the other hand because no reversible couplings need to be neglected. With the ansatz (9.11) whose compatibility with phenomenological hydrodynamics was shown in section 9.5 we will derive DFT expressions for the elastic constants of quasicrystals with $C_{5v}$ point symmetry. On a phenomenological level, elastic constants for that symmetry have already been derived in [Lub88, chapter 7] (see also [Lev+85]). The following discussion aims to identify the phenomenological parameters of these works, based on the considerations from chapter 7, with DFT expressions. Similar has been done for icosahedral hard sphere quasicrystals in [JM87].

Retrieval of Lubensky’s elastic free energy

The starting point is the same DFT free energy expansion as in chapter 6

$$
\delta \mathcal{F} [\{\delta \rho\}] = \delta \mathcal{F}_{\text{lin}} + \sum_{a,b=1}^B \int \int d^d r d^d r \delta \rho (\mathbf{r}) C (\mathbf{r}, \mathbf{r}') \delta \rho (\mathbf{r}') + \mathcal{O} (\delta \rho^3) . \quad (6.1)
$$

We want to relate this to eq. (7.12) of Lubensky’s review,

$$
F (\delta \rho, u_{ij}, \nabla_i w_j, T) = F_0 + F_\rho + F_{\text{el}} \text{ where } \quad F_\rho = \int d^d r \left[ \frac{1}{2} A \left( \frac{\delta \rho}{\rho_0} \right)^2 + B \frac{\delta \rho}{\rho_0} \nabla \cdot \mathbf{u} + B_w \frac{\delta \rho}{\rho_0} \nabla \cdot \mathbf{w} \right] (\mathbf{r}) ,
$$

and

$$
F_{\text{el}} = \frac{1}{2} \int d^d r \left[ K_{\alpha \beta \gamma \delta} u_{\alpha \beta} u_{\gamma \delta} + K_{\alpha \beta \gamma \delta} \nabla_{\alpha} w_{\beta} \nabla_{\gamma} w_{\delta} + 2 K_{\alpha \beta \gamma \delta} u_{\alpha \beta} \nabla_{\gamma} w_{\delta} \right] (\mathbf{r}) .
$$

\(^{1}\text{Working hypothesis 1 provided}\)
\( F_\theta \) is the free energy of the reference state. \( F_\rho \) summarizes the changes in \( F \) due to density fluctuations \( \delta \rho \). Lubensky states that the coupling coefficient \( B_w \) in \( F_\rho \) vanishes for \( C_5 \) symmetry because \( \nabla \) and \( \vec{w} \) transform under different representations of the group \( C_5 \).  

2 DFT expressions for \( B \) and \( A \) which are present in periodic crystals too have been stated in [WF10]. Hence we will focus on the phenomenological elastic free energy \( F_{el} \) with its phonon and phason elastic tensors \( K \). Neglecting couplings to density corresponds to the ansatz

\[
\delta \rho (\vec{r}) = - \left( \vec{u} (\vec{r}) \cdot \nabla + \vec{w} (\vec{r}) \cdot \nabla_i^\perp \right) n (\vec{r})
\]

where \( \nabla_i^\perp n(\vec{r}) \) describes the gradient of \( n \) along perpendicular space, i.e.

\[
\nabla_i^\perp n (\vec{r}) = \lim_{\varepsilon \to 0} \frac{n (\vec{r}, \varepsilon \hat{a}) - n (\vec{r}, \varepsilon \hat{r} = 0)}{\varepsilon} = i \sum_{\vec{g} \in G} g_i^\perp n e^{i \vec{g} \cdot \vec{r}}.
\]

Inserting the ansatz (10.2) into eq. (6.1) up to order \( O (\delta \rho^2) \) yields three contributions to the elastic free energy, \( F_{el} = F^{uu} + F^{uw} + F^{ww} \). \( F^{uw} \) is the contribution known from periodic crystals (cf. [Fuc13, eq. (12)]),

\[
F^{uu} = \frac{k_B T}{2} \iint d^d r \, d^d r' \left[ \frac{\delta (\Delta \vec{r})}{n (\vec{r})} - c (\vec{r}, \vec{r}') \right] u_\alpha (\vec{r}) \nabla_\alpha n (\vec{r}) u_\beta (\vec{r}') \nabla_\beta n (\vec{r}')
\]

\[
= \frac{1}{2} \int d^d r \lambda_\alpha_\beta_\gamma_\delta \nabla_\gamma u_\alpha (\vec{r}) \nabla_\delta u_\beta (\vec{r}) + O (\nabla^2 \vec{u})
\]

\[
\text{with } \lambda_\alpha_\beta_\gamma_\delta = \frac{k_B T}{2V} \iint d^d r \, d^d r' c (\vec{r}, \vec{r}') \nabla_\alpha n (\vec{r}) \nabla_\beta n (\vec{r}') \Delta \gamma \Delta \delta.
\]

From the new phason contributions, first consider the phonon-phason coupling term \( F^{uw} \),

\[
2 \beta F^{uw} = \iint d^d r \, d^d r' \left[ \frac{\delta (\Delta \vec{r})}{n (\vec{r})} - c (\vec{r}, \vec{r}') \right] \times \left[ u_\alpha (\vec{r}) \nabla_\alpha n (\vec{r}) w_\beta (\vec{r}') \nabla_\beta^\perp n (\vec{r}') + \omega_\alpha (\vec{r}) \nabla_\alpha^\perp n (\vec{r}) u_\beta (\vec{r}') \nabla_\beta n (\vec{r}') \right].
\]

Contributions from a constant phason displacement \( \vec{w} \) are eliminated with the phason LMBW equation (9.14). Together with the translational phonon LMBW equation (5.33), eq. (10.3) can be written as

\[
2 F^{uw} = - \int d^d r \frac{k_B T}{2} \int d^d r' c (\vec{r}, \vec{r}') \nabla_\alpha n (\vec{r}) \nabla_\beta^\perp n (\vec{r}') \Delta \gamma \Delta \delta u_\alpha (\vec{r}) \nabla_\gamma \nabla_\delta w_\beta (\vec{r}) + \nabla_\alpha^\perp n (\vec{r}) \nabla_\beta n (\vec{r}') \Delta \gamma \Delta \delta w_\alpha (\vec{r}) \nabla_\gamma \nabla_\delta u_\beta (\vec{r}).
\]

