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Theory of Nonequilibrium Multicomponent Coexistence

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Multicomponent phase separation is a routine occurrence in both living and synthetic systems. Thermodynamics provides a straightforward path to determine the phase boundaries that characterize these transitions for systems at equilibrium. The prevalence of phase separation in complex systems outside the confines of equilibrium motivates the need for a nonequilibrium theory of multicomponent phase coexistence. Here, we develop a mechanical theory for coexistence that casts coexistence criteria into the familiar form of equality of state functions. Our theory generalizes traditional equilibrium notions such as the species chemical potential and thermodynamic pressure to systems out of equilibrium. Crucially, while these notions may not be identifiable for all nonequilibrium systems, we numerically verify their existence for a variety of systems by introducing the phenomenological Multicomponent Active Model B+. Our work establishes an initial framework for understanding multicomponent coexistence that we hope can serve as the basis for a comprehensive theory for high-dimensional nonequilibrium phase transitions.

I. INTRODUCTION

From membrane-less organelles [1–4] to the segregation of cell types during differentiation [5–9], multicomponent phase separation has been implicated as the origin of a number of processes that are essential to living, functional matter. Theoretical treatments of these scenarios have largely borrowed from the equilibrium literature, yet it remains to be seen whether a local equilibrium is achieved in living systems that are decidedly out of equilibrium [10, 11]. In parallel with these efforts, many studies in the field of active matter have been dedicated to generalizing thermodynamic theories of phase coexistence to systems out of equilibrium [12–22]. Much of these investigations have aimed to describe nonequilibrium steady states of phase coexistence: states where two (or more) macroscopic phases coexist (e.g., liquid-liquid coexistence) but energy is constantly consumed at the microscale [see Fig. 1]. The length scales associated with the entities that comprise the phases can differ dramatically and need not be molecular. Both synthetic and biological colloidal systems and even macroscopic living matter can exhibit states of coexistence that are beyond the description of equilibrium thermodynamics [23–26]. While macroscopic *traveling* states are commonly observed in nonequilibrium multicomponent systems [27–29], stationary phase coexistence often persists far from equilibrium across a broad range of conditions [30–36]. A comprehensive predictive framework that describes the macroscopic phase behavior of nonequilibrium mixtures will require an understanding of both stationary and traveling patterns.

While direct measurements of heterogeneous states from experiments or computer simulations can allow for the construction of phase diagrams (both in and out of equilibrium), in equilibrium, thermodynamics allows us to circumvent these approaches and predict the binodals of stationary coexisting phases by simply *equating bulk equations of state* (i.e., func-

tions that depend on the local values, but not the spatial gradients, of the species densities), which are properties of homogeneous states. These coexistence criteria, famously derived by Maxwell, van der Waals, and Gibbs, are obtained variationally from the system free energy [37]. The absence of this variational principle out of equilibrium has obfuscated which (or, if any) bulk state functions are equal between coexisting nonequilibrium phases.

For the above reasons, a genuinely nonequilibrium theory for multicomponent phase coexistence is an outstanding challenge, although much progress has been made towards a theory of *single-component* coexistence. Recently, an entirely mechanical approach for single-component systems has been developed to describe two-phase coexistence while making no appeals to equilibrium notions [17, 22, 38]. The coexistence criteria derived for these systems can be equivalently expressed as a weighted-area construction [38], a generalized common tangent construction [17], or a generalized Maxwell equal-area construction [22]. This approach, however, makes use of several simplifications that are not applicable to multicomponent systems. In fact, we find that one of these simplifications only applies to a subset of one-component systems and that the coexistence theory in Refs. [17, 22, 38] must be extended. While system-specific criteria have been developed for some nonequilibrium multicomponent systems [29, 39–41], there remains an absence of a general theoretical treatment of nonequilibrium multicomponent coexistence.

In this Article, we construct an entirely mechanical theory of phase coexistence applicable to both equilibrium and nonequilibrium systems *in terms of bulk equations of state*. While such criteria were found in single-component nonequilibrium systems, it is not clear *a priori* if equality of state functions is to be generally expected for multicomponent nonequilibrium systems. Indeed, our work allows us to identify systems in which: (i) the criteria are exact and take the form of equality of bulk state functions (equilibrium and select nonequilibrium systems); (ii) the criteria are approximate and take the form of a combination of equality of state functions and a generalized equal-area Maxwell construction on state functions; (iii) no coexistence criteria in terms of bulk state functions exist, exact or approximate. Notably, by rely-

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ing on purely mechanical ideas, we are able to quantitatively predict the phase diagram in a large class of systems where the criteria cannot be expressed as an effective common tangent construction of any sort. We emphasize that our theory encompasses pseudo-thermodynamic approaches, where effective free energies are introduced and Legendre transforms may be used to define quantities that must be equal in coexisting phases [17, 40, 41], while additionally enabling the prediction of phase diagrams in many systems where these ideas do not hold. The utility of our approach is demonstrated through its application to both equilibrium systems, in which we precisely recover the equilibrium coexistence criteria, and a phenomenological nonequilibrium field theory which we term Multicomponent Active Model B+ (MAMB+). Numerical simulations of the full spatial density profiles of a two-component MAMB+ system reveal excellent agreement with our coexistence theory. It is our hope that this approach can provide a practical means by which nonequilibrium phase diagrams with multiple conserved order parameters can be constructed from first principles.

II. MECHANICAL THEORY OF NONEQUILIBRIUM MULTICOMPONENT COEXISTENCE

In this Section, we describe a theory for the bulk coexistence criteria of phase-separated multicomponent systems arbitrarily far from equilibrium. Our perspective is rooted in mechanics and makes no appeals to equilibrium notions. We briefly review the canonical thermodynamic arguments used to derive the familiar equilibrium multicomponent coexistence criteria of equality of chemical potentials and pressure in Section II A. Beginning from the evolution equation of the species densities, we derive generalized coexistence criteria in Section II B in terms of bulk mechanical equations of state. Importantly, while coexistence criteria resembling those of equilibrium systems may not always be identifiable within this framework, in select cases we are able to find the form of species pseudopotentials, analogous to the equilibrium chemical potentials, and a generalized Gibbs-Duhem relation that connects these species pseudopotentials to a global quantity that is analogous to the equilibrium pressure.

A. Equilibrium Multicomponent Coexistence Criteria

Consider a macroscopic system with n_c number of components, n_p number of coexisting phases, and a fixed overall system volume V . We define two sets: $\mathcal{C}$, containing all n_c species in the system, and $\mathcal{P}$, containing all n_p coexisting phases in the system. We use Roman letters to index different species and Greek letters to index different phases. The order parameters that distinguish the coexisting phases are the species densities. We therefore define a vector of species number densities $\boldsymbol{\rho} \equiv [\rho_i \ \rho_j \ \cdots \ \rho_{n_c}]^T$ with length n_c . The overall number density of each species is constrained to a constant, $\boldsymbol{\rho}^{\text{sys}}$, where the i th element is defined as $\rho_i^{\text{sys}} \equiv N_i/V$, where N_i is the total number of particles of species i .

