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Dissipative phenomena and acoustic phonons in isothermal crystals: A density-functional theory study

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We derive the nonlinear transport equations for isothermal crystalline solids using a density-functional theory based free energy and the Poisson bracket formalism. The model is comprised of three characteristic time scales: A fast one of sound waves and two slow ones of diffusive phenomena. It also combines long-range elastic features with a density field ρ having an atomistic resolution. At the level of *linearized hydrodynamics*, our results are identical to transport equations obtained from the Mori projection operator treatment when the coupling of mass density and phonons becomes weak. At the linear level, we also show that Fick's law breaks down without dislocations in accordance with Cahn's theory of stress effects on diffusion in solids. In contrast, with no bilinear couplings between the density and the displacement fields, it is possible to use a *nonlinear local* theory to describe diffusion and elastic effects using just a single scalar field ρ, which is numerically efficient. We show how a variety of phenomenological phase field crystal models—which have recently demonstrated their power in materials science applications—can be derived, and how their parameters can be related to more microscopic ones.

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I. INTRODUCTION

The purpose of this paper is to derive the dynamic laws describing the evolution of slow variables in crystalline solids, and compare the similarities and differences between various theories. Slow variables represent a good set of "thermodynamic quantum numbers," which is relevant for the description of time evolution—after local equilibrium has set in—in an interacting many-body system. They are associated with the conserved and symmetry broken emergent variables.[1] The difference between liquids and solids is that, in addition to the mass density ρ, momentum density $\mathbf{g}$, and energy density $\mathcal{E}$, there are three extra variables associated with the spontaneously broken translational symmetry. These are the acoustic phonons; their action is accounted for by a thermodynamic field called the displacement field $\mathbf{u}$. A great deal of work has been invested in the development of the phenomenological theories of hydrodynamics of solids, in the contexts of liquid crystals and crystals:[2,3] Nondissipative quantum field theoretic models,[4] two-dimensional (2D) melting,[5] and two-fluid description.[6] The phenomenology has reached a certain degree of maturity, but there is more room to improve on our understanding of the valid ranges of different theories, the values of the parameters and mappings between the theories, and how they relate to more fundamental derivations, such as the notable first-principles approach developed by Wadati, and co-workers.[7–9] Equilibrium properties and nondissipative properties have been more the focus of attention; but recently, microscopic Mori projection operator formalism derivations of linearized dissipative hydrodynamics have also been presented.[10]

One of the main motivations behind this work was to derive the so-called phenomenological phase field crystal models, which have already shown their usefulness in materials science applications.[11–13] These models seem to contain all the necessary ingredients for the description of elastic material properties, in terms of a single scalar density, obeying model-B-type diffusive dynamics or a nonlinear wave equation. We will show that indeed it is possible to understand the emergence of these and other phenomenological models from a more fundamental theory comprising more degrees of freedom. One of the aspects, that makes the theory presented here more versatile than most of the existing ones, is the fact that it combines elements on the scale of macroscopic elasticity with information about the dynamics of structures on the atomistic scale. This information is presented in terms of a continuous (probability) density field, the classical one-particle density $\rho(r,t)$, which can be treated as a more or less coarse-grained object depending on how much detailed information is required. The model can also be shown to be thermodynamically consistent; being based on a unique equilibrium free-energy functional derived from classical density functional theory (DFT) or phenomenologically postulated. We also present the valid range of the phenomenological phase field theories based on the linearized hydrodynamics of solids.

II. DERIVATION OF FREE ENERGY

In bridging the gap between more microscopic descriptions and the various phenomenological models, we resort to the use of macroscopic Poisson bracket formalism as a hybrid that can utilize both microscopic information in the construction of the free-energy functional and the reactive currents, and macroscopic irreversible behavior; which guarantees that the correct thermodynamic equilibrium state is attained. The equilibrium distribution is Gibbsian, $\exp(-\beta F')$. As input for the implementation, we need to supply an expression for the free energy and define the macroscopic Poisson brackets. Let us start by considering the generalized free energy

$$F' \equiv F_K + F, \tag{1}$$

where

$$F_K = \frac{1}{2}\int d\mathbf{r}\frac{1}{\rho(\mathbf{r})}g^2(\mathbf{r}) \tag{2}$$

is the kinetic energy[14] and F is the static free-energy functional, which can be derived from microscopics by, e.g., using density-functional theory. For the purpose of explicit calculations, we use

$$F \equiv \int d\mathbf{r}\{\rho(\mathbf{r})\ln[\rho(\mathbf{r})/\bar{\rho}_0] - \delta\rho\} - \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\,\delta\rho(\mathbf{r})C_2(\mathbf{r},\mathbf{r}')\delta\rho(\mathbf{r}'), \tag{3}$$

where $\delta\rho \equiv \rho(\mathbf{r}) - \bar{\rho}_0$, and $\bar{\rho}_0$ is the mean density in the solid phase. Equation (3) has proven to be successful in the description of both liquid–solid transition[15] and liquid-glass transition.[16,17] Since $C_2(\mathbf{r},\mathbf{r}')$ is the direct correlation function at liquid-solid coexistence, the dynamic density-functional theory to be developed below can describe both phases using a single mass and momentum density fields. Indeed, the Euler-Lagrange equation $\delta F/\delta\rho = 0$ can be shown to support both periodic (atomistic) and flat (fluidlike) solutions depending on the values of the parameters of F.[18] Here, we concentrate on the isothermal properties of the solid phase.

From a symmetry-breaking point of view, A "discontinuity" appears when going from the liquid phase to the solid phase: The free energy (3) must be modified to account for a new relevant macrovariable, the displacement field $\mathbf{u}$. Let us first assume that there are no defects in the solid (we are mainly considering point defects in this work). We further assume that the deformed state $\rho(\mathbf{r})$ experiencing a long-range perturbation $\mathbf{u}$ can be generated from the unperturbed perfect crystal density field $\rho_0(\mathbf{r})$ via $\rho(\mathbf{r},t) \approx \rho_0(\mathbf{r}-\mathbf{u}(\mathbf{r},t)) \approx \rho_0 - \nabla\rho_0\cdot\mathbf{u}$. This leads to the following excitation spectrum above the ground state:

$$\tilde{F}[\rho_0,\mathbf{u}] = F[\rho_0] + \frac{1}{2}\int d\mathbf{q}\; u_i(\mathbf{q})K_{ij}(\mathbf{q})u_j(-\mathbf{q}), \tag{4}$$

and the elastic constants can be obtained from

$$K_{ij}(\mathbf{q}) = \tilde{A}^2 \sum \rho_{\mathbf{Q}}\rho_{-\mathbf{Q}}Q_iQ_j[C_2(\mathbf{Q}) - C_2(\mathbf{q}+Q)], \tag{5}$$

where we have expanded the perfect crystal solution (without defects of any kind),

$$\rho_0(\mathbf{r}) = \bar{\rho}_0 + \tilde{A}\sum \rho_{\mathbf{Q}}e^{\imath\mathbf{Q}\cdot\mathbf{r}}, \tag{6}$$

with normalization $\tilde{A}$ and summed reciprocal-lattice vectors $\mathbf{Q}$ over the first Brillouin zone. The values of $\tilde{A}$ and $\mathbf{Q}$ can be found in terms of the parameters of F.[11] The operator K is dependent on scale, and it can be related to scale dependent elastic "constants," which in the limit $q \to 0$ reduce to

$$K_{ij}(\mathbf{q}) = \tilde{A}^2\sum_{\mathbf{Q}} \rho_{\mathbf{Q}}\rho_{-\mathbf{Q}}Q_iQ_j\tilde{C}(\mathbf{q},\mathbf{Q}) \to \lambda_{ijkl}q_kq_l \tag{7}$$

with

$$\tilde{C}(\mathbf{q},\mathbf{Q}) \equiv (1/2)(\mathbf{q}_k\cdot\nabla_{\mathbf{Q}_k})(\mathbf{q}_l\cdot\nabla_{\mathbf{Q}_l})C_2(\mathbf{Q}). \tag{8}$$

Although these results are well documented[10,19] and suffice for our purposes here, we point out that there is a problem when substituting the expansion $\rho \approx \rho_o - \nabla\rho_0\cdot\mathbf{u}(\mathbf{r})$ into F to obtain the excitation spectrum: the (probability) mass is not conserved for an arbitrary $\mathbf{u}$ configuration. Other expansions have been suggested, leading to different values of elastic constants. Mahato *et al.*[20] expand around $\mathbf{u}(\mathbf{R})$, where the displacement field is tied to the equilibrium position $\mathbf{R}$ of the nearest atom. This frees the authors from the mass conservation problem; but consequently, $\mathbf{u}$ cannot be used as a genuine dynamic variable. Kirkpatrick *et al.*[21] used an expansion of the form $\rho \approx \rho_0 - \nabla\cdot(\rho_0\mathbf{u}) + h$, where h is related to controlling the sub-Cauchy scale volume changes. This expression conserves mass but certain ambiguities arise with multiple integrals in the free energy and Poisson bracket terms, if one wishes to use the dynamic formalism presented here. An expansion that fully respects all conservation laws has been used by Wadati[9] based on Umezawa's boson transformation: $\rho \approx \rho_0 + \nabla_i\tilde{\rho}_{ij}(\nabla)u_j$. The mass matrix $\tilde{\rho}_{ij}(\rho_0)$ induces couplings in the equations of motion between the various u_j already at the level of linearized hydrodynamics which, to our knowledge, have not been taken into account in any of the more phenomenological theories dealing with linearized hydrodynamics, of solids. For the following discussion, this feature can be implemented straightforwardly into the final results.

To summarize the discussion above, we have obtained the excitation spectrum for $\mathbf{u}$: $\tilde{F}[\rho_0,\mathbf{u}] = F[\rho_0] + \int(1/2)u_jK_{ij}u_j$, where $\rho_0(\mathbf{r})$ is the atomistic equilibrium density of the crystal and uKu part contains the long-wavelength excitations. However, in our expansion $\rho \approx \rho_0 - \nabla\rho_0\cdot\mathbf{u}$ (or $\rho \approx \rho_0 + \nabla_i\tilde{\rho}_{ij}u_j$) we have made ρ and $\mathbf{u}$ dependent on each other. Equilibrium thermodynamics tells us that two independent state variables (ρ, $\mathcal{E}$ in terms of our conserved fields) are needed *in addition to* $\mathbf{u}$. There are two ways of decoupling ρ from $\mathbf{u}$. First, by introducing a (point) defect density N we can say that $\rho = \rho(N,\mathbf{u})$ instead of $\rho = \rho(\mathbf{u})$ as before. Alternatively, we can define

$$\tilde{F}[\rho,\mathbf{u}] = F[\rho] + \frac{1}{2}\int u_iK_{ij}u_j + \gamma\int(\rho - \rho_0), \tag{9}$$

where ρ and $\mathbf{u}$ can be varied independently, and γ is a Lagrange multiplier enforcing the mass conservation. In fact, the last term can be dropped since it will be invisible in the actual equations of motion. To generalize further, we also introduce a lowest-order coupling term $\alpha_2\rho u_{ii}$ between the mass and the displacement field ($u_{ii} \equiv \nabla\cdot\mathbf{u}$). This type of coupling has been considered before as representative of defect-strain interaction[5] and structural phase transitions.[22] It is also easy to understand how such a coupling term can be derived from Eq. (3) using an expansion of the type $\rho \approx \rho_0 + \nabla_i\tilde{\rho}_{ij}u_j + N$. Later on, we will show how α_2 can be related to chemical inhomogeneity-induced stress of Larche and Cahn.[23] For now, we keep the parameter α_2 free, and write

$$\widetilde{F}[\rho,\mathbf{u}]=F[\rho]+\int\alpha_2\rho u_{ii}+\frac{1}{2}\int u_iK_{ij}u_j. \tag{10}$$

Just as the "original" free energy $F[\rho]$ was valid for all smooth configurations ρ, in the sense that $\exp(-\beta F[\rho])$ gives the "nonequilibrium" probability weight of configuration ρ, $\exp(-\beta\widetilde{F}[\rho,\mathbf{u}])$ can be seen as the mean-field weight obtained from cell averaging of the full partition function. This is subject to the constraint that the microscopic mass density in the cell around $\mathbf{r}$ is $\rho(\mathbf{r})$ and the displacement field takes the value $\mathbf{u}(\mathbf{r})$. Alhough, an important difference remains between the fields ρ and $\mathbf{u}$: The latter cannot be interpreted as a probability density.