\( B_w \) corresponds to the leading linear order \( O (\vec{q}) \mu^\perp (\vec{q}) \) from eq. (9.12). In his notes, C. Walz considered a vanishing of this coupling constant up to at least linear order in \( \vec{q} \) indispensable. But a coupling of density fluctuations to phason strain can occur in incommensurately modulated structures. So a vanishing of \( \mu^\perp (\vec{q}) \) must arise from system-specific symmetries, only.
After renaming the indices $\hat{\alpha} \rightarrow \hat{\beta}$ and $\beta \rightarrow \alpha$ in the second line, a reasoning similar to that in chapter 6 and [Här+15, sec. 3.A.1.] leads to

$$\mathcal{F}_{\mu \nu} = \frac{1}{2} \int d^d r \lambda_{\mu \nu \gamma \delta} w_\gamma (r) \nabla_\delta w_\beta (r) \quad \text{with}$$

$$\lambda_{\alpha \beta \gamma \delta} = \frac{k_B T}{2V} \int d^d r \int d^d r' c (r, r') \left[ \nabla_\alpha n (r) \nabla_\beta^\prime n (r') + \nabla_\beta^\prime n (r) \nabla_\alpha n (r') \right] \Delta r_\gamma \Delta r_\delta.$$ 

This has $\alpha \leftrightarrow \hat{\beta}$ and $\gamma \leftrightarrow \delta$ symmetry which would for the above $D = 4$ example lead to $3 \times 3 = 9$ phason elastic constants in the most general case. The phenomenological prediction however is $(4 \times 4 - 4)/2 + 4 = 10$ which would correspond to a $\gamma \hat{\alpha} \leftrightarrow \delta \hat{\beta}$ symmetry fitting to a symmetric $4 \times 4$ matrix. A possible explanation for this discrepancy seems the elimination of a single phason elastic constant in the absence of dislocations. As reported specifically for $C_5$ symmetry in [Lev+85], the coupling term in $F_{\text{el}}$ proportional to

$$\left( \nabla_x w_x \right) \left( \nabla_y w_y \right) - \left( \nabla_y w_x \right) \left( \nabla_x w_y \right)$$

vanishes by partial integration. At the same time, integration by parts ensures the $\gamma \leftrightarrow \delta$ symmetry in eq. (10.5) which enforces $\lambda_{341|2} = \lambda_{342|1}$. With this and the requirement of a single coupling constant for the term (10.6), $\lambda_{341|2} = -\lambda_{342|1} = 0$ follows immediately. Whether also for $\lambda^{uu}$ and $\lambda^{uw}$ the number of independent elements depends on the presence of dislocations remains to be discussed. That the number of phonon elastic constants is not influenced by dislocations should be related to the additional rotational symmetry absent in complementary space (no phason-rotational LMBW equations). It yields $\lambda^{uu}_{\alpha \beta \gamma \delta} = \lambda^{uu}_{\gamma \delta \alpha \beta}$, and therefore a symmetry in the first index pair $\alpha \beta$ enforces one for the second pair $\gamma \delta$, too. Concerning $\lambda^{uw}_{\alpha \beta \gamma \delta}$, one could examine whether an $\alpha \leftrightarrow \gamma$ symmetry rather than the stated $\gamma \leftrightarrow \delta$ symmetry holds. A rigorous analysis of the integral (10.3) using the mean-value theorem and bearing in mind that $u$ and $w$ may assume their mean value at different points is indicated.

---

3Note that both summands in eq. (10.3) can be discussed separately to obtain $\lambda^{uw} = \lambda^{\parallel \|}$ and $\lambda^{uw} = \lambda^{\perp \perp}$.

4Cf. the next paragraph “Identification of elastic constants” for its origin.
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For now, we stick to the fact that without dislocations the correct number of independent elastic constants is obtained. We consequently identify the three contributions in the phenomenological \( \mathcal{F}_{el} \) in (10.1) with \( \mathcal{F}^u, \mathcal{F}^w \) and \( \mathcal{F}^{uw} \) respectively. The phenomenological phason elastic constants \( K^{uw} \) can be directly obtained from \( \lambda^{uw} \) as

\[
K^{uw}_{\alpha\beta\gamma\delta} = \lambda^{uw}_{\gamma\delta\alpha\beta}.
\]

Concerning \( K^{uw} \) and \( K^{uu} \), linear combinations of \( \lambda^{uw} \) respectively \( \lambda^{uu} \) need to be found that couple to the symmetrized phonon strain \( u = u^T \) employed in eq. (10.1).

For the phonon elastic constants we quote [Här+15, eq. (39c)]

\[
K^{uu}_{\alpha\beta\gamma\delta} = \lambda^{uu}_{\alpha\gamma\beta\delta} + \lambda^{uu}_{\beta\gamma\alpha\delta} - \lambda^{uu}_{\alpha\beta\gamma\delta}.
\]

For the phonon-phason couplings consider

\[
\int d^d r \left( 2\lambda^{uw}_{\alpha\beta\gamma\delta} \right) u_{\alpha\beta} \nabla_\gamma w_\delta = \int d^d r \lambda^{uw}_{\alpha\beta\gamma} \left( 2u_{\alpha\beta} \nabla_\gamma w_\delta - u_{\beta\gamma} \nabla_\alpha w_\delta \right) = \int d^d r \lambda^{uw}_{\alpha\beta\gamma} \left[ \nabla_\alpha u_{\beta\gamma} \nabla_\gamma w_\delta + \nabla_\beta u_{\alpha\gamma} \nabla_\gamma w_\delta - \frac{1}{2} \left( \nabla_\beta u_{\gamma} + u_{\gamma} \nabla_\beta \right) \nabla_\alpha w_\delta \right] = \int d^d r \lambda^{uw}_{\alpha\beta\gamma\delta} \nabla_\gamma u_{\alpha} \nabla_\delta w_\beta = \mathcal{F}^{uw}
\]

where the \( \beta \leftrightarrow \gamma \) symmetry was used on the underdashed terms and the underlined terms were cancelled out by partial integration. With eq. (10.1) follows

\[
K^{uw}_{\alpha\beta\gamma\delta} = \lambda^{uw}_{\alpha\beta\gamma\delta} - \frac{1}{2} \lambda^{uw}_{\gamma\delta\alpha\beta}.
\]

Note that the \( C_{3v} \) symmetry has not entered \( F_{el} \) nor \( \delta p \) in eqs. (10.1) and (10.2) in any way. The derived relations between \( F_{el} \) and \( \mathcal{F}_{el} \) hence hold for arbitrary quasicrystals.

**Identification of elastic constants**

The number of independent coefficients in \( \lambda^{uu}, \lambda^{uw} \) and \( \lambda^{uw} \) is usually reduced by the symmetry relations of a given point group. This means that not all of the index combinations in \( F_{el} \) eq. (10.1) enter with independent coupling coefficients. Those strain components which enter by the same coupling constant can be worked out by methods of group theory [Lax91; Böh02; LF12], bearing in mind that \( F_{el} \) as a scalar must be invariant under symmetry transforms of the system. The number of independent elastic constants is determined by the number of occurrences of the identity representation in the irreducible representations of the symmetry groups of the quadratic strains \( u_{\alpha\beta} u_{\gamma\delta}, u_{\alpha\beta} w_{\gamma\delta} \) and \( w_{\alpha\beta} w_{\gamma\delta} \). Their symmetry groups are obtained as a direct product from those of the strain fields \( u_{\alpha\beta} \) and \( w_{\alpha\beta} \). The
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Figure 10.1.: Stereogram of the $C_5\nu$ point group. $C_5$ symmetry is achieved by removing every second "+" decoration, i.e. the mirror planes are lost.