In equilibrium, for a system with uniform temperature T below the critical temperature T_c , the system can reduce its overall free energy through phase separation. The coexistence curve (or binodal) describes the values of the coexisting densities in each phase as a function of the global system parameters, e.g., T and $\boldsymbol{\rho}^{\text{sys}}$. The coexisting densities can be extracted from the complete spatial species density profiles, $\boldsymbol{\rho}(\mathbf{x})$. Thermodynamics allows us to circumvent solving for these spatially resolved density profiles and, instead, *entirely determine the phase diagram from bulk equations of state*.

With n_p coexisting phases and n_c species densities in each phase, we have $n_c n_p$ unknown species densities. Using the extensivity of the free energy, we can express the total free energy density of a system as $f = \sum_{\alpha}^{n_p} \phi^{\alpha} f^{\text{bulk}}(\boldsymbol{\rho}^{\alpha})$ where $f^{\text{bulk}}(\boldsymbol{\rho})$ is the bulk free energy density of a homogeneous system with densities $\boldsymbol{\rho}$ and ϕ^{α} is the fraction of the system volume occupied by phase α . Here, we have neglected the interfacial free energy which is negligible for phases of macroscopic extent. With the free energy in hand, we can obtain the coexistence criteria by minimizing f with respect to the species densities in each coexisting phase, $\boldsymbol{\rho}^{\alpha}$, and each phase fraction, ϕ^{α} , subject to the constraints of volume ($\sum_{\alpha}^{n_p} \phi^{\alpha} = 1$) and particle number ($\sum_{\alpha}^{n_p} \boldsymbol{\rho}^{\alpha} \phi^{\alpha} = \boldsymbol{\rho}^{\text{sys}}$) conservation. This results in the familiar multicomponent equilibrium coexistence criteria:

$$\boldsymbol{\mu}^{\text{bulk}}(\boldsymbol{\rho}^{\alpha}) = \boldsymbol{\mu}^{\text{coexist}} \quad \forall \alpha \in \mathcal{P}, \quad (1a)$$

$$P^{\text{bulk}}(\boldsymbol{\rho}^{\alpha}) = P^{\text{coexist}} \quad \forall \alpha \in \mathcal{P}, \quad (1b)$$

where $\boldsymbol{\mu}^{\text{bulk}} \equiv [\mu_i^{\text{bulk}} \ \mu_j^{\text{bulk}} \ \cdots \ \mu_{n_c}^{\text{bulk}}]^T$ is a vector of bulk species chemical potentials with $\mu_i^{\text{bulk}} = \partial f^{\text{bulk}} / \partial \rho_i$, $P^{\text{bulk}} = -f^{\text{bulk}} + \boldsymbol{\rho} \cdot \boldsymbol{\mu}^{\text{bulk}}$ is the thermodynamic pressure, and $\boldsymbol{\mu}^{\text{coexist}}$ and P^{coexist} are coexistence values for the chemical potential vector and pressure, respectively. Simply stated, the chemical potential of like species in different phases must be equal and the pressure of each phase must also be equal. The values of these chemical potentials and pressures at coexistence will generally depend on the temperature, T , and overall system composition, $\boldsymbol{\rho}^{\text{sys}}$. Equations (1a) and (1b) constitute $n_c(n_p - 1)$ and $n_p - 1$ equations, respectively. Subtracting the number of equations provided by the coexistence criteria from the number of unknown species densities results in $n_c - n_p + 1$ degrees of freedom, the well-known Gibbs phase rule (with constant temperature) [47].

Equation (1) can be equivalently recast as a Maxwell equal-area construction [37]:

$$\boldsymbol{\mu}^{\text{bulk}}(\boldsymbol{\rho}^{\alpha}) = \boldsymbol{\mu}^{\text{coexist}} \quad \forall \alpha \in \mathcal{P}, \quad (2a)$$

$$\int_{\boldsymbol{\rho}^{\alpha}}^{\boldsymbol{\rho}^{\beta}} [\boldsymbol{\mu}^{\text{bulk}}(\boldsymbol{\rho}) - \boldsymbol{\mu}^{\text{coexist}}] \cdot d\boldsymbol{\rho} = 0 \quad \forall \alpha, \beta \in \mathcal{P}, \quad (2b)$$

which can be straightforwardly recovered by the Gibbs-Duhem relation [48]:

$$dP^{\text{bulk}} = \boldsymbol{\rho} \cdot d\boldsymbol{\mu}^{\text{bulk}}. \quad (3)$$

Equation (2) no longer explicitly contains the thermodynamic pressure and solely contains the species chemical potentials.

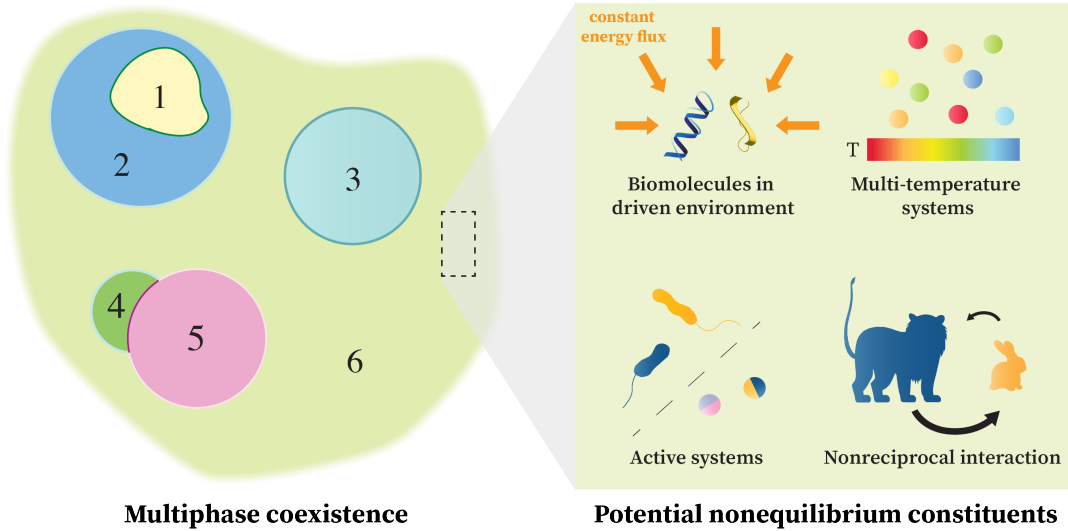


FIG. 1. A schematic of multiphase coexistence (six phases shown) and possible nonequilibrium constituents comprising the phases (including biomolecules in a driven environment [11], multi-temperature particle mixtures [31, 32, 42], active-passive particle mixtures [30, 33, 34, 36, 43–45], and nonreciprocally interacting systems [27, 35, 39, 46]). While curved interfaces are displayed, our theory assumes that the sizes of the phases are such that the radii of curvature far exceed any length scale associated with the constituents and thus the interfaces can be approximated as planar.