In the next section, we use the generalized free energy derived above as the generator of the dynamics. From the static arguments of this section, one may very well question if ρ and $\mathbf{u}$ are really independent of each other. Maybe their appearance in the same free energy (10) leads to some kind of double counting. Specifically, from the derivation of Eq. (4) based on substitution of $\rho\approx\rho_0+\nabla\rho_0\cdot\mathbf{u}$, it appears as if the long-range contribution dependent on $\mathbf{u}$ should be purged from ρ in order for it to be an independent variable from the displacement field. We argue below that whatever relation we assume between ρ and $\mathbf{u}$, when deriving the free energy, no longer matters after the variations are performed in Eqs. (20), (22), and (28): Equations of motion will determine the wavelength content of all fields.

III. EQUATIONS OF MOTION

The remaining task is to determine the nonzero reactive couplings between the slow fields from fluctuating hydrodynamics (see, e.g., Refs. 24 and 25. From our three slow fields, mass and momentum are defined by the microscopic expressions

$$\rho(\mathbf{r},t)\equiv\sum_\alpha m\delta[\mathbf{r}-\mathbf{r}^\alpha(t)]; \tag{11}$$

$$\mathbf{g}(\mathbf{r},t)\equiv\sum_\alpha \mathbf{p}^\alpha(t)\delta[\mathbf{r}-\mathbf{r}^\alpha(t)], \tag{12}$$

where the particle index α runs over all N particles with mass m and microscopic momentum $\mathbf{p}^\alpha$. The nondissipative dynamics of the slow fields will be expressed in terms of Poisson brackets, which we define as

$$\{A(\mathbf{r}),B(\mathbf{r}')\}\equiv\sum_{\alpha j}\left[\frac{\partial A(\mathbf{r})}{\partial r_j^\alpha}\frac{\partial B(\mathbf{r}')}{\partial p_j^\alpha}-\frac{\partial A(\mathbf{r})}{\partial p_j^\alpha}\frac{\partial B(\mathbf{r}')}{\partial r_j^\alpha}\right]. \tag{13}$$

Plugging Eqs. (11) and (12) into Eq. (13) yields

$$\{\rho(\mathbf{r}),g_i(\mathbf{r}')\}=-\rho(\mathbf{r}')\partial_i\delta(\mathbf{r}-\mathbf{r}'), \tag{14}$$

$$\{g_i(\mathbf{r}),\rho(\mathbf{r}')\}=-\rho(\mathbf{r})\partial_i\delta(\mathbf{r}'-\mathbf{r}), \tag{15}$$

where $\partial_i\equiv\partial/\partial r_i$, and similarly for the primed coordinates. For momentum density,

$$\{g_s(\mathbf{r}),g_i(\mathbf{r}')\}=-g_i(\mathbf{r})\partial_s'\delta(\mathbf{r}'-\mathbf{r})+g_s(\mathbf{r}')\partial_i\delta(\mathbf{r}-\mathbf{r}'). \tag{16}$$

The definition of the Poisson brackets for the displacement $\mathbf{u}$ is trickier because unlike momentum and mass, it has no unique microscopic definition. However, a sensible choice turns out to be

$$\{u_i(\mathbf{r}),g_j(\mathbf{r}')\}=+\delta_{ij}\delta(\mathbf{r}-\mathbf{r}'), \tag{17}$$

$$\{g_i(\mathbf{r}'),u_j(\mathbf{r}')\}=-\delta_{ij}\delta(\mathbf{r}-\mathbf{r}'). \tag{18}$$

A more detailed discussion of the microscopic representation [see Eq. (83)] of the displacement field will be provided in Sec. VIII A. Nonlinear extensions of these relations are possible,[17] but in the following, we will consider nonlinearities only in the mass density field.

We will first construct the linearized hydrodynamics for slow fields. We restrict the analysis to the isothermal case and leave out the energy equation (temperature equation). In terms of the generalized free energy $F'=F_K+\widetilde{F}$, and the Poisson brackets above, the mass balance equation becomes

$$\partial_t\rho=\int d\mathbf{r}'\{\rho(\mathbf{r}),g_j(\mathbf{r}')\}\frac{\delta F'}{\delta g_j(\mathbf{r}')} \tag{19}$$

$$=\int\{\rho,g_j\}\frac{\delta F'}{\delta g_j}=-\nabla\cdot\mathbf{g}. \tag{20}$$

Einstein summation convention over repeated indices is implied, and appropriate integration over spatial coordinates is understood. In addition, the integration will always be over the argument of the right-most member of the Poisson bracket. Using this notation, the momentum balance equation reads

$$\partial_t g_i=\Gamma_{g_ig_j}\frac{\delta F'}{\delta g_j}+\int\{g_i,u_j\}\frac{\delta F'}{\delta u_j}+\int\{g_i,\rho\}\frac{\delta F'}{\delta\rho}+(\eta_g)_i \tag{21}$$

$$=L_{ij}g_j+K_{ij}u_j-\bar{\rho}_0\alpha_2\nabla_iu_{jj}-\alpha_3\nabla_i\rho+(\eta_g)_i, \tag{22}$$

where the prefactor

$$\alpha_3\equiv\frac{\bar{\rho}_0}{\beta S(0)}-\alpha_2. \tag{23}$$

The Fourier transform of the structure factor is denoted $S(q=0)=S(0)$. A fluctuation-dissipation theorem fixes the noise correlations as

$$\langle(\eta_g)_i(\mathbf{r},t)(\eta_g)_j(\mathbf{r}',t')\rangle=2T\Gamma_{g_ig_j}\delta(\mathbf{r}-\mathbf{r}')\delta(t-t'), \tag{24}$$

and the dissipative term $\Gamma_{g_ig_j}(\delta F'/\delta g_j)=L_{ij}g_j$, with

$$L_{ij}\equiv\nu_1\delta_{ij}\nabla^2+\nu_2\nabla_i\nabla_j. \tag{25}$$

The bulk and shear viscosities are denoted by ν_1 and ν_2. Of course, the liquid-state-like viscosity is strictly infinite in a solid so ν_i's require a new interpretation. There are two contributions to the viscosity of the solid in the current formulation. One describes the energy transfer between the acoustic and optical (thermal) phonons as will be discussed below. In principle, the viscosities can be computed from the microscopic Green-Kubo expression of the total momentum flux density current as demonstrated in Ref. 10:

$$\nu_{ijkl} = \frac{1}{k_B T V}\int_0^\infty dt \lim_{q\to 0}\langle P_\perp \sigma_{ij}(-\mathbf{q},0)P_\perp \sigma_{kl}(\mathbf{q},t)\rangle_{eq}, \tag{26}$$

where $P_\perp \equiv 1-P$ and P is the projection operator on the subspace of relevant variables. Here $P_\perp \sigma_{ij}=[P_\perp \sigma_{kl}(\mathbf{q})]_{\text{fluid}} -\iota \lambda_{ijkl} u_j(\mathbf{q}) q_l$ is the projected stress tensor[10] and λ_{ijkl} is the elastic tensor to be defined below. To the extent that σ_{ij} is dependent on the defect current, the defects can also contribute to the effective solid-state viscosity. This second contribution to the viscosity links the coefficients ν_1 and ν_2 to the dissipative motion of vacancies. Later on, we will also see that within the linearized hydrodynamics the diffusion coefficient D will not depend on the viscosity explicitly. Implicitly, though, there is a connection through the dissipative current correlator (30) as far as the projected total current depends on the vacancy current.

After discussion of the noise properties of the momentum balance equation, let us take a look at the reactive term $-\alpha_3 \nabla_i \rho$, which is just the pressure gradient. Indeed, in the liquid phase Eq. (22) would reduce to the liquid momentum flux equation with a similar type of lowest-order density dependence. It should also be noted that the corresponding nonlinear pressure term $-\rho \nabla \mu$ can be taken as the *definition* of solid-state pressure (without fluctuating temperature effects in the present case). More detailed comparison with the literature will be presented in Sec. IX A.

Finally, we have the time evolution of the displacement field:

$$\partial_t u_i = \Gamma_{u_i u_j}\frac{\delta F'}{\delta u_j} + \int \{u_i, g_j\}\frac{\delta F'}{\delta g_j} + (\eta_u)_i \tag{27}$$

$$= A_{ij}(K_{js}u_s + \alpha_2 \nabla_j \rho) + (1/\bar{\rho}_0) g_i + (\eta_u)_i, \tag{28}$$

where the noise correlations satisfy

$$\langle (\eta_u)_i(\mathbf{r},t)(\eta_u)_j(\mathbf{r}',t')\rangle = 2TA_{is}K_{sj}\delta(\mathbf{r}-\mathbf{r}')\delta(t-t'). \tag{29}$$

Explicitly, in terms of the elastic constants calculated in Eq. (7), $A_{is}K_{sj}=A_{is}\lambda_{sjrl}k_r k_l$. The dissipative prefactor matrix

$$A_{ij} = \frac{1}{k_B T V}\int_0^\infty dt \lim_{q\to 0}\langle P_\perp \dot{u}_i(-\mathbf{q},0)P_\perp \dot{u}_j(\mathbf{q},t)\rangle_{eq}, \tag{30}$$

where $P_\perp \equiv 1-P$ and P is the projection operator on the subspace of relevant variables.[10] This dissipative coefficient can be interpreted as stemming from scattering effects of various kinds. In the two-fluid theory of Enz,[6] dissipative energy transfer is partly due to the coupling of the acoustic phonons with the dissipative thermal ones. (Here, we use synonymously the expression optical for thermal or dissipative modes: The optical modes are understood as the other vibration modes except the acoustic Goldstone modes.) It should also be noted that the extra (vacancy) density coupling $\alpha_2 \nabla_j \rho$ in our theory, which connects the total momentum with the vacancy dissipation. Exactly, as in the case of the momentum current, the term proportional to α_2 was not obtained from the Mori projection operator formalism of Ref. 10. It is of the same order in powers of q as the elastic term, and thus is relevant. As a possible reason why such a term was not generated, we suspect the use of the geometric projector in the definition of the $\mathbf{u}$ field. The displacement field used by Szamel was defined heuristically using the mass conservation violating assumption $\rho[\mathbf{r}-\mathbf{u}(\mathbf{r})] \approx \rho_0(\mathbf{r}) -\nabla \rho_0 \cdot \mathbf{u}$ through

$$\mathbf{u}(\mathbf{q}) \equiv -\frac{1}{\mathcal{N}}(h_\alpha, \rho) \equiv -\frac{1}{\mathcal{N}}\int d\mathbf{r}\, e^{-\iota \mathbf{q}\cdot\mathbf{r}} \nabla_\alpha \rho_0(\mathbf{r})\rho(\mathbf{r}), \tag{31}$$

where $\mathcal{N}=(h_\alpha, h_\alpha)$ is the normalization and $h_\alpha \equiv \exp(-\iota \mathbf{q}\cdot\mathbf{r})\nabla_\alpha \rho_0$. It is easy to see that this type of density decomposition leads to a zero coupling at least when directly substituted into Eq. (3) and after the long-wavelength limit is taken.