Contributions to $F_{el}$ associated with the different elastic constants are those invariant under the respective identity representations. A step-by-step “pedestrian” approach is outlined in [Lub88, chap. 7]. The $C_5(\nu)$ point group is visualized by the stereograph in figure 10.1 with its 5 mirror planes and the 5-fold rotation axis. The computations are eased by use of the Abelian (commutative) representations of the group $C_5$ where

$$(u/w_x) = \begin{pmatrix} 1 & 1 \\ -i & i \end{pmatrix} \begin{pmatrix} u/w_+ \\ u/w_- \end{pmatrix} \quad \text{with } \theta=2\pi/5 \text{ rotations } R \quad \begin{array}{l} u_\pm \xrightarrow{R(\theta)} e^{\pm i\theta} u_\pm, \\ w_\pm \xrightarrow{R(\theta)} e^{\pm 3i\theta} w_\pm. \end{array}$$

Note that $\nabla$ transforms like the vector $u$. One then finds e.g. invariant components $u_{xx} - u_{yy}$ and $2u_{xy}$ for the irreducible $\Gamma_0^{(2)}$ representation of the phason strain field. Having identified which irreducible representations of the strain fields yield irreducible identities in the direct product space, one can give a symmetry-invariant form for $F_{el}$. For the example of $C_5\nu$ symmetry it reads

$$F_{el} = \int_V d^dr f_{el}(r)$$

where $f_{el} = \frac{1}{2} \lambda (\nabla \cdot u)^2 + \mu u_{\alpha\beta} u_{\alpha\beta} + \frac{1}{2} K^w_{\alpha\beta} \nabla_{\alpha} w_\beta + K^w_2 [\nabla_1 w_3 \nabla_2 w_4 - \nabla_2 w_3 \nabla_1 w_4] + K^{uw} [(u_{11} - u_{22}) (\nabla_1 w_3 + \nabla_2 w_4) + 2u_{12} (\nabla_1 w_4 - \nabla_2 w_3)].$

The identification of DFT expressions for the phenomenological elastic constants is now straightforward: By picking one of the quadratic strain terms to each elastic constant $\lambda, \mu, K^w_{1/2}$ and $K^{uw}$ we obtain from the previous identifications between $K^{xx}$ and $\lambda^{xx}$

$$\lambda = K^{uu}_{1122} = 2\lambda_{1212} - \lambda_{1122}, \quad 2\mu = K^{uu}_{1212} = \lambda_{1122},$$

$$K^w = K^{ww}_{1113} = \frac{1}{2} \lambda^{ww}_{1311}, \quad 2K^w_2 = K^{ww}_{1324} = \lambda^{ww}_{3412}. $$
To compute these expressions, one requires a DFT approach that yields a (hypothetically) stable two-dimensional equilibrium density $n$ with $C_{5v}$ symmetry.
Conclusion and Outlook

This thesis set out on a generalization of the reversible, isothermal Zwanzig–Mori crystal hydrodynamics from [WF10] to binary systems. The successful inclusion of optical phonons on that way led to a dynamical block matrix $\Lambda(q)$. Its consistency with phenomenological hydrodynamics could be shown in so far as acoustic phonons were obtained. Nevertheless, the elastic constants could not unambiguously be identified due to additional couplings without clear phenomenological counterpart. As a means of clarification, a comparison with an equivalent thermodynamic route to crystal elasticity was carried out. Table 10.1 lists the main aspects of that comparison to which chapter 8 gave a detailed discussion.

The second generalization of [WF10] aimed for was that to acoustic phonons in quasicrystals. Due to the challenges imposed by the peculiar structure in reciprocal space, no rigorous description could be identified. Nonetheless, a clearer view on the problem could be obtained, which may serve as a starting point to future studies in that direction.

Leaving aside the questions still open about the correct handling of the projection operator approach in quasicrystals as well as in periodic crystals, further research is possible in many directions. To begin with, a natural generalization to phonons and

| Table 10.1.: Synopsis of the key aspects of part II for the Zwanzig–Mori hydrodynamics and the thermodynamic DFT approach. |
| Aspect | Approach | Zwanzig–Mori hydrodyn. | cf. | thermodynamic DFT | cf. |
| output/results | dispersion relations | 5.2 | elastic constants | 6 |
| scope gained | binary periodic crystals | $\text{eq. (5.11)}$ | bin. periodic cryst. of arbitrary symmetry | $\text{eq. (6.11)}$ |
| | optical phonons | 7.1.2 | point defects | $\text{eq. (6.11)}$ |
| | point defects | 7.1.3 | | |
| limitations | nonprimitive & 1 species | 8.1 | nonprimitive & 1 species | 8.1 |
| internal strains | optical couplings?! | C | sublattice displacements | $\text{eq. (6.19)}$ |
| classical $\lim_{T \to 0}$ | discrepancies to [Wal98] | 8.2 | similarities to [Wal98] | 8.2 |
elasticity in the presence of point defects seems the inclusion of topological defects to the treatment. In the context of this work, this would enhance the understanding of the symmetries of the elastic tensor $\lambda^{\omega\nu}$ from chapter 10 and thus of its number of independent elements. In view of the connection between optical modes and piezoelectricity pointed out by [MA67] for crystals without inversion symmetry, considerations in this thesis could lead to the identification of DFT-based expressions for additional material parameters. On a more applied level, implementation of a crystal-specific DFT into the present approach — e.g. from the fundamental measure theory for binary HS crystals in [GS15] — seems desirable. This will allow to study the full expression (7.14) of the dynamical matrix and, on a longer term, to aim for the prediction of martensitic displacive\(^5\) phase transitions. Such transitions can be expected to gain in importance in crystals of anisotropic particles — a tendency that has already been observed for the vacancy concentration in simulations of crystals of truncated hard cubes [Gan+13]. In addition to that, anisotropic particles will come along with rotational degrees of freedom and the potential for additional symmetry-restoring hydrodynamic variables.

\(^5\)Martensitic instabilities can be detected from imaginary phonon eigenfrequencies $\omega < 0$ in the dispersion relations. They correspond to negative restoring forces w.r.t. a certain strain component. See, e.g. [Dov03, chap. 3] for an introduction.
The lack of a unique, classical microscopic reference state impedes the study of elasticity in non-ideal crystals at finite temperature. Not only do thermal lattice vibrations contribute to that lack for their part but they also promote the creation of point defects. Moreover, phason flips cause an ambiguity of the reference configuration intrinsic to quasicrystals. These processes crucially go along with an unclear microscopic definition of the displacement field $u$.