We note that for *one-component* systems, the coexistence criteria can be expressed entirely with *either* the chemical potential *or* pressure as chemical potential equality can be expressed through the appropriate Maxwell construction on the pressure. For multicomponent systems, this symmetry is lost: there is no way to express the coexistence criteria without $n_c - 1$ species chemical potentials. Next, we seek to determine the nonequilibrium analogs of the species chemical potentials and Gibbs-Duhem relation in order to express our coexistence criteria solely in terms of bulk equations of state.

B. Nonequilibrium Multicomponent Coexistence Criteria

The phase diagram, for both equilibrium and nonequilibrium systems, can always be obtained by determining (e.g., through experiment, simulation, or theoretically) the spatially resolved species density profiles, $\rho(\mathbf{x})$, during coexistence. We aim to develop a framework that, much like equilibrium thermodynamics, allows us to circumvent the often difficult task of obtaining the complete spatial $\rho(\mathbf{x})$ and, instead, obtain nonequilibrium phase diagrams through a procedure that solely requires bulk equations of state. We take the following approach:

1. Develop the mechanical conditions necessary for stationary multicomponent phase coexistence.
2. Perform a formal expansion of the terms appearing in the mechanical conditions with respect to species density gradients.
3. Perform a series of linear operations on the expanded mechanical conditions to recover coexistence criteria in terms of bulk equations of state.

Our approach is able to reproduce the criteria derived in the previous section for equilibrium systems while also describing a large class of nonequilibrium systems.

We begin by considering the spatial and temporal dynamics of each species density field. We aim to describe states of macroscopic phase coexistence and therefore consider a quasi-1D geometry where spatial variations only occur in the z -dimension with translational invariance in the other dimensions. This choice will ensure that z will be the normal direction to the interface for phase-separated states and amounts to neglecting the effects of interfacial curvature. Such an approximation is justified for macroscopic phases where the radius of curvature far exceeds any other length scale. The evolution equations for the species densities, in the absence of chemical reactions, satisfy the continuity equation:

$$\partial_t \rho = -\partial_z \mathbf{J}, \quad (4)$$

where $\partial_t \equiv \partial/\partial t$, $\partial_z \equiv \partial/\partial z$, and the i th element of $\mathbf{J}$ is the z -component of the number density flux of species i . The fluxes in the directions orthogonal to z are neglected, consistent with our quasi-1D geometry and translational invariance in these directions. We now require a description of the species density flux, $J_i = \rho_i v_i$ (where v_i is the average velocity of species i in the z -direction). We can appreciate that the flux of species i is directly proportional to the momentum density of species i , differing only by a factor of the species mass, m_i [22]. The evolution equation for the flux of each species i is governed by linear *species momentum balance*:

$$m_i \partial_t J_i + m_i \partial_z (J_i J_i / \rho_i) = \partial_z \sigma_i + b_i \quad \forall i \in \mathcal{C}, \quad (5)$$

where $\sigma_i(z; t)$ and $b_i(z; t)$ are the stresses (zz -component of the full spatial stress tensor) and body forces (z -component

of the spatial body force vector) acting on species i , respectively. We emphasize that even for passive systems, the species momentum density is not a conserved quantity, and body forces (sources/sinks of momentum) are thus anticipated to be present. It is only the total momentum density (i.e., $\sum_i^{n_c} m_i J_i$) that is conserved for passive systems (in the absence of external forces).

The coupled continuity equations and species momentum balances, along with *constitutive relations* for the stresses and body forces, can in principle be used to describe the spatial and temporal evolution of the density fields in 1D. Here, as we are interested in stationary states of phase coexistence, we can simplify the continuity equation to $\partial_z \mathbf{J} = \mathbf{0}$. With zero-flux boundary conditions, the flux of each species must vanish everywhere, $\mathbf{J} = \mathbf{0}$, for the coexistence to be stationary: macroscopic phase coexistence is a flux-free stationary state in both equilibrium and nonequilibrium systems. This reduction enables us to simplify the species linear momentum balance [Eq. (5)] to a static species mechanical force balance:

$$\mathbf{0} = \partial_z \boldsymbol{\sigma} + \mathbf{b}. \quad (6)$$

Equation (6) represents the *species-level mechanical conditions* for flux-free stationary states, including macroscopic phase coexistence.

While the distinction between stresses and body forces can be essential [49], here we define an *effective body force* and restate the static mechanical balance:

$$\mathbf{b}^{\text{eff}} \equiv \partial_z \boldsymbol{\sigma} + \mathbf{b} = \mathbf{0}, \quad (7)$$

which are n_c exact mechanical conditions for any planar coexistence scenario. Any further analysis requires a form for $\mathbf{b}^{\text{eff}}$. In detail, the exact microscopic form can be obtained from an Irving-Kirkwood procedure [50], or, in equilibrium, variationally using the methods of classical density functional theory [51]. The exact form of $\mathbf{b}^{\text{eff}}$ often results in integro-differential equations, with the non-local contributions arising from, for example, long-range particle interactions and correlations. Solving these equations for the complete spatial profiles can be an arduous challenge that we aim to circumvent.

To make analytical progress, we first propose performing a general expansion of the effective body forces with respect to spatial gradients of the species densities. Such an expansion can be formally performed (as will later be done for passive systems). Here, we retain terms up to third-order in spatial gradients and neglect even gradients as the body force must be odd with respect to spatial inversion. The accuracy of this expansion will depend on the degree to which the non-local terms can be approximated with local terms. Our body force now takes the form:

$$\mathbf{b}^{\text{eff}} \approx \mathbf{b}^{(1)} + \mathbf{b}^{(3)}, \quad (8a)$$

where:

$$\mathbf{b}^{(1)} = \mathbf{b}^{(1,1)} : \partial_z \boldsymbol{\rho}, \quad (8b)$$

$$\begin{aligned} \mathbf{b}^{(3)} = & -\mathbf{b}^{(3,1)} : \partial_z \boldsymbol{\rho} \partial_z \boldsymbol{\rho} \partial_z \boldsymbol{\rho} \\ & -\mathbf{b}^{(3,2)} : \partial_{zz}^2 \boldsymbol{\rho} \partial_z \boldsymbol{\rho} - \mathbf{b}^{(3,3)} : \partial_{zzz}^3 \boldsymbol{\rho}, \end{aligned} \quad (8c)$$