IV. LINEARIZED HYDRODYNAMICS

We will now rewrite the linearized hydrodynamics of our theory in terms of new variables, which will help us to better understand the diffusive phenomena and which will make it easier to compare our results with those of Larche and Cahn presented in Sec. IX D. We first introduce a different density decomposition:

$$\rho = \rho_0 - \bar{\rho}_0 u_{ii} + N = \tilde{N} - \bar{\rho}_0 u_{ii}, \tag{32}$$

where we have defined a different defect density:

$$\tilde{N} \equiv \rho_0 + N. \tag{33}$$

Note that this expansion is taken to be an exact definition of $N(\tilde{N})$. Everything else—from point defects to higher powers of the $\mathbf{u}$ field—is lumped into $\tilde{N}$. As discussed in Sec. III, due to our practical definition, $N=\rho(\mathbf{r})-\rho_0(\mathbf{r})+\bar{\rho}_0 u_{ii}$, N can contain contributions other than *just* the actual coarse-grained density of the vacancies, such as nonlinear contributions from $\mathbf{u}$, density of dislocations, etc. Therefore, it is possible that N/ρ is larger than $\mathcal{O}(5.0\times 10^{-5})$, which holds for the Lennard-Jones system near triple point.[26] In the new variables $\mathbf{u}$ and $\tilde{N}$ we can write our balance equations as

$$\partial_t \tilde{N} = -\nabla \cdot \mathbf{g}_N, \tag{34}$$

$$(\partial_t - L)\mathbf{g}_L + (\partial_t - L)\mathbf{g}_N = K_3 u - \alpha_3 \nabla \tilde{N}, \tag{35}$$

$$\mathbf{g}_L \equiv \bar{\rho}_0 \partial_t \mathbf{u}; \tag{36}$$

$$(\mathbf{g}_N)_i \equiv -\bar{\rho}_0 A_{ij}(K_2 u + \alpha_2 \nabla \tilde{N})_j, \tag{37}$$

where we have defined acoustic phonon current $\mathbf{g}_L$ and the defect current $\mathbf{g}_N$, the sum of which equals the total momentum as dictated by Eq. (28):

$$\mathbf{g} = \mathbf{g}_L + \mathbf{g}_N. \tag{38}$$

We point out that it is easy to generalize the phonon current to the form $\mathbf{g}_L = \nabla_i \tilde{\rho}_{ij} u_j$, corresponding to strictly mass conserving excitation, if necessary. We have also defined two new operators:

$$K_2 u \equiv Ku - \bar{\rho}_0 \alpha_2 \nabla u_{ii}, \tag{39}$$

$$K_3 u \equiv Ku + \bar{\rho}_0(\alpha_3 - \alpha_2)\nabla u_{ii}. \tag{40}$$

In fact, in view of the comments above concerning the slowness of the vacancy diffusion in metals, the maximum contribution to the current $\mathbf{g}_N$ can come from the dissipative phononic processes, and in this sense, it may be somewhat misleading to talk about defect current. However, to facilitate the comparison, especially with Ref. 5, we will stick to this nomenclature.

Next, we solve from our linearized equations of motion for $\mathbf{u}(\tilde{N})$, and obtain from Eqs. (34)–(37)

$$\partial_t \tilde{N}(\mathbf{q}) = - D_{\alpha\beta}(\hat{\mathbf{q}}) q_\alpha q_\beta \tilde{N}(\mathbf{q}), \tag{41}$$

where we have defined the diffusion tensor consisting of two parts,

$$D_{\alpha\beta} = \bar{\rho}_0 \alpha_2 A_{\alpha\beta} + \tilde{D}_{\alpha\beta}; \tag{42}$$

$$\tilde{D}_{\alpha\sigma} = \bar{\rho}_0 \alpha_3 A_{\alpha\eta} (K_2)_{\eta\gamma}(\hat{\mathbf{q}}) (K_3)^{-1}_{\gamma\beta}(\hat{\mathbf{q}}). \tag{43}$$

The unit vector has been denoted $\hat{\mathbf{q}}$, $K_{\alpha\beta}(\hat{\mathbf{q}}) \equiv -\lambda_{\alpha\beta\gamma\delta}\hat{q}_\gamma \hat{q}_\delta$, and

$$(K_3)_{\alpha\beta}(\hat{\mathbf{q}}) = K_{\alpha\beta}(\hat{\mathbf{q}}) - \bar{\rho}_0(\alpha_3 - \alpha_2)\hat{q}_\alpha \hat{q}_\beta \tag{44}$$

is the wave propagation matrix of dissipationless phonons. In the limit $\alpha_2 \to 0$ the diffusion constant reduces exactly to the one obtained from the Mori projection analysis.[10] The results (41) and (42) implies the breakdown of Fick's law because the diffusion equation becomes nonlocal. This has been verified numerically.[27] Nonlocal behavior results from the presence of the $K_2 u$ term in the diffusion equation (100). One first has to solve the elastic fields from the force balance equation (momentum equation) and substitute the nonlocal result back into Eq. (100). Nonlocality always results for crystals with symmetry lower than cubic,[23] except for some very special geometries. In particular, these conditions are never realized under experimental circumstances such as polycrystalline grain growth or solidification: The grains do not have a regular shape on average and one may expect nonlocal effects always to manifest themselves. However, in an *infinite* system with no boundaries to complicate the expression of $\mathbf{u}$ in terms of $\tilde{N}$, and with isotropic elastic operator of the form $\lambda_1 \delta_{ij}\nabla^2 + \lambda_2 \nabla_i \nabla_j$, the ensuing diffusion equation will be local (but anisotropic) even if the dissipative operator A_{ij} is not diagonal:

$$D_{\alpha\beta} = \bar{\rho}_0 A_{\alpha\beta}\left(\alpha_2 + \frac{\alpha_3(\lambda - \alpha_2\bar{\rho}_0)}{\lambda + \bar{\rho}_0(\alpha_3 - \alpha_2)}\right), \tag{45}$$

where $\lambda \equiv \lambda_1 + \lambda_2$. For nonisotropic crystal the direction cosines would appear in the expression for the diffusion constant as is evident from the more general result (42).

V. NONLINEAR DENSITY INTERACTIONS

The Poisson bracket formalism allows us to consider arbitrary nonlinearities in density, momentum density, and elastic fields. In order to establish the connection with other theories, we will now take consider of the nonlinear effects in the mass density ρ. Keeping elastic self-interactions linear but retaining all bilinear terms of the theory, and fully nonlinear density self-interactions, we obtain the following set of equations from Eqs. (20), (22), and (28):

$$\partial_t \rho = - \nabla \cdot \mathbf{g}; \tag{46}$$

$$\partial_t g = Lg + Ku + \alpha_2 \nabla \rho - \rho \nabla \mu(\rho, u) + \eta_g; \tag{47}$$

$$\partial_t u = (1/\bar{\rho}_0) g + A(Ku + \alpha_2 \nabla \rho) + \eta_u, \tag{48}$$

where we have defined $\mu(\rho,u) = \delta\tilde{F}[\rho,\mathbf{u}]/\delta\rho$. Assuming diagonality of the dissipative matrix A (a condition which can be relaxed, if needed) we can take the divergence on both sides of Eqs. (47) and (48). Using Eq. (46) we can then express the dynamics in terms of a new field,

$$\epsilon \equiv \bar{\rho}_0 u_{ii}, \tag{49}$$

as follows:

$$\partial_t \rho + \partial_t \epsilon = a\lambda \nabla^2 \epsilon + c_2 \nabla^2 \rho, \tag{50}$$

$$\partial_t^2 \rho - \nu \nabla^2 \partial_t \rho = - (\lambda/\bar{\rho}_0)\nabla^2 \epsilon - \alpha_2 \nabla^2 \rho + \alpha_2 \nabla \left(\frac{\rho}{\bar{\rho}_0}\nabla \epsilon\right) + \nabla[\rho \nabla \mu(\rho)], \tag{51}$$

where $\mu(\rho)$ is only a function of ρ. In other words, $\mu(\rho) \equiv \delta\tilde{F}[\rho,\mathbf{u}=0]/\delta\rho$. We have also dropped the noise terms and defined the following symbols:

$$c_2 \equiv \bar{\rho}_0 a \alpha_2, \tag{52}$$

$$\lambda \equiv \lambda_1 + \lambda_2, \tag{53}$$

$$\nu \equiv \nu_1 + \nu_2. \tag{54}$$

The third term on the right-hand side (RHS) of Eq. (51) results from the action of $\delta/\delta\rho$ on the coupling term $\alpha_2 \rho u_{ii}$ in $\tilde{F}[\rho,\mathbf{u}]$, and it has been explicitly separated from μ. The term $\alpha_2 \nabla[(\rho/\bar{\rho}_0)\nabla\epsilon]$ is the only bilinear coupling between two different fields, and responsible for the fact that the two equations (50) and (51) cannot be combined into one third-order equation in time. This would be expressed solely in terms of density and would be local in real space. If the bilinear coupling is linearized such that

$$\alpha_2 \nabla \left(\frac{\rho}{\bar{\rho}_0}\nabla \epsilon\right) \approx \alpha_2 \nabla^2 \epsilon \tag{55}$$

(or, if $\alpha_2 = 0$), then the entire theory is representable in terms of a single local equation for the density field ρ. This is easy to see by operating on both sides of Eq. (51) with

$$L_1 \equiv \partial_t - a\lambda\nabla^2, \tag{56}$$

and using Eq. (50) and the approximation (55). We obtain

$$L_1\partial_t^2\rho - \nu L_1\nabla^2\partial_t\rho = (-\lambda/\bar{\rho}_0 + \alpha_2)\nabla^2(-\partial_t\rho + c_2\nabla^2\rho) - \alpha_2 L_1\nabla^2\rho + L_1\nabla[\rho\nabla\,\mu(\rho)]. \tag{57}$$

This is a fully local scalar equation in time and space (given that local free-energy functional is used) with third-order time derivatives. It can be easily simulated by decomposing it into three first-order equations in time, for instance. We made no other assumptions other than requiring all elastic couplings (self-couplings and couplings with other fields) to be linear (not bilinear) and the dissipative matrix A_{ij} to be diagonal. Thus, within linear elasticity, effects of the set of five equations in two dimensions (seven in three dimensions) given in Eqs. (46)–(48) can be exactly packaged into Eq. (57) Despite the simple appearance of Eq. (57) it is, of course, impossible to simulate it on diffusive time scales with realistic values of the materials parameters for which the time scale separation of the phononic and dissipative timescales is several orders of magnitude. Bringing these two time scales artificially closer to each other but still keeping them well separated leads to qualitatively reasonable results for many phenomena, such as those studied in Ref. 12. For more quantitative results, a quasistationarity condition for the phonons can be utilized.