This thesis generalizes previous approaches to isothermal crystal elasticity, focusing on the periodic case discussed in Part II. The two equivalent approaches considered can be distinguished by their nature as static/thermodynamic respectively hydrodynamic. Primarily, the linear, dissipationless and isothermal Zwanzig–Mori equations of motion from [WF10] are generalized to binary periodic crystals. This includes the derivation of a dynamical block matrix $\mathbf{A}$ whose diagonalization yields both acoustic and optical phonon dispersion relations. The elastic constants follow from the acoustic branches by the method of long waves. The central input parameter to the theory is the direct correlation function which can be obtained from classical Density Functional Theory (DFT). As a proof of principle, dispersion relations are computed for several binary hard sphere model systems, based on a simple DFT approach to freezing. Dispersion relations are further computed from the equilibrium statistics of a binary hard sphere crystal Molecular Dynamics simulation. To that end, the definition of the linear response displacement field from [WF10] is generalized in a species-wise manner.

A discussion of the properties of the dynamical matrix $\mathbf{A}$ in the long-wavelength limit is performed with the result of potential couplings of the total momentum density to non-hydrodynamic variables. While these couplings can be ruled out in systems with inversion symmetry, there are strong indications for a lowering of the elastic constants in the opposite case. This seems in conflict with phenomenological hydrodynamics of crystals and raises fundamental questions about the correct application of the Zwanzig–Mori formalism. More specifically, the presence of reversible contributions in the memory matrix comes into question. In reaction to that, two working-hypotheses are formulated that allow to apply the formalism in the conventional way, yet appear incompatible in the light of the findings.

Therefore, a “second witness is called to court” in the form of the thermodynamic DFT approach to crystal elasticity. It is formulated for binary periodic crystals of
arbitrary symmetry. By dropping the requirement of inversion symmetry and by the inclusion of point defect fluctuations, this thesis adds to the scope of previous binary approaches. Additionally, the equilibrium condition at given external strain and defect fluctuations is discussed on the level of arbitrary internal strain. This is expected to provide a straightforward access to the treatment of more complicated internal strains. The subsequent example includes only a single sublattice displacement as “optical” internal strain parameter. Its coupling to external strain is derived and related to results known from the classical low-temperature potential expansion. Whether this potential expansion approach has been correctly recovered by [Wal09] in the case of lattices without inversion symmetry is studied on the example of the honeycomb lattice.

In a separate part, approaches to the description of acoustic phonons in quasicrystals within the same Zwanzig–Mori formalism are explored. The characteristic “dense” structure of the reciprocal lattice for such systems poses challenges to which no conclusive answer could be given. The author hopes that the approaches made may serve as a starting point for future research. Nonetheless, encouraged by earlier works in that direction, the thermodynamic approach to elasticity is modified from periodic crystals and applied to a specific two-dimensional quasicrystal example.

Deutsch  Das Fehlen einer eindeutigen, klassischen mikroskopischen Referenzkonfiguration steht der Elastizitätstheorie nichtidealer Kristalle bei endlichen Temperaturen im Wege. Thermische Gitterschwingungen tragen nicht nur ihren Teil zu dieser Problematik bei, sondern begünstigen auch die Entstehung von Punktdefekten. Darüber hinaus bewirken Phasonenflips eine Quasikristallen intrinsische Mehrdeutigkeit der Referenzkonfiguration. Entscheidend ist, dass diese Prozesse mit einer unklaren mikroskopischen Definition des Verschiebungsfeldes \( u \) einhergehen.


Ansätze zur Beschreibung akustischer Phononen in Quasikristallen im Rahmen des Zwanzig–Mori-Formalismus werden in einem separaten Teil untersucht. Die charakteristische “dichte” Struktur des reziproken Gitters in solchen Systemen bringt Herausforderungen mit sich, auf die keine abschließende Antwort gegeben werden konnte. Der Autor hofft, dass die gemachten Ansätze als Ausgangspunkt zukünftiger Forschung diesen können. Ermüdigt von früheren Arbeiten in dieselbe Richtung wird gleichwohl die thermodynamische Herangehensweise an Elastizität von periodischen Kristallen modifiziert und auf das Beispiel eines einfachen zweidimensionalen Quasikristalls angewandt.
Danksagung


It was a great pleasure both scientifically and personally to collaborate with the group of Prof. Marjolein Dijkstra from Utrecht University. I am particularly indebted to Dr. Anjan Prasad Gantapara who provided the simulation results for section 7.2.


Mit Abstand am meisten verdanke ich auf dem Weg hierher meinen Eltern. Ihnen widme ich diese Arbeit und schließe mit einem Gebet der Hl. Edith Stein [Ste08]:

Ohne Vorbehalt und ohne Sorgen
Leg’ ich meinen Tag in Deine Hand.
Sei mein Heute, sei mein gläubig Morgen,
Sei mein Gestern, das ich überwand.

Frag mich nicht nach meinen Sehnsuchtswegen,
Bin aus Deinem Mosaik ein Stein.
Wirst mich an die rechte Stelle legen,
Deinen Händen bette ich mich ein.

Amen.
A. Projectors with non-slow variables

This appendix examines under which conditions Working hypothesis 2 can be shown to hold. Assume a set of slow variables $A_0 = \{A_1, A_2, \ldots, A_\ell\}$ that meets the requirements of Working hypothesis 1 and a second set of non-slow variables $A_1 = \{A_{\ell+1}, \ldots, A_\sigma\}$. W.l.o.g., we can assume for the static correlation functions $\langle A_i^* (k) A_{i+j} (k) \rangle = O(k^2)$ with $i \in \{1, \ldots, \ell\}$ and $j \in \{\ell+1, \ldots, \sigma\}$. The Zwanzig–Mori formalism for the set $A_0 \cup A_1 = \mathcal{A}$ starts from a matrix of correlation functions as

$$
C(z, k) = \begin{pmatrix}
C_{11} & C_{12} & \cdots & C_{1\ell} & \cdots & C_{1\sigma} \\
C_{21} & C_{22} & \cdots & C_{2\ell} & \cdots & C_{2\sigma} \\
\vdots & \vdots & \ddots & \vdots & & \vdots \\
C_{\ell 1} & C_{\ell 2} & \cdots & C_{\ell \ell} & \cdots & C_{\ell \sigma} \\
\vdots & \vdots & \ddots & \vdots & & \vdots \\
C_{\sigma 1} & C_{\sigma 2} & \cdots & C_{\sigma \ell} & \cdots & C_{\sigma \sigma}
\end{pmatrix}(z, k).
$$

The missing of the second wave vector argument $k'$ has been be found for periodic crystals in eqs. (5.11) and is used in advance for simplicity. The top-left $\ell \times \ell$ block yields all modes whose relaxation times $\tau_j$ become, in the long-wavelength limit $k \to 0$, much larger compared to the remaining dynamics. As discussed in paragraph 3.2.1, in the present case of hydrodynamic slow variables this time scale separation becomes infinitely large as $k$ goes to 0. Consequently, all hydrodynamic modes can be obtained from the Zwanzig-Mori formalism with the conventional projection operators

$$
P_0 = \sum_{i,j=1}^{\ell} A_i \langle A_i^* A_j \rangle^{-1} \langle A_j^* \rangle, \quad Q_0 = 1 - P_0.
$$

Note that, at finite $k$, $C(z, k)$ does generically not take block-diagonal form and a coupling between the sets $A_0$ and $A_1$ will occur. In order to obtain generalized reversible modes, in the following a frequency matrix $\Omega$ will be obtained from $C$ with a projection operator $\mathcal{P}$ that projects on all variables in $\mathcal{A}$ (and $Q = 1 - \mathcal{P}$). But is it still justified in this context to obtain sound velocities and elastic constants from a discussion of the frequency matrix $\Omega$ alone? In other words can neglecting the memory matrix $\mathcal{F}$ introduce artificial contributions to these quantities? The

\[1\] This can always be ensured by projecting out the respective orders in $q$ from the variables in $A_1$. 