with definition $\partial_{zz}^2 \equiv \partial^2 / \partial z^2$ and $\partial_{zzz}^3 \equiv \partial^3 / \partial z^3$. Our proposed form of the body force now contains a number of equations of state. $\mathbf{b}^{(1,1)}$, $\mathbf{b}^{(3,1)}$, $\mathbf{b}^{(3,2)}$, and $\mathbf{b}^{(3,3)}$ are tensors of rank 2, 4, 3, and 2, respectively, where each element of these tensors is a state function, i.e., they depend on $\boldsymbol{\rho}$ but not its spatial gradients. We further note that not every component of $\mathbf{b}^{(3,1)}$ is unique as certain anti-symmetric components will vanish upon contraction with $\partial_z \boldsymbol{\rho} \partial_z \boldsymbol{\rho} \partial_z \boldsymbol{\rho}$. This is more readily appreciated by adopting Einstein indicial notation, which makes clear that, when triple contracting into the tensor with components $\partial_z \rho_i \partial_z \rho_j \partial_z \rho_k$, we only retain the contributions to $b_{ijk}^{(3,1)}$ that are symmetric under the exchange of any pair of the i, j , and k indices. We define $\mathbf{b}^{(3,1)}$ to satisfy this symmetry. In total, the expanded body force contains $2n_c^2 + n_c^3 + \frac{1}{6}n_c^2(n_c + 1)(n_c + 2)$ equations of states. For a one-component system, only four state functions are required but this number grows quartically with the number of components.

It was demonstrated that in one-component systems, the mechanical balance always and immediately results in one coexistence criterion for both equilibrium and nonequilibrium systems: equality of pressure [22]. For one-component phase separation, there is a single order parameter (the density), which *always* allows the z -component of the static momentum balance to be expressed as $\partial_z \sigma + b = b^{\text{eff}} \equiv \partial_z \Sigma = 0$ where Σ is the relevant component of the dynamic (or effective) stress tensor. Simple integration of the one-component mechanical balance results in the condition of uniform dynamic stress. The uniform density within the macroscopic coexisting phases coupled with the uniform stress condition results in the coexistence criterion of equality of the bulk contribution to the stress (i.e., pressure) between phases.

Multicomponent systems stand in contrast to one-component systems as the mechanical balance of each species *generally* does not result in a condition of a spatially uniform mechanical property. All (true and effective) body forces will vanish within the phases where no density gradients are present, precluding the immediate identification of a bulk state function that is equal between phases. We seek to perform a linear, bijective *transformation* of the mechanical balance:

$$\mathbf{b}^{\text{eff}} = \mathbf{0} \rightarrow \partial_z \mathbf{u} = \mathbf{0}, \quad (9)$$

where we have introduced the vector of species pseudopotentials, $\mathbf{u}$, whose elements generally depend on $\boldsymbol{\rho}$ and its spatial gradients up to second order. Consistent with the effective body forces being odd with respect to spatial inversion, each species pseudopotential must be even. Before proposing a specific transformation relating the species pseudopotentials to the effective body forces (see Eq. (12) for this transformation), let us consider the expanded form of $\mathbf{u}$:

$$\mathbf{u} \approx \mathbf{u}^{\text{bulk}} + \mathbf{u}^{\text{int}}, \quad (10a)$$

where:

$$\mathbf{u}^{\text{int}} = -\mathbf{u}^{(2,1)} : \partial_z \boldsymbol{\rho} \partial_z \boldsymbol{\rho} - \mathbf{u}^{(2,2)} : \partial_{zz}^2 \boldsymbol{\rho}. \quad (10b)$$

Here, we explicitly delineate the bulk (i.e., gradient-independent) and interfacial contributions to the species pseudopotentials as $\mathbf{u}^{\text{bulk}}$ and $\mathbf{u}^{\text{int}}$, respectively. $\mathbf{u}^{\text{bulk}}$, $\mathbf{u}^{(2,1)}$,

and $\mathbf{u}^{(2,2)}$ are tensors of rank 1, 3, and 2, respectively, where each element of these tensors is a state function dependent on ρ but not its spatial gradients. Not every element of $\mathbf{u}^{(2,1)}$ is unique as certain anti-symmetric components vanish upon contraction with $\partial_z \rho \partial_z \rho$. In indicial notation, considering $u_{nij}^{(2,1)}$, only contributions symmetric under the exchange of the i, j indices are retained when doubled contracted into the tensor with components $\partial_z \rho_i \partial_z \rho_j$. We define $\mathbf{u}^{(2,1)}$ to satisfy this symmetry. In total, the expanded species pseudopotentials contain $n_c + n_c^2 + \frac{1}{2}n_c^2(n_c + 1)$ equations of state that each generally depend on ρ .

If the form of the species pseudopotentials can be identified, we immediately recover the majority of our coexistence criteria. Integration of the steady-state condition, $\partial_z \mathbf{u} = \mathbf{0}$, results in the condition of spatially uniform species pseudopotentials. The absence of density gradients in the bulk phases then allows us to identify that the bulk contribution of each species pseudopotential is equal in each of the coexisting phases:

$$\mathbf{u}^{\text{bulk}}(\rho^\alpha) = \mathbf{u}^{\text{coexist}} \quad \forall \alpha \in \mathcal{P}. \quad (11)$$

As we will later show, these coexistence criteria reduce to equality of species chemical potentials for systems at equilibrium.

The central task is now to determine the precise form of the transformation symbolically proposed in Eq. (9). We introduce a *transformation tensor*, $\mathcal{T}$, defined such that:

$$\mathcal{T} \cdot \mathbf{b}^{\text{eff}} = \partial_z \mathbf{u}. \quad (12)$$

Here, $\mathcal{T}$ is an invertible second-rank tensor whose elements are state functions that depend on ρ but not its spatial gradients. Substituting the expanded forms of $\mathbf{b}^{\text{eff}}$ [Eq. (8)] and $\mathbf{u}$ [Eq. (10)] into Eq. (12) (detailed in Appendix A 1) results in:

$$\mathcal{T} \cdot \mathbf{b}^{(1,1)} = \partial_\rho \mathbf{u}^{\text{bulk}}, \quad (13a)$$

$$\mathcal{T} \cdot \mathbf{b}^{(3,1)} = [\partial_\rho \mathbf{u}^{(2,1)}]^S, \quad (13b)$$

$$\mathcal{T} \cdot \mathbf{b}^{(3,2)} = (\partial_\rho \mathbf{u}^{(2,2)} + 2\mathbf{u}^{(2,1)}), \quad (13c)$$

$$\partial_\rho(\mathcal{T} \cdot \mathbf{b}^{(3,3)}) = \partial_\rho \mathbf{u}^{(2,2)}, \quad (13d)$$

where $\partial_\rho \equiv \partial/\partial \rho$ and $[\partial u_{nij}^{(2,1)} / \partial \rho_k]^S \equiv \frac{1}{6}(\partial u_{nij}^{(2,1)} / \partial \rho_k + \partial u_{nik}^{(2,1)} / \partial \rho_j + \partial u_{nji}^{(2,1)} / \partial \rho_k + \partial u_{njk}^{(2,1)} / \partial \rho_i + \partial u_{nki}^{(2,1)} / \partial \rho_j + \partial u_{nkj}^{(2,1)} / \partial \rho_i)$ extracts the symmetric (with respect to exchange of the i, j , and k indices) portion of the fourth rank tensor $\partial_\rho \mathbf{u}^{(2,1)}$ with components $\partial u_{nij}^{(2,1)} / \partial \rho_k$.