Next, we will study two limits of the full model. The first one, (Sec. V A) is the limit where the familiar (viscosity damped) wave equation for the phonons becomes detectable. The second one is the limit, where the dissipative features of the phonon current dominate (Sec. V B)

A. Limit of nondissipative current domination

Let us consider a weak coupling α_2 such that $c_2\nabla^2\rho \ll a\lambda\nabla^2\boldsymbol{\epsilon}$, where $c_2 \propto \alpha_2$. By the same token, we can also assume that the bilinear term, which is approximated as $\alpha_2\nabla^2\boldsymbol{\epsilon}$ is much smaller than the first term on the RHS of Eq. (51) and can be dropped. Then, Eq. (50) reduces to $\partial_t\rho \approx -\partial_t\boldsymbol{\epsilon} + a\lambda\nabla^2\boldsymbol{\epsilon} \approx -\nabla\cdot\mathbf{g}_L - \nabla\cdot\mathbf{g}_N$. When the nondissipative phonon current $\mathbf{g}_L$ dominates mass transport, $\partial_t\rho \approx -\partial_t\boldsymbol{\epsilon}$, or $\rho \approx -\boldsymbol{\epsilon}$ [leaving out the time independent $\rho_0(\mathbf{r})$], and the original condition $c_2\nabla^2\rho \ll a\lambda\nabla^2\boldsymbol{\epsilon}$ yields the condition for the magnitude of α_2: $|\alpha_2| \ll |-\lambda/\bar{\rho}_0|$. Equation (51) reduces to

$$\partial_t^2\boldsymbol{\epsilon} - \nu\nabla^2\partial_t\boldsymbol{\epsilon} = (\lambda/\bar{\rho}_0)\nabla^2\boldsymbol{\epsilon} - \nabla\{[\rho_0(\mathbf{r}) - \boldsymbol{\epsilon}]\,\nabla\mu[\rho_0(\mathbf{r}) - \boldsymbol{\epsilon}]\}, \tag{58}$$

which, apart from the last term on the right-hand side, is nothing but the divergence of the familiar wave equation where $-\nu\nabla^2\partial_t\boldsymbol{\epsilon}$ gives the damping of the phonon fluctuations. In fact, there is linear contribution in $\boldsymbol{\epsilon}$ originating from

$$\nabla\{[\rho_0(\mathbf{r}) - \boldsymbol{\epsilon}]\,\nabla\mu[\rho_0(\mathbf{r}) - \boldsymbol{\epsilon}]\}, \tag{59}$$

which can be absorbed into the redefinition of the diagonal elastic constant, that is, the sum $\lambda = \lambda_1 + \lambda_2$. Nevertheless, the form of the wave equation is not changed by this fact. The nonlinear interactions of $\boldsymbol{\epsilon}$, originating from the term (59), can be interpreted as a higher-order scattering effect. However, due to the reasons discussed in the beginning of this section, we only consider the linear contribution in the displacement field $\boldsymbol{\epsilon}$. It should be noted that, since ρ and $\mathbf{u}$ are independent in the Poisson bracket formalism, there is no problem in expanding the nonlinear chemical potential term in $\boldsymbol{\epsilon}$. The linear contribution, which renormalizes the elastic constants and sound velocity—should not be set to zero, even if we set the coupling $\alpha_2 = 0$.

B. Limit of dissipative current domination

In the opposite limit, $\nabla\cdot\mathbf{g}_N \gg \nabla\cdot\mathbf{g}_L$, or $-a\lambda\nabla^2\boldsymbol{\epsilon} \gg -\partial_t\boldsymbol{\epsilon}$. From the linear analysis of Sec. IV, we obtain the following condition

$$\frac{1}{|\bar{\rho}_0 a^2\lambda|} \ll k^2 \ll \frac{1}{|\bar{\rho}_0\nu a|}, \tag{60}$$

where we have used the quasistationarity of the momentum current and the late time condition $\omega \ll 1/|(a\bar{\rho}_0)|$ characteristic of diffusive time scales. Then, Eq. (50) gives $\partial_t\rho = a\lambda\nabla^2\boldsymbol{\epsilon}$, and subsititution into Eq. (51) yields

$$\partial_t^2\rho - \nu\nabla^2\partial_t\rho = -\frac{\bar{\rho}_0\alpha_2 - \lambda}{\bar{\rho}_0 a\lambda}\partial_t\rho - \alpha_2\nabla^2\rho + \nabla[\rho\nabla\mu(\rho)]. \tag{61}$$

Simple power counting tells us that the left-hand side (LHS) of Eq. (61) is negligible in the long time limit, and therefore, a nonlinear (vacancy) diffusion equation results:

$$\partial_t\rho = \frac{\bar{\rho}_0\alpha_2 a\lambda}{\bar{\rho}_0\alpha_2 - \lambda}\nabla^2\rho + \frac{\bar{\rho}_0 a\lambda}{\lambda - \bar{\rho}_0\alpha_2}\nabla[\rho\nabla\mu(\rho)] \tag{62}$$

$$\approx a\bar{\rho}_0\nabla[\rho\nabla\mu(\rho)] \tag{63}$$

in the limit of weak coupling, $\alpha_2 \to 0$. The only simplifying assumption in the derivation of the nonlinear diffusion equation (63) was that $A_{\alpha\beta} = a\delta_{\alpha\beta}$. If diagonality holds, we obtain in the limit of large times $\partial_t\rho \approx a\bar{\rho}_0\nabla(\rho\nabla\mu)$, which is the locally conserved representation in variable ρ. It is important to note that the diffusion coefficient of the defect part $\tilde{N}$ in Eq. (42) is slightly different than the factor in front of the chemical potential term in Eq. (63) due to the splitting of ρ into two contributions in Eq. (32). Moreover, the condition (60) is only needed to impose a strict dominance of the diffusion current over the nondissipative part. Even if it is relaxed, the full model presented in Sec. V does have a diffusive pole in its hydrodynamic determinant for arbitrarily small k values. This is not the case with the modified phase field crystal model (MPFC) to be presented in Sec. VII: If one insists that it is derivable from the fundamental model of Sec. V with the same (physical) parameter values, then condition (60) is necessary.

VI. MULTISCALE MODELING AND ELASTIC COEFFICIENTS

We have considered two types of coarse graining in this work: Coarse graining in time and space. The time scale hierarchy leading to the evolution equation (57) consists in increasing order of the momentum relaxation time $\tau_m(k) \sim (\nu k^2)^{-1}$ [Eq. (51)], the sound propagation time scale $\tau_s \sim (\bar{\rho}_0/\lambda)^{1/2}k^{-1}$ [Eq. (58)], and the diffusive time scale of defects and other dissipative processes,

$$\tau_d \sim \left(\frac{a\bar{\rho}_0 k^2}{\beta S(0)}\right)^{-1} \tag{64}$$

[cf. Eqs. (75) and (41)]. For a hard sphere gas (radius r_o, mass m) one can approximate $\tau_m \sim (\beta m)^{1/2}/(r_0^2\rho_0)$, independent of k.[28] Also, the processes of most rapid variation time τ_T due to the thermal fluctuations have all been lumped into the noise terms. Thus, in this sense, the fields entering the Poisson bracket formalism have already been averaged over time scales shorter than τ_T, although, this is not explicitly shown.

Various spatial scales also arise. The field ρ varies as a probability density on scales having atomistic resolution. The exact precision in the spatial form of ρ is set by the correlation function C_2 in the free energy. As it is directly related to the structure factor of the system, whose precise form depends on the experimental methods (or simulation technique), it can be concluded that the type (energy) of radiation, quasielastic nature of collisions, multiple scattering, and other factors all play a role in the interpretation of the fine structure of the ρ field. For explicit calculations, we have also utilized various analytical approximations, which make ρ more diffuse than it would be in an ideal situation. For example, fuzziness of ρ is common to all theories having a free energy that has been obtained through a gradient expansion. If one is only interested in phenomena where the density field varies slowly on the scales of the correlation length of the direct correlation function (pair potential in low temperatures), one can expand[29,30]

$$\rho(\mathbf{r}') = \rho(\mathbf{x}) + [(\mathbf{r}-\mathbf{r}')\cdot\nabla]\rho(\mathbf{r}) + \frac{1}{2}[(\mathbf{r}-\mathbf{r}')\cdot\nabla]^2\rho(\mathbf{r}) + \dots \tag{65}$$

in Eq. (3). This leads to the local free-energy density whose gradient interaction term derives from the second term on the RHS of Eq. (65):

$$\int d\mathbf{r}\, \tilde{c}_0(\bar{\rho}_0)|\nabla\rho|^2 \equiv \int d\mathbf{r} \frac{1}{12\beta}\int d\mathbf{r}'\,(r')^2 C_2(r',\bar{\rho}_0)|\nabla\rho|^2, \tag{66}$$

where we have indicated that the coefficient $\tilde{c}_0$ depends weakly on the density (and temperature) because C_2 does. Even though the gradient expansion is sometimes used outside of its domain of validity, it can be expected to give quantitatively accurate results only for slow density variations, such as a binary alloy close to spinodal or liquid-gas systems[31] close to the critical point. For example, in order to get quantitatively reliable results for fluids in the vicinity of solid walls, the full nonlocal form of interaction should be considered.[26] Thus, any gradient interaction theory, such as the phase field crystal models given in Refs. 11 and 12, has already been coarse grained to a coarser scale than Eq. (3) and consequently, the probability density is not the atomistic one anymore. The coefficients in these expansions can be related to the more microscopic ones by, e.g., relating the elastic coefficients or other parameters to each other, as explained in Sec. VII. Of course, by adding higher-order gradient terms and suitable nonlinearities, shorter scale features can be mimicked approximately.

Now let us consider the spatial scales beyond the cell scale above which a sensible gradient interaction theory can be defined for a liquid-gas system.[14] The most relevant ones for the present purposes are the widths of the phase boundaries and the average domain size of the polycrystalline grains. For example, the grain size grows like $\sim t^{1/2}$ in time for a nonconserved order parameter even though the underlying dynamics of ρ is conserved. There are several correlation lengths that can be determined for the roughening domain boundaries as well. Also, the various diffusion lengths are important for understanding the macroscopic materials properties.