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inclusion of the set $A_1$ into the set of considered variables can by construction not affect the slowest eigenmodes obtained alone from the set $A_0$. To illustrate this, we refer to the appendix of [GL89] where Götze and Latz introduce a reduced resolvent operator $R_0(z)$ as

$$R_0(z, k) = Q_0 [Q_0 L Q_0 - z]^{-1} Q_0.$$  

The correlation function $C_{ij}(z) = \langle A_i^* R(z) A_j \rangle$ is then expressed in terms of the reduced resolvent $R_0(z)$ in [GL89, eq. (A14)] which can be used to rewrite the coupling between slow and non-slow variables in the long-wavelength limit. With slightly adapted notation, that eq. (A14) reads

$$C_{XY}(z, k) = \sum_{i,j=1}^\ell \langle X^* A_i \rangle \langle A_i^* R(z) A_j \rangle \left( \langle A_j^* L R_0(z) Y \rangle - \langle A_j^* Y \rangle \right).$$

(A.1)

With $X \in A_0$ and $Y \in A_1$ arbitrary\(^2\), the expression (A.1) simplifies strongly as $R_0(z)$ applied to $X$ vanishes by construction.

$$C_{XY}(z, k) = \sum_{i,j=1}^\ell \langle X^* A_i \rangle \langle A_i^* R(z) A_j \rangle \langle A_j^* L R_0(z) Y \rangle.$$  

(A.2)

The first two terms of eq. (A.2)

$$\sum_{i=1}^\ell \langle X^* A_i \rangle \langle A_i^* R(z) A_j \rangle (k) = \sum_{i=1}^\ell \langle X^* A_i \rangle (k) C_{ij}(z, k)$$

form a linear combination of the entries of $C_0$. The subsequent limit $\lim_{z \to 0} \lim_{k \to 0}$ can thus be inferred from standard results (here: of hydrodynamics). The remaining third term has the hydrodynamic poles removed by the projector $Q_0$ and gives only a renormalization factor. The separate discussion of its hydrodynamic limit follows [For74, section 7] and [Mis]: The projector $Q_0$ can be omitted from the time-evolution operator $\exp(-i Q_0 L Q_0 t)$ in the limit $k \to 0$. One then finds, neglecting terms of order $O(k^2)$,

$$\lim_{z \to 0} \lim_{k \to 0} \langle A_j^* L R_0(z) Y \rangle (k) = \lim_{z \to 0} \lim_{k \to 0} \langle A_j^* L Q_0 \frac{1}{L - z} Y \rangle (k)$$

$$= -i \lim_{t \to 0} \lim_{k \to 0} \int_0^\infty dt e^{-it} \langle A_j^* L Q_0 Y(t) \rangle (k)$$

$$= 0 \text{ by construction.}$$

(A.3)

To obtain eq. (A.3) bear in mind that the $A_j$ and $Q_0$ contain only slow variables. It seems fair to assume — e.g. from a continuity equation for conserved variables —

\(^2\)Consideration of $C_{YX}(z, k)$ becomes obsolete for the hydrodynamic modes if $C(z, k)$ can be shown to be triangular up to (and including) terms of $O(k)$. 

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A.1 Reversible terms in the memory matrix

that \( A^*_i \mathcal{L} \mathcal{Q}_0 = \mathcal{O}(q) \) and that the remaining time integral stays finite because \( Y \) decays fast.\(^3\)

In summary, this eliminates contributions to the poles of \( C_0 \) from the coupling term \( C_{XY} \) which is the expected result. To justify Working hypothesis 2 however, \( \Omega \) and \( \Gamma \) need to take an approximate block-diagonal form separately in the hydrodynamic limit. This is to rule out that neglecting \( \Gamma \) while considering \( \Omega \) induces artificial terms of \( \mathcal{O}(q) \) that would cancel out when considering both of these contributions. So we still need to argue that \( \Gamma_{XY} (z, k) = \mathcal{O} \left( k^2 \right) \) which we can then use for

\[
\Gamma_{XY} (z, k) = \mathcal{O} \left( k^2 \right) \quad \leftrightarrow \quad \Omega_{XY} (k) = \mathcal{O} \left( k^2 \right). \quad (A.4)
\]

At this point we resort to a physical argument: The hydrodynamic limit will not be altered if only the slow component of each variable is considered. This corresponds to the replacement \( A_i \to \mathcal{P}_0 A_i \), \( i = 1, 2, \ldots, \sigma \) which was used in the beginning to (approximately) block-diagonalize the matrix of static correlation functions \( C_{i\ell} (k) \) and consequently also its inverse\(^4\),

\[
C_{XY} (k) = \langle X^* Y \rangle (k) = \langle X^* \mathcal{P}_0 (k) Y \rangle (k) = \mathcal{O} \left( k^2 \right). \quad (A.5)
\]

The approximate form here stresses the wave vector dependency of the projection operator itself. By applying the substitution \( A_i \to \mathcal{P}_0 A_i \) to

\[
\Omega_{XY} (k) = \sum_{i=1}^{\sigma} \left\langle A^*_X \mathcal{L} A_i \right\rangle (k) C^{-1}_{iY} (k) \quad \text{or} \quad \Gamma_{XY} (z, k) = \sum_{i=1}^{\sigma} \left\langle A^*_X \mathcal{L} \frac{1}{Q \mathcal{L} Q - z} Q \mathcal{L} A_i \right\rangle (k) C^{-1}_{iY} (k).
\]

we obtain either side of eq. (A.4).

### A.1. Reversible terms in the memory matrix

The following considerations are motivated by the findings for nematic liquid crystals by Forster, presented in [For74] and [For90, chapter 9]. There, the continuous orientational symmetry is spontaneously broken by a non-conserved quantity — the particle orientation (“director”)\(^5\). This leads to reversible contributions in the memory matrix and corrections to the speed of sound obtained from the frequency

\(^3\)If \( Y \) on the contrary still contained slow components, the remaining integral might diverge as they would not be projected out by \( \mathcal{Q}_0 \). It is therefore crucial to project out the complete slow dynamics in the Zwanzig–Mori formalism.