Crucially, the system of equations presented in Eq. (13) is overdetermined, with $n_c^2 + 2n_c^3 + \frac{1}{6}n_c^2(n_c + 1)(n_c + 2)$ linear, first-order, homogeneous PDEs, and $n_c + 2n_c^2 + \frac{1}{2}n_c^2(n_c + 1)$ unknown functions (the elements of both $\mathcal{T}$ and $\mathbf{u}$). The number of equations $[\mathcal{O}(n_c^4)]$ exceeds the number of unknown functions $[\mathcal{O}(n_c^3)]$ and hence Eq. (13) is overdetermined when $n_c > 1$, meaning a solution is not guaranteed to exist, except for when there is a single component and Eq. (13) becomes a system of ODEs where the number of unknowns is precisely the number of equations.

To find solutions for both $\mathcal{T}$ and $\mathbf{u}$, one approach may be to eliminate $\mathbf{u}$ from Eq. (13) through a series of linear operations, obtaining a set of equations solely in terms of $\mathcal{T}$ and the known body force coefficients. Proceeding this way, we must ensure that certain conditions are met, namely, that the order of partial differentiation with respect to the species densities of the elements of both $\mathcal{T}$ and $\mathbf{u}$ is inconsequential (this is more formally referred to as involutivity [52]). These conditions ensure that the resulting state functions, i.e. the components of $\mathcal{T}$ and $\mathbf{u}$, are continuous and differentiable functions of the species densities. The general relations that emerge from stipulating these conditions are difficult to determine for an arbitrary number of components. Nevertheless, Eq. (13) is the starting point for any approach to determine solutions for $\mathcal{T}$ and $\mathbf{u}$. Any solutions that satisfy Eq. (13) can subsequently be checked to ensure that partial differentiation with respect to species density is indeed commutative – we will later show that the form of the body force coefficients for passive equilibrium systems results in solutions $[\mathcal{T}_{ij} = -\rho_i^{-1} \delta_{ij}]$ (where δ_{ij} is the Kronecker delta) and u_i is simply the equilibrium chemical potential of species i] that are clearly consistent with this property.

It is important to mention that many phenomenological models for nonequilibrium dynamics take as a starting point the existence of species pseudopotentials (sometimes defined as nonequilibrium chemical potentials) whose gradients drive the species flux [14, 28]. The present work makes clear that the existence of species-level chemical potential-like quantities is not at all guaranteed for nonequilibrium systems. This undoubtedly limits the number of microscopic systems that can be mapped to species-potential based phenomenological theories for multicomponent systems. When there is a single-component, however, a solution for $\mathbf{u}$ and $\mathcal{T}$ can always be found and the coexistence theories in Refs. [17, 22, 38] can be subsequently applied. In the absence of finding a full-rank solution (where all n_c columns/rows of $\mathcal{T}$ are linearly independent) for $\mathcal{T}$, the species pseudopotentials cannot be rigorously defined using the transformation proposed in this work. Importantly, the absence of a well-defined $\mathbf{u}$ for a particular system does not necessarily signify the absence of phase coexistence scenarios. However, if a full-rank solution of $\mathcal{T}$ can be found, we can use Eq. (13) to identify the form of $\mathbf{u}$ as:

$$\mathbf{u}^{\text{bulk}} = \int \mathcal{T} \cdot \mathbf{b}^{(1,1)} \cdot d\rho, \quad (14a)$$

$$\mathbf{u}^{(2,1)} = \frac{1}{2}(\mathcal{T} \cdot \mathbf{b}^{(3,2)} - \partial_\rho(\mathcal{T} \cdot \mathbf{b}^{(3,3)})), \quad (14b)$$

$$\mathbf{u}^{(2,2)} = \mathcal{T} \cdot \mathbf{b}^{(3,3)}. \quad (14c)$$

For systems in which the species pseudopotentials can be found, we still require additional coexistence criteria that are analogous to the equality of pressure between phases in equilibrium systems. To identify the remaining coexistence criteria, we make an ansatz of a generalized multicomponent Gibbs-Duhem relation, mapping the species pseudopotentials, $\mathbf{u}$, to a global quantity (i.e., a quantity that is not on a per-species basis), $\mathcal{G}$, that depends on ρ and its spatial gradients up to second order:

$$\mathcal{E} \cdot d\mathbf{u} = d\mathcal{G}, \quad (15)$$

where we define a generalized Maxwell construction vector, $\mathcal{E}$, containing n_c elements, each of which is a state function that depends on ρ but not its spatial gradients. The connection of this vector to a Maxwell construction will be made evident in Eq. (21). Consistent with our second-order expansion of $\mathbf{u}$, we expand $\mathcal{G}$:

$$\mathcal{G} \approx \mathcal{G}^{\text{bulk}} + \mathcal{G}^{\text{int}}, \quad (16a)$$

where:

$$\mathcal{G}^{\text{int}} = -\mathcal{G}^{(2,1)} : \partial_z \rho \partial_z \rho - \mathcal{G}^{(2,2)} \cdot \partial_{zz}^2 \rho. \quad (16b)$$

Here, we again explicitly delineate the bulk and interfacial contributions to the global quantity as $\mathcal{G}^{\text{bulk}}$ and $\mathcal{G}^{\text{int}}$, respectively. Note that $\mathcal{G}^{\text{bulk}}$ is a scalar function while $\mathcal{G}^{(2,1)}$ and $\mathcal{G}^{(2,2)}$ are tensors of rank 2 and 1, respectively, where each element is a state function dependent on ρ but not its spatial gradient. Not every element of $\mathcal{G}^{(2,1)}$ is unique as anti-symmetric components vanish upon contraction with $\partial_z \rho \partial_z \rho$. In indicial notation, $\mathcal{G}_{ij}^{(2,1)}$ is symmetric under the exchange of the i, j indices, just as $u_{nij}^{(2,1)} \forall n \in \mathcal{C}$. We define $\mathcal{G}^{(2,1)}$ to only include terms that satisfy this symmetry. In total, the expanded global quantity contains $1 + n_c + \frac{1}{2}n_c(n_c + 1)$ equations of state that each generally depend on ρ .