Of all our dynamic fields, it is the smooth part of $\mathbf{u}$ that varies on the largest scales. For smooth elastic effects using the elastic free energy given in Eq. (10) means that we have washed out all legth scales in the limit $k \to 0$ and, therefore, the elastic fields do not see, e.g., individual grains. The resolution can in principle, at least, be increased by retaining the dependence of the elastic constants on the field $\rho(\mathbf{r})$. Using the fact that at zero strain, the Euler-Lagrange equation for ρ should give rise to the microscopic density distribution $\rho_0(\mathbf{r})$ and the assumption that when $\rho_0(\mathbf{r})$ is replaced by $\rho(\mathbf{r})$ (with microscopic resolution) in Eq. (4), one obtains the correct generator $\tilde{F}[\rho,\mathbf{u}]$ for strained density evolution. One is immediately led to the following expression for the elastic energy density:

$$F_{el}[\rho,\mathbf{u}] = \int d\mathbf{k}\, u_i(\mathbf{k})\tilde{K}_{ij}[\rho,\mathbf{k}]u_j(-\mathbf{k}), \tag{67}$$

where the scale dependent elastic constants are given by

$$\tilde{K}_{ij} = \int d\mathbf{r} \int d\mathbf{r}'\,\nabla_i\rho(\mathbf{r})C_2(\mathbf{r}-\mathbf{r}')(1-e^{\imath\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')})\nabla'_j\rho(\mathbf{r}'). \tag{68}$$

In other words, it is possible that the elastic constants given by $\tilde{K}_{ij}$ can assume a different value on the grain scale (determined by setting the coarse-graining level of ρ) from their values on a much larger scale of the entire crystal. Also, the ρ dependence can be utilized when modeling coexisting liquid and solid phases (see Sec. VIII A). From the mathematical point of view, the admissibility of elastic continuum for materials with hierarchical structure is a more complex question, which cannot be separated from the determination of macroscopic boundary conditions. Thermomechanical considerations related to this observation have been presented in Ref. 32.

VII. RELATION TO PHASE FIELD CRYSTAL MODELS

In this section, we will demonstrate under what kinds of conditions the equations of motion (46)–(48) will give rise to two different variants of the phase field crystal models. A purely diffusive model, which contains a single diffusive time scale, has been introduced by Elder and one of us in Ref. 11 where it was demonstrated that the PFC model has the capability to describe various features of nonequilibrium materials processing ranging from epitaxial growth to softening of nanocrytalline materials. Precisely the same model has also appeared in the context of block copolymer systems and it is known as the Landau-Brazovskii theory of weak crystallization.[33] A long-range version of the theory was proposed by Kawasaki and Ohta.[34,35] Another variant of the PFC model was introduced, recently, by Stefanovic, Haataja, and Provatas, who considered an extension of the diffusive PFC model by introducing a second time scale, by adding a double time derivative term into the model of Ref. 11. Various case studies were performed in Ref. 12 where it was shown, that due to the fast time scale, the mass transport was more realistic on the time scales of the simulation. A very similar model with two time scales has previously been proposed also by Teramoto *et al.*[36]

To be able to derive the PFC models, we need to first simplify our driving force $\nabla(\rho\nabla\mu)$ by replacing it with $\bar{\rho}_0\nabla^2\mu$ in the momentum balance equation. The term $\nabla(\rho\nabla\mu)$ plays a dual role: It originates from the reactive Poisson bracket and can be argued to be essential for obtaining the reversible mode coupling due to driving force.[28] On the other hand, the same term can appear in a dissipative role, such as in the description of the coarse-grained dynamics of colloidal suspensions.[37] The exact nature and consequences of the approximation, $\nabla(\rho\nabla\mu)\approx\bar{\rho}_0\nabla^2\mu$, can be revealed through numerical simulations not pursued in the present work. We will also set the coupling term $\alpha_2=0$ for simplicity. Equations (47) and (48) now reduce to the form

$$\partial_t g = Lg + Ku - \rho\nabla\mu; \tag{69}$$

$$g = \bar{\rho}_0\partial_t u - \bar{\rho}_0 AKu = g_L + g_N. \tag{70}$$

Taking divergence on both sides of Eq. (69) and using the mass conservation equation (46), we obtain

$$\partial_t^2\rho - \nu\nabla^2\partial_t\rho - (a\bar{\rho}_0)^{-1}\nabla\cdot g_N = \nabla(\rho\nabla\mu) \approx \bar{\rho}_0\nabla^2\mu, \tag{71}$$

where, for simplicity, we have assumed that $A_{ij}^{-1}=(1/a)\delta ij$. In order to obtain the MPFC model of Ref. 12, one consideres the regime ($\omega \ll a\lambda k^2$) where the dissipative flux dominates,

$$\nabla\cdot\mathbf{g}_N \gg \nabla\cdot\mathbf{g}_L \Rightarrow \nabla\cdot\mathbf{g}_N \approx \nabla\cdot\mathbf{g}. \tag{72}$$

In more rigorous terms, the wave vector window (60) is now necessary for the existence of diffusive pole, unlike for the full model of Sec. V. With the approximation (72), it is possible to use again the mass balance equation to express $\nabla\cdot\mathbf{g}$ in terms of $\partial_t\rho$. Equation (71) becomes

$$\partial_t^2\rho + [1/(a\bar{\rho}_0) - \nu\nabla^2]\partial_t\rho = \bar{\rho}_0\nabla^2\mu, \tag{73}$$

where for large enough length scales, we can drop $\nu\nabla^2$ in comparison with the constant $1/(a\bar{\rho}_0)$. The "wave equation"[12] follows:

$$\partial_t^2\rho + (a\bar{\rho}_0)^{-1}\partial_t\rho = \bar{\rho}_0\nabla^2\mu. \tag{74}$$

The parameters of this model are now known in terms of the more microscopic expressions, as will be detailed below.

Finally, as pointed out in Sec. V, since the first term on the LHS of Eq. (74) is negligible to the second one at late times $\omega\ll 1/(a\bar{\rho}_0)$, the original diffusive PFC equation[11] emerges in this limit:

$$\partial_t\rho = a\bar{\rho}_0{}^2\nabla^2\mu. \tag{75}$$

Thus, we have been able to express the unknown time rescaling τ of Ref. 11 in terms of $a\bar{\rho}_0{}^2$, with a given by the microscopic expression in Eq. (30). We point out that it is possible to obtain the same diffusive pole—both from the linearized hydrodynamics of the full model (57) and from Eq. (75) directly without first reducing the full model to the MPFC form.[38] It is also important to note that if the diffuse mass current dominated limit as given in the approximation (72) is a clean one, then our diffusion coefficient (45) should reduce to $D_{\alpha\beta}^{PFC}$ of the original PFC model in the dimensionless units where $a\bar{\rho}_0{}^2$ can be set to 1 (absorbed into dimensionless time) and $\alpha_2=0$.[11]

$$D_{\alpha\beta}^{PFC} = \delta_{\alpha\beta}\left(1 + r + 3\bar{\rho}_0^2 + \frac{9}{8}\tilde{A}^2\right) \equiv \delta_{\alpha\beta}d_2, \tag{76}$$

where $r\equiv b\Delta T/\lambda_A q_0^4$ is the parameter that determines the deviation from criticality. In the dimensionful numbers $D_{\alpha\beta}^{PFC}=a\bar{\rho}_0 d_2\delta_{\alpha\beta}$ is, indeed, obtained from the result of Eq. (42) by setting an extra constraint

$$|-\lambda/\bar{\rho}_0| \gg |d_2|. \tag{77}$$

Despite the fact that the static elastic properties contained in the free energy in both cases are the same, the elastic constants appear explicitly only in Eq. (45). In both cases, the phonons affect the diffusion constant implicitly through the prefactor a.

In Refs. 11 and 12 the phenomenological Swift-Hohenberg free energy was utilized. Its parameters can be matched with the more fundamental DFT free energy, for example, by considering the elastic constants or the diffusion constant. The parameters of the phenomenological Swift-Hohenberg F_{SH} free energy,[11]

$$F_{SH}[\rho] \equiv \int d\mathbf{r}\left(\frac{1}{2}\rho(\mathbf{r})w(\nabla^2)\rho(\mathbf{r}) + \frac{\lambda_B}{4}\rho^4(\mathbf{r})\right), \tag{78}$$

$$w(\nabla^2) \equiv b\Delta T + \lambda_A(q_0^2 + \nabla^2)^2, \tag{79}$$

can now be mapped onto the DFT results using our results for the elastic constants derived in Sec. II. In particular, we obtain the following result:

$$K_{ij} = \tilde{A}^2\sum_Q \rho_Q\rho_{-Q}Q_iQ_j\tilde{C}(\mathbf{q},\mathbf{Q}), \tag{80}$$

where we have defined similarly to Eq. (5) the kernel $\tilde{C}$ function

$$\tilde{C}(\mathbf{q},\mathbf{Q}) = \lambda_A[(-2q_0^2 + 2Q_iQ_j)q^2 + 4Q_iQ_jq_iq_j]. \tag{81}$$

The results in 2D hexagonal were obtained by direct evaluation of the free energy under compressive, shear, and deviatoric deformations considered in Ref. 11. Elder and Grant found that the Swift-Hohenberg free energy sustains only isotropic stresses with fixed Poisson ratio $\nu_P = 1/3$. Moreover,

$$K_{11}/3 = K_{12} = K_{14} = \frac{1}{3}\lambda_A q_0^4 \tilde{A}^2. \tag{82}$$

When the DFT form (5) for determination of the elastic coefficients is used, it is possible to obtain an arbitrary Poisson ratio unlike with Swift-Hohenberg free energy. It is also important to notice that the simple gradient expansion of the nonlocal DFT free energy (3) will not produce the gradient terms of the Swift-Hohenberg free energy (78) because the lowest order Laplacian (∇^2) has a different sign. Therefore, the lowest order gradient expansion will not directly yield the phenomenological PFC parameters in terms of the DFT parameters. Alternatively, one can utilize the phase-amplitude representation[39] of the density field on large scales, as will be discussed in Sec. VIII A.

We conclude that the MPFC model of Ref. 12 is derivable from our model by replacing the dissipative momentum current g_N with the total momentum. Consequently, as stated by Stefanovic *et al.*, the waves described by Eq. (73) are not real acoustic-phonon excitations but quasiphonons, whose purpose is to move (probability) mass from one place to another at a faster rate than pure diffusion would be able to. Contrary to the real acoustic-phonon excitations, which live on large spatial scales, the quasiphonons manifest themselves only for small times and distances.[12] We also point out that the dispersion relation characteristic of the quasiphonon equation is similar to the dispersion relations derived from the two-fluid equations of Enz[6] of optical phonons in the second sound domain on a rigid lattice $\mathbf{u} = 0$.