\(^4\)For the inversion of block matrices cf. [GL89, and references therein].

\(^5\)This opposes, e.g., the magnetization in a ferromagnet which also breaks orientational symmetry but originates from a conserved density, viz. the electron spin.
matrix, alone. The translational symmetry that is spontaneously broken inside a crystal apparently constitutes no conserved quantity either. Based on Forster’s reasoning and paragraph 3.2.1, we analyze possible contributions to the memory matrix in a single-species crystal. Equation (3.17) generalizes to

\[ \Gamma_{ij}(z, k) C_{ij}(k) = \left\langle A^*_i \mathcal{L} Q \frac{1}{\mathcal{Q} - z} \mathcal{Q} A_j \right\rangle(k) . \]

For the given set of hydrodynamic variables, we will replace the observable indices by \( \tilde{j} \) and \( \delta \tilde{\rho} \) as appropriate. The vector symbol is used as a shorthand notation for vectors whose components are indexed by \( g \in G \sim N \). Also in the multivariate case, the reduced dynamics \( \mathcal{Q} \mathcal{L} \mathcal{Q} \) can be replaced by \( \mathcal{L} \) in the long-wavelength limit \( k \to 0 \). This yields

\[
\lim_{z \to 0} \lim_{k \to 0} \Gamma_{il}(z, k) C_{lj}(k) = - \lim_{z \to 0} \lim_{k \to 0} \left\langle A^*_i Q \frac{1}{\mathcal{L} - z} Q A_j \right\rangle(k) = -i \lim_{\varepsilon \to 0} \int_0^\infty dt e^{-\varepsilon t} \lim_{k \to 0} \left\langle A^*_i(k) Q(t = 0) Q(t) A_j(k) \right\rangle_{\mathcal{T}(t)} = -i \lim_{\varepsilon \to 0} \int_0^\infty dt e^{-\varepsilon t} \lim_{q \to 0} \left\langle \left( \frac{\partial^{*}(q) \mathcal{T}(t) \tilde{\mathcal{J}}(q) \mathcal{T}(t) \delta \tilde{\rho}(q)}{\delta \tilde{\rho}^{*}(q) \mathcal{T}(t) \tilde{\mathcal{J}}(q) \mathcal{T}(t) \delta \tilde{\rho}(q)} \right) \right\rangle .
\]

In order to obtain eq. (3.18), we assumed a continuity equation holds for \( a \). For \( \delta \tilde{\rho} \), one has to use eq. (5.2) instead so that

\[
\lim_{z \to 0} \lim_{k \to 0} \Gamma_{il}(z, k) C_{lj}(k) = -i \lim_{\varepsilon \to 0} \int_0^\infty dt e^{-\varepsilon t} \lim_{q \to 0} \times \left( \frac{q \cdot \sigma^{*}(q) \mathcal{T}(t) q \cdot \sigma(q) - q \cdot \sigma^{*}(q) \mathcal{T}(t) (\mathbf{g} + \mathbf{q}) \cdot \tilde{\mathbf{j}}(q)}{m^2 (\mathbf{g} + \mathbf{q}) \cdot \tilde{\mathbf{j}}(q) \mathcal{T}(t) (\mathbf{g} + \mathbf{q}) \cdot \tilde{\mathbf{j}}(q)} \right) \right\rangle .
\]

For the detailed reasoning behind the expressions (A.6a) and (A.6b) refer to [For74] and [Mis]. The equilibrium correlation matrix \( C \) becomes block diagonal by use of the opposite time inversion symmetries of \( j \) and \( \delta \tilde{n} \). We find

\[
C(q) = \left( \frac{j^* j}{\delta \tilde{\rho}^{*} \delta \tilde{\rho}} \right)(q)
\]

whose inverse is known from eqs. (5.5) and (5.23a). Whether the expressions (A.6) have nonvanishing terms of \( \mathcal{O}(q) \) in their off-diagonal blocks, needs further investigation. A coupling of the strain tensor \( \sigma \) to generalized currents \( j_g \) seems to fit into the picture of internal strains from chapter 6.
B. Another proof of property (5.41)

As one easily convinces oneself from eq. (5.39), $P A^{(\text{tot})} (q) = P A^{(\text{tot})\dagger} (q) = P A^{(\text{tot})} (-q)$ is self-adjoint and antisymmetric in $q$. The former implies the existence of a unitary matrix $R (q)$, $R^{-1} = R^\dagger$, such that the associated (eigen)basis transform reads

$$R (q) \cdot P A^{(\text{tot})} (q) \cdot R^{-1} (q) = \text{diag} (\lambda_1 (q), \lambda_2 (q), \ldots, \lambda_d (q))$$

with diag a shorthand for a diagonal matrix and $\lambda_1 (q), \ldots, \lambda_d (q) \in \mathbb{R}$. Because the antisymmetry in $q$ of $P A^{(\text{tot})} (q)$ holds irrespective of a particular coordinate system, $\lambda_\sigma (q) = \lambda_\sigma (-q) = O (q^2)$. Making use of the normalization of the elements of $R$, it is now easy to give an upper bound to the elements of $P A^{(\text{tot})} (q)$ as

$$\left| P A^{(\text{tot})}_{\alpha\beta} (q) \right| = \left| R^{-1}_{\alpha\sigma} (q) \lambda_\sigma (q) R_{\sigma\beta} (q) \right| \leq \left| R^{-1}_{\alpha\sigma} (q) \right| \left| \lambda_\sigma (q) \right| \left| R_{\sigma\beta} (q) \right| \leq \sum_{\sigma=1}^{d} \left| \lambda_\sigma (q) \right| = O \left( q^2 \right).$$

This shows that the leading order in $q$ exponent of the eigenvalues of $P A^{(\text{tot})}_{\alpha\beta} (q)$ has a lower bound of 2.

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C. Approximate diagonalization of dynamical matrix $\Lambda$

Inspired by [Wal98, chap. 15], we will see that an additional coordinate transform $U$ diagonalizes the binary $p_2^2\Lambda$ from eq. (5.32) into an acoustic and an optical $d \times d$ block, coupling only by terms of $O(q^3)$. The transformation matrix $U$ takes the following form

$$U = \begin{pmatrix} I_d - \frac{1}{2}q^2\delta^\dagger \cdot \delta & -q\delta^\dagger \\ q\delta & I_d - \frac{1}{2}q^2\delta \cdot \delta^\dagger \end{pmatrix} \tag{C.1}$$

where $\delta = p_2^2\Lambda_0^{(22)-1} \cdot p_2^2\Lambda_1^{(21)} = \left[p_2^2\Lambda_1^{(12)} \cdot p_2^2\Lambda_0^{(22)-1}\right]^\dagger \tag{C.2}$

and $p_2^2\Lambda_n^{(ab)}(q) := \lim_{q \to 0} \frac{1}{q^n} p_2^2\Lambda_n^{(ab)}(q\hat{q})$.