If a global quantity can be found, we identify our remaining coexistence criteria by substituting the spatial uniformity of species pseudopotentials into the generalized Gibbs-Duhem relation [Eq. (15)], finding $\partial_z \mathcal{G} = 0$ and consequently $\mathcal{G}$ must also be spatially constant. As the species densities are homogeneous within the bulk phases, we recognize that $\mathcal{G}^{\text{bulk}}$ must be equal across phases:

$$\mathcal{G}^{\text{bulk}}(\rho^\alpha) = \mathcal{G}^{\text{coexist}} \quad \forall \alpha \in \mathcal{P}, \quad (17)$$

providing our final $n_p - 1$ coexistence criteria. In equilibrium, this set of criteria reduces to equality of pressures [Eq. (1b)] between phases.

To determine the elements of the Maxwell construction vector, we insert the expanded forms of both $\mathbf{u}$ [Eq. (10)] and $\mathcal{G}$ [Eq. (16)] into our proposed generalized Gibbs-Duhem relation [Eq. (15)] and identify the following system of equations (see Appendix A 2 for details):

$$\mathcal{E} \cdot \partial_\rho \mathbf{u}^{\text{bulk}} = \partial_\rho \mathcal{G}^{\text{bulk}}, \quad (18a)$$

$$\partial_\rho (\mathcal{E} \cdot \mathbf{u}^{(2,2)}) = \partial_\rho \mathcal{G}^{(2,2)}, \quad (18b)$$

$$\mathcal{E} \cdot (2\mathbf{u}^{(2,1)} + \partial_\rho \mathbf{u}^{(2,2)}) = 2\mathcal{G}^{(2,1)} + \partial_\rho \mathcal{G}^{(2,2)}, \quad (18c)$$

$$\mathcal{E} \cdot [\partial_\rho \mathbf{u}^{(2,1)}]^{S'} = [\partial_\rho \mathcal{G}^{(2,1)}]^{S'}, \quad (18d)$$

where $[\partial \mathcal{G}_{ij}^{(2,1)} / \partial \rho_k]^{S'} \equiv \frac{1}{6}(\partial \mathcal{G}_{ij}^{(2,1)} / \partial \rho_k + \partial \mathcal{G}_{ji}^{(2,1)} / \partial \rho_k + \partial \mathcal{G}_{ik}^{(2,1)} / \partial \rho_j + \partial \mathcal{G}_{ki}^{(2,1)} / \partial \rho_j + \partial \mathcal{G}_{jk}^{(2,1)} / \partial \rho_i + \partial \mathcal{G}_{kj}^{(2,1)} / \partial \rho_i)$ extracts the components, $\partial \mathcal{G}_{ij}^{(2,1)} / \partial \rho_k$, of $\partial_\rho \mathcal{G}^{(2,1)}$ that are symmetric with respect to exchanging i, j , and k . The system of PDEs in Eq. (18) is again overdetermined, with $n_c + 2n_c^2 + \frac{1}{6}n_c(n_c + 1)(n_c + 2)$ linear, first-order, homogeneous PDEs

and $1 + 2n_c + \frac{1}{2}n_c(n_c + 1)$ unknown functions, as described in Appendix A 2. Again, just as was the case with Eq. (13), we have an excess of equations in comparison to our unknowns for $n_c > 1$. When $n_c = 1$, the system of ODEs reduces to that of Refs. [17, 22, 38] and a solution can always be found. In multicomponent systems, solutions for $\mathcal{G}$ and $\mathcal{E}$ that satisfy Eq. (18) will again need to be checked to ensure that partial differentiation with respect to species densities is commutative for every state function in $\mathcal{G}$ and $\mathcal{E}$. As shown in the Supporting Information (SI) [53], for a two-component system with $n_c = 2$, we can differentiate (or, formally, prolong [52]) Eq. (18) twice to obtain a system of PDEs where the commutativity of partial differentiation is guaranteed. However, since this system is overdetermined, a consistent solution to all equations may not exist, including those found after differentiating Eq. (18). Importantly, this means a solution for $\mathcal{E}$ generally may not exist, even when a full-rank solution for $\mathcal{T}$ can be found. If a solution of $\mathcal{E}$ can be found, we can use Eq. (18) to identify the form of $\mathcal{G}$ as:

$$\mathcal{G}^{\text{bulk}} = \mathcal{E} \cdot \mathbf{u}^{\text{bulk}} - \int \mathbf{u}^{\text{bulk}} \cdot d\mathcal{E}, \quad (19a)$$

$$\mathcal{G}^{(2,1)} = \left(\mathcal{E} \cdot \mathbf{u}^{(2,1)} - \frac{1}{2} \mathbf{E}^T \cdot \mathbf{u}^{(2,2)} \right), \quad (19b)$$

$$\mathcal{G}^{(2,2)} = \mathcal{E} \cdot \mathbf{u}^{(2,2)}, \quad (19c)$$

where $\mathbf{E} \equiv \partial_\rho \mathcal{E}$. In addition to solving Eq. (18), for Eq. (17) to provide a unique criterion that is distinct from Eq. (11), $\mathcal{G}^{\text{bulk}}$ must not be expressible solely in terms of the elements of $\mathbf{u}^{\text{bulk}}$, i.e., $\mathcal{G}^{\text{bulk}}$ must be functionally independent from the elements of $\mathbf{u}^{\text{bulk}}$ (more formally, $\mathcal{G}^{\text{bulk}}$ cannot factor through the elements of $\mathbf{u}^{\text{bulk}}$). For example, Eq. (17) is not distinct from Eq. (11) when every component of $\mathcal{E}$ is a constant (including zero) or when $\mathcal{E} = \mathbf{R} \cdot \mathbf{u}^{\text{bulk}}$ for some constant matrix $\mathbf{R}$, where $\mathcal{G}^{\text{bulk}}$ is respectively a linear and quadratic function of $\mathbf{u}^{\text{bulk}}$ in these cases.

For systems at equilibrium, $\mathbf{u}$ is simply the species chemical potentials and Eq. (15) reduces to the equilibrium Gibbs-Duhem relation with the Maxwell construction vector as the species densities, $\mathcal{E} = \rho$, and the pressure as the global quantity, $\mathcal{G} = P$. These solutions are indeed shown to be consistent with Eq. (18) in the SI [53]. We emphasize that while the mechanical interpretation of the global quantity is clear for systems at equilibrium, this may not always be the case out of equilibrium.