VIII. CONNECTIONS WITH OTHER PHASE FIELD MODELS

A. Amplitude expansion

We have discussed the hydrodynamics of solids using four fields: mass, momentum, and energy represent the conserved slow variables and the displacement field $\mathbf{u}$ describes the long-wavelength excitations of the crystal. It is fundamentally different from the first three for several reasons: it is not conserved, it is constrained to the solid phase only, and it does not have a unique microscopic expression in terms of particle positions and momenta. The last point is usually overlooked and the displacement vector of the αth particle is presented as a vector that points from the closest equilibrium lattice position $\mathbf{R}^\alpha$ of the perfect equilibrium crystal lattice to the actual (displaced) position of the atom. However, at any finite temperature, the crystal is necessarily defected and, therefore, there is no unique origin for the displacement vector.[4] For the purposes of the Poisson bracket formalism, approximative microscopic definitions, such as[17]

$$\rho(\mathbf{r},t)u_i(\mathbf{r},t) \equiv m\sum_{\alpha=1}^{N} u_i^\alpha(t)\,\delta[\mathbf{r} - \mathbf{r}^\alpha(t)], \tag{83}$$

where $\mathbf{r}^\alpha(t) \equiv \mathbf{R}^\alpha + \mathbf{u}^\alpha(t)$, can be used to fix the brackets of $\mathbf{u}$ with the other fields.

Also, $\mathbf{u}$ cannot be seen simply as the order parameter of the solid. It certainly fulfills the requirement of the order parameter in the sense that it is nonzero in the ordered (solid) phase and zero, or vanishing, in the disordered (liquid) phase. However, we cannot present $\mathbf{u}$ as an expectation value of a symmetry breaking operator, which would single out an (unambigious) reference state. Usually, the real order parameters of the crystalline solid are defined as the various Fourier amplitudes $\rho_G \propto \int_V d\mathbf{r}\,\rho(\mathbf{r})\exp(\imath\mathbf{G}\cdot\mathbf{r})$.[15,18] This definition clearly makes sense and is microscopically well defined. Yet, what makes the derivation of hydrodynamical description of the solid slightly discomforting, using this definition, is not only the fact that there are infinitely many order parameters, but also the entanglement of the order parameters with the conserved density field. The latter clearly comprises the former, and these fields cannot be separated at the microscopic level *at least*. Other definitions in the same vein include the one introduced in the context of the boson transformation:[7] $\rho_0(\mathbf{r}) = \bar{\rho}_0 + A\phi_0(\mathbf{r})$. If we use the lowest order modes for the spatially periodic part of the ground state $\phi_0(\mathbf{r})$, the density field of the perfect crystal without defects is expanded as

$$\rho_0(\mathbf{r}) = \bar{\rho}_0 + A\sum_Q \rho_Q e^{-\imath\mathbf{Q}\cdot\mathbf{r}}, \tag{84}$$

and the amplitude of the periodic part is taken to be the order parameter. Obivously, $A = 0$ in the liquid. It should also be noted that in the case of liquid-gas coexistence, which was not considered in Ref. 7, A should be considered to be a function of $\mathbf{r}$, not merely a constant. Thus, A is very much analogous to the amplitude used in the amplitude-phase expansion of nonlinear dynamical systems,[40] which can serve as the basis fields of a systematic renormalization-group (RG) theory:[39]

$$\rho(\mathbf{r},t) = \bar{\rho}_0 + \sum_i A_i(\mathbf{r},t)e^{\imath\mathbf{Q}_i\cdot\mathbf{r}}, \tag{85}$$

where A_i are the complex amplitudes in the directions of the basis vectors (3 for the 2D hexatic crystal[39]). These complex amplitudes can be considered as the order parameters of the solid. In fact, they are more than that, because knowing them allows one to exactly reconstruct[39] the (microscopic) density field and its excitations above the ground state through Eq. (85).

In order to provide some insight into how to derive the phenomenological order-parameter models of solidification and domain coarsening,[41,42] as well as more recent ones, which describe strain relief mechanisms in thin solid films coexisting with liquid or gas,[43,44] we try to extract the order-parameter dynamics from the known dynamics of the density field. At first sight, this attempt seems to suffer from the same problem as the attempt to try to obtain the dynamics of the displacement field from Eq. (57): After all, not all features of the vector field ($\mathbf{u}$) can be inferred from the equation of motion of the scalar field ρ, which can only contain certain contractions of the components of $\mathbf{u}$. While this is correct, it is also true that making an extra assumption about the form the vector variable $\mathbf{u}$ is encoded in the nonlinear self-interactions of the ρ field, recovering an approximate equation of motion for $\mathbf{u}$ is possible.[45] Of course, we do not need to back engineer the phonon equations of motion from Eq. (57) since we have an independent means of deriving it, as shown in Eq. (28). This line of reasoning suggests—that it might be possible to obtain the dynamics of the amplitude fields A_i in Eq. (85) by substituting the density expansion $\rho(A_i)$ into the free energy (3). Then, treating A_i as variationally independent variables in the Poisson bracket formalism, in the same manner, as we proceeded with the displacement field when substituting the expansion $\rho \approx \rho_0 - \nabla \rho_0 \cdot \mathbf{u}$ into F. In general, if a dynamics of a system is potential, i.e., it obeys gradient flow, there is no guarantee that it stays potential[40] upon a change of collective variables. However, by explicit computation it can be shown, in the present case, that a potential condition to lowest order is obeyed.

There is a more rigorous way, however, of obtaining the amplitude equations.[39] In this approach, one starts directly from the equations of motion of the density field and substitutes the expansion (85). To get an exact presentation, the complex nature of all A_i's has to be taken into account. Below, we make the following simplification: It is assumed, that on large enough scales, all amplitudes are the same. Also, we only retain the norm of the amplitudes. Since the conservation of mass is violated by leaving out the phases, the traditional phase field models, with a single amplitude order parameter, will not give a precise description of dynamics on smaller scales, or close to phase boundaries where the solid must orient itself. However, some of these features can be taken into account phenomenologically, e.g., by introducing an orientation dependent surface tension.[46] The approximation, which only includes amplitude(s), is generally expected to work only close to the bifurcation threshold, where nonlinearities are weak.[40] As most of the traditional order-parameter models of solid-liquid systems do not include phase degree of freedom of the amplitude, we expect that there are regimes where the amplitude dynamics is sufficiently well given by $A \equiv |A_i|$. Indeed, Shih *et al.* have shown that, by making all the amplitudes the same, one is still able to obtain a very good quantitatively correct result for the isotropic part of the surface tension[47] (see also Ref. 48). To account for the (small) anisotropy, one needs to take into account the differences in the amplitudes as demonstrated in Ref. 49. The validity and implications of these assumptions for sharp interface dynamics will also be studied in future work.[50] Thus, we approximate

$$\rho(\mathbf{r},t) \approx \bar{\rho}_0 + A(\mathbf{r},t)\sum_i e^{\imath \mathbf{Q}_i \cdot \mathbf{r}}. \tag{86}$$

Substitution into Eq. (75) leads to lowest order in derivatives to

$$\partial_t A = b_0 \nabla^2 A + b_1 A + b_2 A^2 + b_3 A^3, \tag{87}$$

which can be written in the form of nonconserved dynamics,

$$\partial_t A = -M \frac{\delta F_{SH}}{\delta A} \tag{88}$$

with constant mobility M. Direct substitution of expansion (86) into the local Swift-Hohenberg free energy and rescaling of variables does, indeed, follow an equation of the form (78), which suggests that we can try a similar substitution in more general cases, as well.

B. Models with and without line defects

A more complicated model can be obtained by taking into account the smooth elastic degrees of freedom. Substitution of expansion (86) into $\tilde{F}[\rho,\mathbf{u}]$ in Eq. (10) leads to the free-energy density

$$f[A,\mathbf{u}] = \frac{b_0}{2}|\nabla A|^2 + \frac{b_1}{2}A^2 + \frac{b_2}{3}A^3 + \frac{b_3}{4}A^4 + \alpha_2 A u_{ii} + \frac{1}{2}u_i K_{ij} u_j, \tag{89}$$

which can be seen to contain the same physics as the phenomenological model presented in Ref. 43 (cf. Ref. 51) with free-energy density

$$f(\phi,\mathbf{u}) = \frac{l}{2}|\nabla \phi|^2 + \frac{1}{a}\phi^2(\phi^2-1)^2 + \frac{\epsilon_2^2}{2\kappa}g^2(\phi) + \epsilon_2 g(\phi) u_{ii} + f_{el}(\phi,\mathbf{u}), \tag{90}$$

where ϕ is the liquid-solid order parameter, ϵ_2 is related to external stress, and κ is the compressibility. The elastic free-energy density is given by

$$f_{el}(\phi,\mathbf{u}) \equiv \frac{\kappa}{2}u_{ii}^2 + g(\phi)\mu_2 \sum_{ij} [u_{ij} - (1/d)\delta_{ij}\nabla \cdot \mathbf{u}]^2. \tag{91}$$

The similarities and differencies between the free energy of Eqs. (89) and (90) are as follows: Interpreting A as the liquid-solid order parameter ϕ, the first two terms on the RHS of Eq. (90) are seen to correspond to the first four in Eq. (89). In the latter, the first-order transition is enforced using a sixth-order potential with three wells, whereas in the former two wells, with an asymmetric ϕ^3 term, ensure the first-order nature of liquid-solid transition. The third term on the RHS of Eq. (90) balances the wells, such that, the coupling with elastic degrees of freedom given by $\epsilon_2 g(\phi) u_{ii}$ does not change the bulk free energy of the pure phases. In Eq. (89) there is no apparent Kobayashi contribution. However, we should also keep in mind that the coupling term $\alpha_2 A u_{ii}$ is the lowest-order approximation to the coupling $\mu(0,\rho)u_{ii}$ introduced in the end of Sec. IX D. Also, the quartic polynomial in A only results from the fact that we have used the Swift-Hohenberg free energy for the amplitude expansion. Had we used a more accurate DFT result, such as Eq. (3), there would be higher-order nonlinearities present. It is not certain that these nonlinear contributions sum up effectively to a Kobyashi type of term. At liquid-gas coexistence, the form of the coupling term plays a role since the force generated by the variation $\delta(\alpha_2 \rho u_{ii})/\delta\rho$ or $\delta(\mu(0,\rho)u_{ii})/\delta\rho$ of the chemical potential is nonvanishing.

The elastic free energy of Eq. (89) is essentially the same as given in Eq. (91) in the solid phase. At coexistence, there are differences in the two formulations. First, the elastic energy in Eq. (89) was derived under the assumption of infinite solid ($k \to 0$ limit). Obviously, this assumption breaks down when liquid coexists with the solid. In this situation, one can either introduce a multiplier function, such as the Kobayashi function in Eq. (91), or one can force the displacement field **u** to be ineffective in the liquid phase. This requirement is satisfied if one uses the density dependent (scale dependent) elastic free energy introduced in Sec. VI. Indeed, Eq. (67) with Eq. (68) reduces to $(1/2)u_i K_{ij} u_j$ in the long-wavelength limit because $\nabla_i \rho$ coherently sum up in the solid phase. In the liquid phase, however, when one goes towards larger scales, the contribution from $\nabla_i \rho$ is incoherent by definition and there is no contribution from this term. On atomistic scales, there could be a nonvanishing contribution from Eq. (67) when the liquid is highly inhomogeneous. We also point out, that using the density dependent elastic free energy (67) the bulk compressibility mediated by the **u** field vanishes in the liquid as it should. This is not the case in Eq. (91). There is no other mechanism in Ref. 43, such as the coupling with the momentum density field in our case, to give rise to the free-energy cost due to bulk compression.