The transformation matrix $U$ in eq. (C.1) is constructed from the leading terms of an expansion of $p_2^2\Lambda(q)$ in $q$. Concerning the existence of the inverse $p_2^2\Lambda_0^{(22)-1} = p_2^2\Lambda^{(22)-1}(q = 0)$ bear in mind the self-adjointness of $p_2^2\Lambda^{(22)}$. Its invertibility is equivalent to the requirement of nonvanishing eigenvalues.\(^1\) The inverse $U^{-1}$ can be approximated by $U^\dagger$ because $U(q)$ is unitary up to terms of $O(q^4)$,

$$U^\dagger \cdot U = \begin{pmatrix} I_d - q^2\delta^\dagger \cdot \delta + q^2\delta^\dagger \cdot \delta + O(q^4) & 0 \\ 0 & I_d + O(q^4) \end{pmatrix} \cdot$$

\(^1\)Under the condition that the diagonalizable $\Lambda(q = 0)$ has no more than $m$ degenerate vanishing eigenvalues with eigenvectors $\hat{j}_1, \hat{j}_2, \ldots, \hat{j}_m$, $\Lambda_0$ becomes invertible in the orthogonal complement of $\{\hat{j}_1, \hat{j}_2, \ldots, \hat{j}_m\}$. With a physical stability argument and eq. (5.44), this yields the invertibility of $p_2^2\Lambda_0$ in the general $B$-species case.
For the transformed matrix $\mathbf{DP}_2 \mathbf{A} = \mathbf{U} \cdot \mathbf{P}_2 \cdot \mathbf{A} \cdot \mathbf{P}_2^{-1} \cdot \mathbf{U}^\dagger$ yields, up to terms of $O(q^3)$

\[
\mathbf{DP}_2 \mathbf{A}(q) + O(q^3) = \mathbf{U} \cdot \begin{pmatrix}
q^2 \mathbf{p}_2 \mathbf{A}_2^{(11)} & q^2 \mathbf{p}_2 \mathbf{A}_1^{(12)} & \left(1 + \mathbf{d} - \frac{1}{2} q^2 \delta^\dagger \cdot \delta - q \delta^\dagger \right) \\
q^2 \mathbf{p}_2 \mathbf{A}_2^{(21)} & \mathbf{p}_2 \mathbf{A}_0^{(12)} & \left(1 + \mathbf{d} - \frac{1}{2} q^2 \delta^\dagger \cdot \deltaight) \\
q^2 \left(\mathbf{p}_2 \mathbf{A}_2^{(11)} - \mathbf{p}_2 \mathbf{A}_0^{(22)} \cdot \delta \right) & q^2 \mathbf{p}_2 \mathbf{A}_0^{(22)} & \left(\delta \cdot \mathbf{p}_2 \mathbf{A}_1^{(12)} - \frac{1}{2} \delta \cdot \delta^\dagger \cdot \mathbf{p}_2 \mathbf{A}_0^{(22)}ight) + q^2 \left(\delta \cdot \mathbf{p}_2 \mathbf{A}_1^{(12)} - \frac{1}{2} \delta \cdot \delta^\dagger \cdot \mathbf{p}_2 \mathbf{A}_0^{(22)}\right)^\dagger
\end{pmatrix}
\]

The off-diagonal blocks in eq. (C.3) vanish with the definition (C.2) of $\delta$,

\[
\delta^\dagger \cdot \mathbf{p}_2 \mathbf{A}_0^{(22)} = \mathbf{p}_2 \mathbf{A}_1^{(12)} \cdot \mathbf{p}_2 \mathbf{A}_0^{(22)}^{-1} \cdot \mathbf{p}_2 \mathbf{A}_0^{(22)} = \mathbf{p}_2 \mathbf{A}_1^{(12)}
\]

such that $\mathbf{DP}_2 \mathbf{A}(q)$ takes, up to $O(q^3)$, a block-diagonal form with blocks

\[
\mathbf{DP}_2 \mathbf{A}^{(11)}(q) = \mathbf{A}^{\text{sound}}(q) + O(q^3)
\]

where

\[
\mathbf{A}^{\text{sound}}(q) = q^2 \mathbf{p}_2 \mathbf{A}_2^{(11)} - q^2 \left[\mathbf{p}_2 \mathbf{A}_1^{(12)} \cdot \mathbf{p}_2 \mathbf{A}_0^{(22)}^{-1} \cdot \mathbf{p}_2 \mathbf{A}_1^{(21)} + \left(\ldots\right)^\dagger\right]
\]

\[
\mathbf{DP}_2 \mathbf{A}^{(22)}(q) = \mathbf{A}^{\text{opt}}(q) + O(q^3)
\]

where

\[
\mathbf{A}^{\text{opt}}(q) = \mathbf{p}_2 \mathbf{A}_0^{(22)} + q^2 \left[\mathbf{p}_2 \mathbf{A}_0^{(22)}^{-1} \cdot \mathbf{p}_2 \mathbf{A}_1^{(21)} \cdot \mathbf{p}_2 \mathbf{A}_1^{(12)} - \frac{1}{2} \left[\mathbf{p}_2 \mathbf{A}_1^{(12)} \cdot \mathbf{p}_2 \mathbf{A}_0^{(22)}^{-1} \cdot \mathbf{p}_2 \mathbf{A}_1^{(21)} \cdot \mathbf{p}_2 \mathbf{A}_1^{(12)}\right]^\dagger \cdot \mathbf{p}_2 \mathbf{A}_0^{(22)} \cdot \mathbf{p}_2 \mathbf{A}_0^{(22)}^{-1}\right] + q^2 \left[\ldots\right]^\dagger.
\]

A relation of $\mathbf{A}^{\text{sound}}_{\alpha\beta\gamma\delta} := \partial_q \partial_{\eta_\beta} \mathbf{DP}_2 \mathbf{A}^{(11)}(q=0)$ to the phenomenological elastic constants $K_{\alpha\beta\gamma\delta}^{c}$ requires the fourth-rank tensor $\mathbf{A}^{\text{sound}}$ to obey “Voigt-like” symmetries. “Voigt-like” indicates that the number of independent elements (21 in 3d) has to be the same while the $\alpha \leftrightarrow \beta$, $\gamma \leftrightarrow \delta$ and $\alpha \beta \leftrightarrow \gamma \delta$ symmetries may be only obeyed by a linear superposition of elements with appropriate index permutations. Compare the phenomenological wave equation (3.54b)

\[
\frac{\partial^2}{\partial q^2} \tilde{j}_\alpha(q,t) = -\frac{1}{\varrho_0} \frac{K_{\alpha\beta\gamma\delta}^{c} q_\beta \tilde{q}_\delta \tilde{j}_\beta(q,t)}{q_\gamma}
\]