Our nonequilibrium multicomponent coexistence criteria are thus:

$$\mathbf{u}^{\text{bulk}}(\rho^\alpha) = \mathbf{u}^{\text{coexist}} \quad \forall \alpha \in \mathcal{P}, \quad (20a)$$

$$\mathcal{G}^{\text{bulk}}(\rho^\alpha) = \mathcal{G}^{\text{coexist}} \quad \forall \alpha \in \mathcal{P}, \quad (20b)$$

which can be expressed in alternate forms. We can recast Eq. (20b) as a generalized Maxwell equal-area construction with respect to $\mathcal{E}$:

$$\int_{\mathcal{E}^\alpha}^{\mathcal{E}^\beta} [\mathbf{u}^{\text{bulk}}(\mathcal{E}) - \mathbf{u}^{\text{coexist}}] \cdot d\mathcal{E} = 0 \quad \forall \alpha, \beta \in \mathcal{P}. \quad (21)$$

We can further replace $d\mathcal{E}$ with $\mathbf{E} \cdot d\rho$ to obtain the “weighted-

area” construction with respect to the species densities:

$$\int_{\rho^\alpha}^{\rho^\beta} [\mathbf{u}^{\text{bulk}}(\rho) - \mathbf{u}^{\text{coexist}}] \cdot \mathbf{E}(\rho) \cdot d\rho = 0 \quad \forall \alpha, \beta \in \mathcal{P}. \quad (22)$$

As shown in Section II A, one can derive the equilibrium coexistence criteria [Eq. (1)] by minimizing a free energy subject to the constraints of particle number and volume conservation. This results in the well-known common tangent construction. When every component of $\mathcal{E}$ is nonconstant, we can similarly express our criteria as a common tangent construction on an effective bulk free energy defined as $w^{\text{bulk}} \equiv \int \mathbf{u}^{\text{bulk}} \cdot d\mathcal{E}$. The common tangent construction on w^{bulk} is with respect to $\mathcal{E}$ and takes the form:

$$\mathbf{u}^{\text{coexist}} = \left. \frac{\partial w^{\text{bulk}}}{\partial \mathcal{E}} \right|_{\rho=\rho^\alpha} \quad \forall \alpha \in \mathcal{P}, \quad (23a)$$

$$\mathcal{G}^{\text{coexist}} = \mathbf{u}^{\text{coexist}} \cdot \mathcal{E}(\rho^\alpha) - w^{\text{bulk}}(\rho^\alpha) \quad \forall \alpha \in \mathcal{P}. \quad (23b)$$

While w^{bulk} can always be defined when every component of $\mathcal{E}$ is nonconstant, we emphasize that a solution to Eq. (18) for $\mathcal{E}$ does not guarantee one can define an effective free energy functional, $\mathcal{W}$, that the species pseudopotentials are derived from, $\mathbf{u} = \delta\mathcal{W}/\delta\mathcal{E}$. This can be trivially seen in the case where at least one component of $\mathcal{E}$ is constant or zero (Eq. (23) cannot be used as the coexistence criteria in these systems as well), however there are many systems where every element of $\mathcal{E}$ has a dependence on ρ but $\mathcal{W}$ still cannot be defined. In Appendix C, we derive the conditions for $\mathcal{W}$ to exist and demonstrate that the existence of $\mathcal{W}$ implies the existence of the generalized Gibbs-Duhem relation but that the converse is only true when $n_c = 1$.

Before concluding this Section, it is important to note that there are cases in which a full solution to $\mathcal{E}$ [from Eq. (18)] does not exist but approximate coexistence criteria can still be formulated. To see this, we first separately consider the bulk and interfacial contributions to the generalized Gibbs-Duhem relation and distinguish the Maxwell construction vectors that satisfy each relation with:

$$\mathcal{E}^{\text{bulk}} \cdot d\mathbf{u}^{\text{bulk}} = d\mathcal{G}^{\text{bulk}}, \quad (24a)$$

$$\mathcal{E}^{\text{int}} \cdot d\mathbf{u}^{\text{int}} = d\mathcal{G}^{\text{int}}. \quad (24b)$$

The global quantity is rigorously defined with Eq. (18) when $\mathcal{E} = \mathcal{E}^{\text{bulk}} = \mathcal{E}^{\text{int}}$. Then, the generalized Gibbs-Duhem relation holds and equality of $\mathcal{G}^{\text{bulk}}$ between coexisting phases is recovered. We now consider two approximations to equality of $\mathcal{G}^{\text{bulk}}$ [Eq. (20b)] when $\mathcal{E}^{\text{bulk}} \neq \mathcal{E}^{\text{int}}$, both of which rely on the existence of a $\mathcal{E}^{\text{int}}$ that satisfies Eq. (24b). When this is the case, as shown in Appendix D, the weighted-area construction (with $\mathbf{E} = \mathbf{E}^{\text{int}}$) [Eq. (22)] is no longer equal to the difference in $\mathcal{G}^{\text{bulk}}$ between phases and hence generally depends on the selected integration path. Notably, this construction vanishes if the integrals are performed along the path where the relationships between the species densities coincides with the full spatial solution of the coexisting densities, $\rho^c(z)$, which we initially set out to avoid determining. This constitutes the first approximation for the coexistence criteria corresponding to

equality of $\mathcal{G}^{\text{bulk}}$: the weighted-area construction [Eq. (22)] with $\mathbf{E} = \mathbf{E}^{\text{int}}$ allows one to approximate the coexistence densities, with the approximation gaining accuracy as the selected integration path approaches the actual coexistence profiles.

We can also introduce a second approximate criterion when $\mathcal{E}^{\text{bulk}} \neq \mathcal{E}^{\text{int}}$, now using the $\mathcal{E}^{\text{bulk}}$ that satisfies Eq. (24a). Defining the bulk contribution to the global quantity as $\mathcal{G}^{\text{bulk}} \equiv \mathcal{E}^{\text{bulk}} \cdot \mathbf{u}^{\text{bulk}} - \int \mathbf{u}^{\text{bulk}} \cdot d\mathcal{E}^{\text{bulk}}$, we arrive at our second approximation: equality of this $\mathcal{G}^{\text{bulk}}$ across phases [Eq. (20b)], or equivalently the weighted-area construction [Eq. (22)] with $\mathbf{E} = \mathbf{E}^{\text{bulk}}$. Equality of this $\mathcal{G}^{\text{bulk}}$ across phases is not guaranteed in these scenarios, as the weighted-area construction only vanishes along the path corresponding to the coexistence profiles when using $\mathbf{E} = \mathbf{E}^{\text{int}}$. However, the weighted-area construction using $\mathbf{E} = \mathbf{E}^{\text{bulk}}$ is path-independent, as its value is the difference in $\mathcal{G}^{\text{bulk}}$ across the phases being considered. This difference is generally unknown but can be expressed as (detailed in Appendix D):

$$\begin{aligned} \Delta^{\alpha\beta} \mathcal{G}^{\text{bulk}} &\equiv \mathcal{G}^\alpha - \mathcal{G}^\beta \\ &= \int_{\rho^\alpha}^{\rho^\beta} [\mathbf{u}^{\text{bulk}}(\rho^c) - \mathbf{u}^{\text{coexist}}] \cdot (\mathbf{E}^{\text{bulk}}(\rho^c) - \mathbf{E}^{\text{int}}(\rho^c)) \cdot d\rho^c, \end{aligned} \quad (25)$$

where the integrals are evaluated along the coexistence profiles, $\rho^c(z)$. Clearly, the approximation of equality of $\mathcal{G}^{\text{bulk}}$ across phases improves as the integrals in Eq. (25) decrease. Notably, the validity of this approximation is unalterable for a given system, as it depends on the value of the right-hand side of Eq. (25). This contrasts with the first approximation (the weighted-area construction with $\mathbf{E} = \mathbf{E}^{\text{int}}$), as its accuracy can be tuned by altering the selected integration path. A schematic of the above framework to obtain either the exact or approximate coexistence criteria is shown in Fig. 2.