Finally, we note that by taking into account a possible multivaluedness of the displacement field via separation of the total strain $\mathbf{u}^t$ strain,

$$\mathbf{u}^t = \mathbf{u}^s + \mathbf{u}^p, \tag{92}$$

into a smooth $\mathbf{u}^s$ and plastic component $\mathbf{u}^p$, leads immediately to the free energy studied in Ref. 44. In the rest of this work, we have used $\mathbf{u}^t = \mathbf{u}^s = \mathbf{u}$ without any contribution from topological defects. The decomposition (92) can be naturally motivated—either by using the defect gauge argument by Kleinert[4] or by using the boson transformation method,[9] where the plastic fields are seen as the multivalued special solution of the **u** evolution equation. Both interpretations lead to the same result. As compared to Ref. 44, the most notable difference is the fact that Haataja *et al.* have left out the momentum density field of the solid, the fluid and replaced its evolution equation with the condition of mechanical equilibrium. While it is true, that as a conserved field, it is relevant for hydrodynamic description, some conserved fields relax still more rapidly to a steady state than some others, and in this case, the diffusive modes related to mass conservation (giving rise to the nonconserved order-parameter relaxation) and the defect diffusion are still much slower processes. Yet, giving up **g** means that, at coexistence, the compressibility has not been taken into account via the pressure term present in the momentum equation.

As for other differences, in Ref. 44 the authors had to introduce a term which made the dislocation fields massive in the fluid phase, and thus effective only in the solid. Using the dependence of the elastic constants on the density field ρ (67), the same effect is incorporated in our theory without an extra coupling term. Moreover, any effective boundary condition for the Airy stress function, which in Ref. 44 is mediated by the massive coupling χ^2, should in the present treatment arise automatically from the interaction of the bulk fields **u** and ρ (A), if the free energy is correctly derived from microscopics. As we have pointed out in Sec. VIII A, especially the shorter scale dynamics and local orienting features of the phase boundary are expected to depend on the interaction of all the amplitude fields A_i and the phases of these complex fields. Higher-order strain fields in the free energy, which have also been left out of the present level of sophistication, can also play a role in the formation of the effective boundary conditions, especially as what comes to the boundary phenomena at grain boundaries in solid-solid transformations.

From the multiple time scales, only the slowest diffusive ones have been retained in Ref. 44: The equations of motion result from assuming conserved relaxation for the dislocation density and nonconserved type of relaxation for the order parameter. The Poisson bracket formalism advocated here does not give a fully satisfactory answer as to what comes to the extraction of the dynamics of the dislocation density from the density $\rho(\mathbf{r},t)$. Despite the fact that the Poisson bracket formalism can reproduce the diffuse regime obtained by more phenomenological means, it is not clear from our derivation to which extent the topological defects can really be treated as independent degrees of freedom. The problem is similar to the one we faced when separating the smooth strains and order parameter amplitude from the density field ρ. This problem is not easily overcome in any continuum theory, as there is no unique well-defined way of relating the continuum representation of elasticity to microscopically discrete structure of the lattice, where the defects really manifest themselves. Given that Kleinert's lattice gauge theory[4] and the boson transformation[9] both give rise to a similar time dependence of the defect density fields in the action (free energy), it should be possible to apply the field-theoretic methods to address the more fundamental formulation of dislocation dynamics.

IX. COMPARISONS

A. Momentum balance equation

Let us now compare our theory with results from the literature. We start with the so-called two-fluid theories of solids.[6] Even though, we have not explicitly separated out the thermal phonon fluid used in these theories, the pressure term is consistent with the two-fluid theory of Enz[6] in the sense that, the total momentum current here plays the role of the optical momentum in Ref. 6 responsible for the dissipative effects. On the contrary, there is no pressure term in the "superfluid" momentum equation (for acoustic phonons) in Enz's theory. When only reversible Hamiltonian dynamics is considered, the reason for the disappearance of the pressure gradient (at low temperatures) can be understood through the following double counting argument. At zero temperature the free-energy density becomes the energy density. Correspondingly, the reversible parts of the equations of motion generated via the Poisson bracket formalism contain only a variation with respect to the energy density and no additional variational derivative with respect to the density ρ, thus leading to vanishing of $-\rho\nabla\mu = -\nabla p$ from the momentum balance equation. However, for finite temperatures, this argument does not justify leaving out the pressure part due to the variations of density.

In the momentum balance equation (3.34) of Ref. 5, all the reactive terms can be generated using only $\int\{g_i,u_j\}\delta F'/\delta u_j$, and the defect pressure term corresponding to our $\int\{g_i,\rho\}\delta F'/\delta\rho$ does not appear. Specifically, in Ref. 5 the defect pressure only enters as a driving force in equation of motion of dislocation density. Some reasons for leaving out the pressure gradient have been contemplated in Ref. 21: Diffusion of vacancies, at least in typical metals, is extremely slow with diffusion constant of about 10^{-10} cm^2/s. Both sound propagation and thermal diffusion take place on a much faster time scale, consequently, the authors of Ref. 21 retain only the temperature gradient part of the pressure term, $-(\partial p/\partial_T)_{\rho_0}\nabla\delta T$. However, if one defines a density (change) through a relation, such as $\delta\rho\equiv\rho-\rho_0=-\bar{\rho}_0u_{ii}+N$, where the defect density N in principle contains everything else but the long-range volume changes given by $-\bar{\rho}_0u_{ii}$, then N can possibly contain through $\delta\rho$ also faster modes of mass propagation, e.g., nonlinear $\mathbf{u}$ interactions. Therefore, one should expect at least $\nabla\delta\rho$, if not N, to appear as a driving pressure gradient in the momentum balance equation. Indeed, to lowest order both in the nondissipative[52] and dissipative[10] cases, the $-(\partial p/\partial\rho)_T\nabla\delta\rho$ compressibility term due to the pressure field, appears in the momentum balance equation derived via the projection operator formalism. A pressure term similar to ours also appears in the phenomenological theory of Kim.[53]

Finally, we make a few remarks on the nonlinear momentum dependence. Taking into account, the convective momentum flux resulting from the bracket $\{g_i,g_j\}$ given in Eq. (16) would lead to conservation of momentum at order $\mathcal{O}(g^2)$ without dissipation and defects in contradiction with Enz's two-fluid theory for the acoustic momentum component, which is only conserved at linear level $\mathcal{O}(g)$. Choosing to leave out the convective momentum contribution enables one to obtain the well-known wave equation for the field $\mathbf{u}$ when no dissipation takes place. However, there can be other types of nonlinearities resulting from self-interactions of the $\mathbf{u}$ field. Therefore, it is not *a priori* certain that the convective momentum term can be dropped if, at the same time, nonlinearities in $\mathbf{u}$ are taken into account.

B. Displacement field

Similar to Eq. (28), dissipative terms proportional to $\nabla_i\nabla\cdot\mathbf{u}$ and ∇_iN were obtained from the phenomenologically postulated displacement field evolution equation of Ref. 5 with different coefficients, however. This is due to the fact that Zippelius *et al.* define the dissipative part of $\partial_t\mathbf{u}$ through a phenomenologically postulated total momentum current $\mathbf{g}=\bar{\rho}_0\partial_t\mathbf{u}+\mathbf{J}_N$, which is then solved for $\partial_t\mathbf{u}$ to give the dynamics of the displacement field,

$$\partial_tu_i=(1/\bar{\rho}_0)g_i+(J_N)_i \tag{93}$$

with $\mathbf{J}_N=\tilde{\Gamma}\nabla\delta\tilde{F}/\delta N$ as the defect current. On the other hand, our corresponding expression (28) gives a slightly different dissipative part because we differentiate $\tilde{F}$ with respect to u_j, not N (ρ). Rewriting the displacement field evolution equation (93) of Ref. 5 in the Poisson bracket form,

$$\partial_tu_i=(1/\bar{\rho}_0)g_i+\Gamma_{u_iN}\frac{\delta\tilde{F}}{\delta N}, \tag{94}$$

where $\Gamma_{u_iN}\equiv\tilde{\Gamma}\nabla_i$, it appears that Onsager's reciprocity relations are violated since the coupling term $\Gamma_{Nu_i}\delta\tilde{F}/\delta u_i$ is missing from the defect evolution equation in Ref. 5. In general, unless special transformation rules are attached to the dissipative operators Γ in the single generator formalism based on the free energy $\tilde{F}$, it is possible that Onsager's reciprocity appears to be violated because of a variable transformation from one set of thermodynamic variables to another. Variable transformations in a single generator framework can be self-consistently addressed in the Fokker-Planck representation as shown in Ref. 54. In a more refined double generator formalism of irreversible thermodynamics, such as GENERIC,[55] all transformations, automatically, respect the reciprocity requirement. Our (single generator) theory does respect Onsager's reciprocity because the diffusive coupling in Eq. (28) is of the form $\Gamma_{u_iu_j}$, which is a self-coupling mixing no variations in other variables than components of $\mathbf{u}$. Similar dissipative terms, with only self-couplings, also appear in the free volume diffusion context of amorphous solids.[56]

C. Comparison with linear diffusion equation from Mori formalism

It is interesting to note that, even if we leave out the explicit $\mathbf{u}$ dependence from the diffusion equation (100), the phononic scattering effects manifest themselves in the dissipative coefficient $A_{ij}\propto\langle\dot{u}_i|\dot{u}_j\rangle_{eq}$ appearing in the expression of the diffusion coefficient D_{ij}. Consequently, even though one can argue that there are no explicit activated jumps from potential well to another for vacancies in our model due to its probabilistic nature, the coefficient A_{ij} provides a link between the diffusional motion through activation and phonons. As shown in Eq. (42), the diffusion coefficient is directly proportional to a Kubo-type current correlator A_{ij}. In the traditional diffusion theory, one identifies various regimes of tracer diffusion with different dependence of the diffusion constant D on the viscosity, and thus current correlations.[57] Energy transfers between the bulk modes and the diffusing atom leads to viscous dissipation. In this context, viscosity (η_{tr}) means the damping coefficient present in the effective Langevin equation, which describes the dynamics of the adatom obtained, by projecting out the bulk degrees of freedom via Mori formalism. More importantly, it can be shown[58] that η_{tr} contains the phonon correlation function $\langle u_i(t)u_j(0)\rangle_{tr}$ similar to our expression (30). In the quantum-mechanical case of Ref. 58 the definition of the phonons (and projectors) is, of course, different from the classical continuum version of Ref. 10 that we are using. For single-particle diffusion, one can furthermore show[58] that in the high viscosity regime $D\propto1/\eta_{tr}$, and in the low viscosity regime $D\propto\eta_{tr}$ in the nomenclature of Combs and Kuntz. In other words, if we were to take A_{ij} analogous to η_{tr}, our collective diffusion coefficient would be indicative of the low viscosity regime. However, this comparison is not really appropriate because, for collective phenomena, the same dependency of the diffusion constant on the friction coefficient does not have to hold. Gortel and Turski[59] have extracted the diffusion constant D_{gt} of the collective density fluctuations and shown that for a dense adsorbate

$$D_{gt} = \lim_{|\mathbf{k}|\to 0} \frac{R(\mathbf{k})}{\eta_{gt}(|\mathbf{k}|,0)}, \tag{95}$$

where R plays the role of the interparticle potential and η_{gt} is proportional to the current correlator of the normal coordinates Q_j of phonons. Thus $D_{gt}\propto[\langle Q_j(t)Q_{-j}(0)\rangle_{eq}]^{-1}$. In contrast, our diffusion coefficient $D_{\alpha\beta}$ is directly proportional to the current correlation function. Finally, in the case of boundary lubrication theory, the collective diffusion coeffcient D_c is related, as in the theory of Gortel and Turski, to the macroscpic density fluctuations. In this case, the diffusion constant turns out to be inversely proportional to the sliding friction η_s, $D_c\propto 1/\eta_s$ in the linear-response regime.[60] However, since in this case the friction coefficient is inversely proportional to the current (J) correlator, we obtain the familiar Green-Kubo relation $D\propto\int_0^\infty\langle J(t)J(0)\rangle_{eq}$, which would indicate the analogy $J=P_\perp\dot u$ motivated by Eq. (30).