with

\[
\frac{\partial^2}{\partial q^2} j_\alpha(q,t) = -\frac{1}{\varrho_0} \mathbf{A}^{\text{sound}}_{\alpha\beta\gamma\delta} q_\beta q_\delta \tilde{j}_\beta(q,t)
\]
where the exact acoustic eigenvector differs from $\delta j(q, t)$ only by terms of $O(q)$. The part $P^2 A_{(11)}$ of $A_{\text{sound}}(q)$ in eq. (C.4a) stems from the coupling internal to the total momentum subspace in eq. (5.32). It appears plausible that an identification with elastic constants can be performed much in parallel to that by C. Walz in [Wal09; WF10]. We therefore consider only the index structure of the additional contribution to $A_{\text{sound}}(q)$:

$$A_{\alpha\beta\gamma\delta}^{\text{sound}} q_\gamma q_\delta - P^2 A_{(11)} = - \left[ P^2 A_{(12)} P^2 A_{(22)}^{-1} P^2 A_{(21)} + P^2 A_{(12)^*} P^2 A_{(22)^*}^{-1} P^2 A_{(21)^*} \right] q_\gamma q_\delta =: \kappa_{\alpha\beta\gamma\delta}$$

where $P^2 A_{(ab)} := \frac{\partial}{\partial q_\gamma} P^2 A_{(ab)}(q = 0)$.

For $P^2 A_{(12)}$ in eq. (5.32) we take from eq. (5.38)

$$P^2 A_{(12)} = \frac{q_0}{\theta_0} \sum_{s=1}^{\frac{5.32}{\beta V}} (A^{(s1)} - A^{(s2)}) = \frac{q_0}{\theta_0} \sum_{s=1}^{\frac{5.32}{\beta V}} \left( \frac{1}{\theta_0} A^{(1s)} + \frac{1}{\theta_0} A^{(2s)} \right) \theta_0 = \frac{q_0}{\beta V} q_7 \int d^d r \sum_s \left[ \frac{i}{\theta_0} \nabla n^{(1)}(r) \int d^d r' c^{(1s)}(r, r') \Delta r \nabla n^{(s)}(r') + \frac{-i}{\theta_0} \nabla n^{(2)}(r) \int d^d r' c^{(2s)}(r, r') \Delta r \nabla n^{(s)}(r') \right] + O(q^2).$$

Equation (C.6) was written in a form suggestive for an application of the species-wise rotational LMBW equation,

$$r \times \nabla \left[ \ln n^{(a)}(r) + \beta V^{(a)}(r) \right] = \sum_b \int d^d r' c^{(ab)}(r, r') r' \times \nabla n^{(b)}(r') .$$

We state it without a derivation — it should be straightforward along the lines of [Wal09; WF10]. Further following these works, eq. (C.7) yields

$$0 = \sum_b \int d^d r' c^{(ab)}(r, r') \Delta r \times \nabla n^{(b)}(r')$$

which shows that the antisymmetric component of $\Delta r, \nabla n^{(s)}(r')$ in eq. (C.6) vanishes. Hence,

$$P^2 A_{(12)}^{(12)} = \frac{-i}{\theta_0} \frac{q_0}{\beta V} \int d^d r d^d r' \sum_s c^{(1s)}(r, r') \nabla n^{(s)}(r) \Delta r \nabla n^{(s)}(r') + \frac{i}{\theta_0} \cdots$$

$$= P^2 A_{(12)^*} = P^2 A_{(21)^*} = P^2 A_{(21)^*}.$$

Note that $P^2 A_{(12)}^{(21)}$ is symmetric in the last two indices instead. Further, because it is purely imaginary, conjugation corresponds to a sign change. Finally, the block $P^2 A_{(22)}^{(22)}$
from the self adjoint $P_2 \Lambda$ is purely real and therefore symmetric with a symmetric inverse. $\kappa$ can now be rewritten as

$$\kappa_{\alpha\beta\gamma\delta} = P_2 A_{\alpha\gamma}(12) P_2 A_{\alpha\gamma}(22)^{-1} P_2 A_{\gamma\beta}(21) + P_2 A_{\beta\delta}(12) P_2 A_{\beta\delta}(22)^{-1} P_2 A_{\gamma\delta}(21) = \kappa_{\gamma\delta\alpha\beta} = \kappa_{\alpha\delta\gamma\beta} = \kappa_{\gamma\delta\alpha\beta}.$$

The symmetric index pairs here are $\alpha \leftrightarrow \gamma$ and $\beta \leftrightarrow \delta$ from rotational invariance, and the self-adjoint combination in eq. (C.4a) yields an additional $\alpha \beta \leftrightarrow \gamma \delta$ symmetry. Note that the $\gamma \leftrightarrow \delta$ symmetric summation in eq. (C.5) will further reduce the number of independent contributions and allow the introduction of $\tilde{\kappa}$ symmetrized w.r.t. $\alpha \leftrightarrow \beta$ and $\gamma \leftrightarrow \delta$. $\tilde{\kappa}$ can then be treated like $\lambda$ in [Wal09; WF10] to obtain the elastic constants proposed in this thesis.


Bibliography


Nomenclature

Abbreviations

DFT     Density Functional Theory
h.o.t.   higher order terms
QC      Quasicrystal
w.l.o.g. without loss of generality
e.o.m.  equation(s) of motion
MD      Molecular Dynamics
TD      thermodynamics
HS      hard sphere

Mathematical notations, first used on page...

\[ \Lambda \] ordinary matrix
\[ \Lambda \] block matrix, page 50
\[ \mathbf{R} = \frac{\mathbf{r} + \mathbf{r}'}{2} \] center coordinate, page 52
\[ \Delta \mathbf{r} = \mathbf{r} - \mathbf{r}' \] relative coordinate, page 52
\[ \hat{\alpha} \] internal space cartesian index, page 114
\[ \lambda \] tensor
\[ v = \|\mathbf{v}\| \] vector magnitude
\[ \hat{\mathbf{v}} = \mathbf{v}/v \] unit vector
Nomenclature

\( q \)  
Reciprocal vector from the first Brillouin zone

**Physical constants, first used on page...**

\( \varrho_0^{(s)} = m_0^{(s)} n_0^{(s)} \)  
average mass density of species \( s \), page 31

\( \varrho_0^{(ab)} = \sqrt{\varrho_0^{(a)} \varrho_0^{(b)}} \)  
average mass density matrix, page 54

\( \chi \)  
binary liquid stoichiometry, page 76

\( \tau \)  
golden ratio, \( \tau = \frac{1+\sqrt{5}}{2} \)

\( h \)  
Planck’s constant, \( h \approx 6.626070040 \cdot 10^{-34} \) Js

\( k_B \)  
Boltzmann’s constant, \( k_B \approx 1.38064852 \cdot 10^{-23} \) J/K

\( a, a_0 \)  
conventional/primitive lattice constant

\( \zeta \)  
hard sphere size ratio, page 71