D. Diffusion of vacancies in elastic network: Larche and Cahn theory

We will now show that with a nonzero coupling α_2 between the (defect) density and longitudinal component of the displacement field, our linearized model of Sec. IV reduces to a model introduced by Larche and Cahn[23] for self-stress effects on diffusion in solids. They considered diffusion of composition changes that were representative of vacancies in a background matrix, the network of occupied lattice sites. To enable the comparison with the Larche and Cahn theory, we reproduce the diffusion equation of Ref. 23:

$$\partial_t c = \nabla_i B_{ij}\nabla_j M(\sigma,c); \tag{96}$$

$$M(\sigma,c) = M(0,c) - \frac{1}{\bar\rho_0}\left(\frac{du^c_{ij}}{dc}\sigma_{ij} + \frac{ds_{ijkl}}{dc}\sigma_{ij}\sigma_{kl}\right), \tag{97}$$

where $u_{ij}\equiv(1/2)(\partial_i u_j+\partial_j u_i)$. Here, $\bar\rho_0$ is the density of lattice sites in the reference state. The stress free strain $u^c_{ij}=\eta\Delta c\,\delta_{ij}$ is for simplicity taken to be diagonal tensor linearly dependent on the thermal-expansion coefficient η and on the composition difference $\Delta c\equiv c-c_0$ from the reference composition c_0. Finally, s_{ijkl} is the compliance tensor. Leaving out the nonlinear stress contribution for the moment, Eq. (96) becomes

$$\partial_t c = \nabla_i B_{ij}\nabla_j(M(0,c) - (\eta/\bar\rho_0)\sigma_{kk}), \tag{98}$$

where the stress is given in terms of the tensor of elastic coefficients:

$$\sigma_{ij} = \lambda_{ijkl}(u_{kl}-u^c_{kl}) = Ku - \frac{Y}{1-2\nu_P}\eta\Delta c\,\delta_{ij}, \tag{99}$$

where Y is Young's modulus and ν_P is the Poisson ratio.

We can now identify the variables in the two theories. Substituting Eq. (37) into Eq. (34) we get

$$\partial_t\tilde N = \bar\rho_0\nabla_i A_{ij}(K_2 u + \alpha_2\nabla\tilde N)_j. \tag{100}$$

Taking $\tilde N$ to be c (Δc), Eq. (100) can be seen to be of the same form as the diffusion equation of Larche and Cahn [Eq. (98)] [$\tilde N$ can be trivially replaced by N because $\rho_0(\mathbf{r})$ part vanishes in the long-wavelength limit from (100)]. The phenomenological mobility matrix B_{ij} is associated with the phonon current correlator $A_{ij}\propto\langle\dot u_i\dot u_j\rangle_{eq}$. The remaining term $\alpha_2\nabla\tilde N$ can be associated with the self-stress term of Eq. (99) provided that we set

$$\alpha_2 \propto -\frac{Y\eta}{1-2\nu_P}. \tag{101}$$

The only difference is that, in the diffusion equation (100), the elastic operator K_2 appears in the current $\mathbf{g}_N$, whereas in Eq. (99) there is K. In other words, we have an extra contribution to the diagonal part of the elastic tensor proportional to the coefficient of thermal expansion. However, this can be absorbed into the redefinition of elastic coefficients.

Finally, we point out that the nonlinear density (concentration c) contributions entering via the chemical potential $M(0,c)$ of the interstitial species—in Larche's and Cahn's theory[23]—can be generated by keeping higher-order coupling terms in the expansion of the free energy (10). In other words, when deriving $\tilde F$ from F in Eq. (3) through expansion $\rho=\rho_0+\Delta\rho$, we obtain

$$F[\rho] = F[\rho_0] + \int d\mathbf{r}\frac{\delta F}{\delta\rho(\mathbf{r})}\Delta\rho(\mathbf{r}) + \frac{1}{2}\int d\mathbf{r}\int d\mathbf{r}'\Delta\rho(\mathbf{r})E(\mathbf{r},\mathbf{r}')\Delta\rho(\mathbf{r}') + \cdots, \tag{102}$$

where the variations are to be evaluated at $\rho=\rho_0$. Thus, the last term, $E=(\delta^2F/\delta\rho\delta\rho)|_{\rho=\rho_0}$, gives rise to the term $(1/2)u_iK_{ij}u_j$ in Eq. (10). Proceeding as in Sec. II, and making the replacement $\rho_0(\mathbf{r})\to\rho(\mathbf{r})$, whose relevance and motivation based scale dependent elastic energy will be further discussed in Sec. VI, we get

$$\left.\frac{\delta F}{\delta\rho}\right|_{\rho=\rho_0} \equiv \mu_1[\rho_0(\mathbf{r})] \to \mu_1[\rho(\mathbf{r})]. \tag{103}$$

In order to cast the coupling term in the form that is needed to reproduce the nonlinear defect density dependent part of the diffusion potential of Ref. 23, we evaluate μ_1 at $\epsilon=0$ [corresponding to $\Delta\rho=0$, or, equivalently, $\rho=\rho_0$ in Eq. (102)]. This yields

$$\int d\mathbf{r}\mu_1\,[\rho(\mathbf{r})]|_{\epsilon=0}\Delta\rho(\mathbf{r}) = \int d\mathbf{r}\ \mu_1[\tilde N(\mathbf{r})]\epsilon(\mathbf{r}), \tag{104}$$

because $\rho=\tilde N-\epsilon$. Rewriting $\mu_1(\tilde N)\equiv M(0,\tilde N)$, leads to the diffusion potential of Larche and Cahn. It should be noted that since $\tilde F[\rho,\mathbf{u}]=F[\rho]+\mu_1(\rho)u_{ii}+(1/2)u_iK_{ij}u_j$, for nonzero

u it follows that $\delta\tilde{F}/\delta\rho \neq \delta F/\delta\rho$. Only $\delta F/\delta\rho$ can be related to the chemical potential used in Ref. 23. Also, one should be careful in the construction of the diffusion potential when using the thermodynamic identities together with the variable transformation $\rho=\tilde{N}-\epsilon$: $\sigma_{ij}=\delta\tilde{F}/\delta u_{ij}|_{\rho}$ will give a different result from $\sigma_{ij}=\delta\tilde{F}/\delta u_{ij}|_{\tilde{N}}$. These different definitions of the stress tensor are obsolete in our case, since the Poisson bracket formalism we utilize assumes that ρ is the fundamental variable. We chose not to use $\tilde{N}$ due to the lack of unambious microscopic representation for it. Finally, to account for nonlinear strain fields in the diffusion potential (97) requires the introduction of composition dependent strain fields.

X. DISCUSSION AND CONCLUSIONS

Let us make a few additional comments on how to extend the model presented in the previous sections. At the present stage of the model, we have only considered nonlinearities that are present in the self-couplings of the density field in the chemical potential $\mu(\rho)$ and in the bilinear coupling term $\alpha_2\nabla[(\rho/\bar{\rho}_0]\nabla\epsilon)=\alpha_2\nabla(\rho\nabla u_{ii})$ of Eq. (55). If one wants to include nonlinear elastic interaction in the model, one should also start considering the inclusion of plastic strain effects. Therefore, the theory should also include the dynamics of various types of line defect densities, such as dislocations and disclinations. The mechanisims via which they can be incorporated into the model, already at the level of linearized elasticity, are briefly discussed in Sec. VIII B. For solid-fluid coexistence, the main elastic features are included at the quadratic level in strains. Higher-order (smooth) strains are needed, for example, when describing various solid-solid transformations.[61]

The current model does not properly describe the coexistence of solid and liquid, despite the fact that the direct correlation function C_2 appearing in the free energy is determined at coexistence (see Sec. II). Thus, the solid correlation function is approximated to a sufficient degree of accuracy by the correlations of an inhomogenous liquid. In a more quantitative model, we would have to make the two-point correlation functions dynamical variables along with the conserved one-point functions (mass, momentum, and energy) and the order parameters of the model. This would facilitate not only the more accurate description of spatially inhomogeneous coexistence region, but also the possiblity of seeing how the constants (such as transport coefficients or parameters related to gradient expansion C_2) change when the phase-transition region is crossed. In the phenomenological approaches different means have been employed to kill the solidlike features of the fields in the liquid domain. In other words, the problem reduces to making the field **u** ineffective in the liquid, which is then described by only the mass, momentum, and energy. Rigorously speaking, **u** should not exist in the liquid, but in the current formulation presented in this work, it is simply decoupled from the other fields in the liquid domain, such that it can still evolve in time, and take a nonzero value in the liquid. Nevertheless, the remaining conserved fields do not interact with it in the liquid phase when Ku vanishes in Eq. (47) and $-\rho\nabla\mu(\rho,\mathbf{u})\rightarrow-\rho\nabla\mu(\rho)$. The actual vanishing of the displacement field can be achieved if we introduce it only as collective parameter characterizing the excitations of the real order-parameter field ψ by using a more fundamental field-theoretic description.[62]

Finally, we summarize our main results. We have derived the hydrodynamical evolution equations for isothermal solids. The generalization to include temperature effects can be done along the lines given in Ref. 55 consistent with the Poisson bracket formulation presented here. We have generalized the diffusion equation for point defects given by Mori formalism in Ref. 10. Furthermore, we have given an alternative derivation of Larche's and Cahn's diffusion theory in self-stressed solids, with an interpretation of the phenomenological constants. It was also shown how two important variants of the phase field crystal model[11,12] can be obtained from our theory under particular conditions. It was also demonstrated how a variety of elastic continuum models[43,44] can be obtained using the amplitude-phase expansion and a more microscopic free energy. Finally, an expression for scale dependent elastic free energy was presented, which can be utilized in multiscale modeling of polycrystalline materials.

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