III. GENERALIZED GIBBS PHASE RULE

For systems with exact coexistence criteria [Eq. (20)], it can be straightforwardly shown that the Gibbs phase rule holds. For a system with n_c species and n_p coexisting phases, we have $n_c n_p$ unknown species densities (n_c in each phase) and n_p unknown phase fractions. Our generalized coexistence criteria [Eq. (20)] result in a total of $(n_c + 1)(n_p - 1)$ equations that solely contain the $n_p n_c$ unknown densities (i.e., the phase fractions do not appear in these equations). We always have an additional equation, arising from volume conservation, that solely contains the phase fractions:

$$\sum_{\alpha}^{n_p} \phi^\alpha = 1, \quad (26a)$$

and an additional n_c equations that contain both the unknown densities and phase fractions, arising from particle number conservation:

$$\sum_{\alpha}^{n_p} \rho^\alpha \phi^\alpha = \rho^{\text{sys}}. \quad (26b)$$

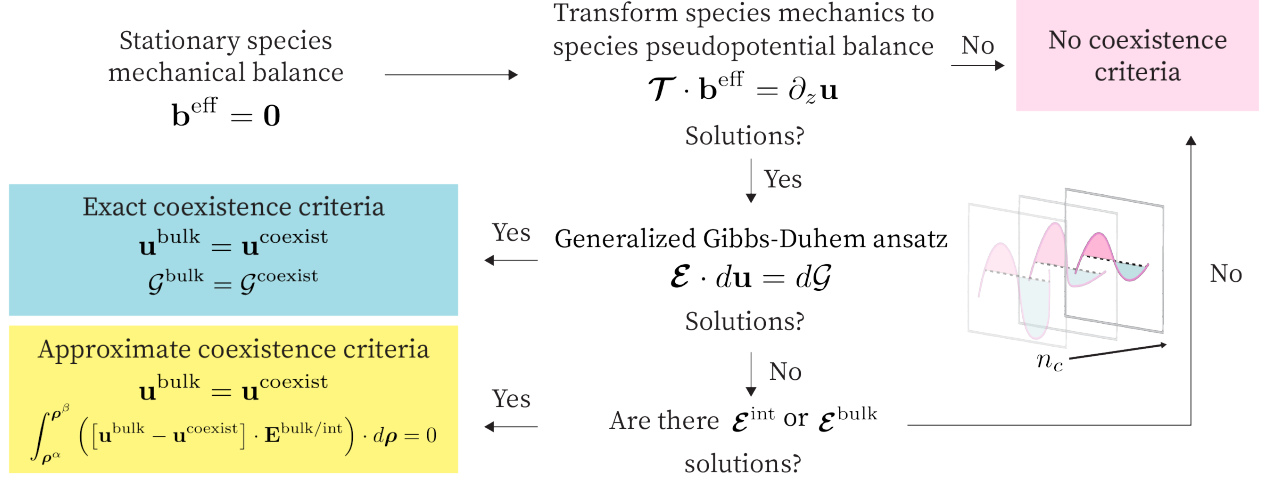


FIG. 2. A visual procedure to obtain the coexistence criteria for multicomponent nonequilibrium systems. First, determine the stationary species mechanical balance [Eq. (7)]. Next, transform the effective body forces to species pseudopotentials with the transformation tensor $\mathcal{T}$ [Eq. (12)]. Only proceed if solutions for $\mathcal{T}$ and $\mathbf{u}$ can be found. If so, identify the Maxwell construction vector, $\mathcal{E}$, used in the generalized Gibbs-Duhem relation [Eq. (15)]. If solutions for $\mathcal{E}$ and $\mathcal{G}$ can be found, we have exact coexistence criteria [Eq. (20)]. If $\mathcal{E}^{\text{bulk}} \neq \mathcal{E}^{\text{int}}$ but solutions for $\mathcal{E}^{\text{bulk}}$ and/or $\mathcal{E}^{\text{int}}$ can be found, we can approximate the coexistence criteria.

While at first glance, we have precisely the same number of equations as unknowns, we can gain insight by examining the precise dependencies of the state function criteria [Eq. (20)], volume conservation equation [Eq. (26a)], and particle conservation equations [Eq. (26b)]. We begin by subtracting the number of unknown species densities from the number of coexistence criteria that solely contain the species densities. We denote this quantity as the “degrees of freedom” [54], $n_{\text{dof}} = n_c - n_p + 1$. When $n_{\text{dof}} = 0$, the number of coexistence criteria is the same as the number of unknown species densities, allowing for the determination of the coexisting densities *without* referring to the conservation constraints [Eq. (26)]. The conservation constraints can then be used to determine the remaining unknowns, the phase fractions. This is known as the lever rule. In these scenarios, the independence of the constraints and the coexistence criteria indicates that the coexisting densities are *fixed and cannot be adjusted by altering the global constraints*. It is in this sense that the system has zero degrees of freedom.

The picture changes when $n_{\text{dof}} > 0$. Here, there are fewer coexistence criteria than the number of unknown densities, and the conservation constraints must be solved simultaneously with the coexistence criteria to obtain the unknown phase densities and phase fractions. In these scenarios, in contrast to $n_{\text{dof}} = 0$, the constraints on the global species densities *do* impact the coexisting densities.

Finally, when $n_{\text{dof}} < 0$, the number of coexistence criteria exceeds the number of unknown species densities while there are fewer conservation constraints than unknown phase fractions. Only in pathological cases can one solve the coexistence criteria for the species densities in each of the n_p phases, however, these cases can generally be accessed by tuning system-level control parameters. While the coexisting densities can be solved for in these pathological scenarios,

the conservation constraints are underspecified with respect to the phase fractions, and thus $|n_{\text{dof}}|$ phase fractions can be chosen arbitrarily while satisfying our coexistence criteria. This has the consequence that, in practice, one will always observe fewer than n_p phases (with finite phase fractions) simultaneously coexist as this reduces the overall interfacial area of the system. For example, in a single-component system, while a state of three phase coexistence can be predicted (a “triple point”), one of the phase fractions will always be zero to minimize the interfacial area, and two-phase coexistence will be the dominant form of coexistence that is observed. While these surface energy arguments may appear to not be extendable to active or nonequilibrium systems, it has been recently demonstrated that many active interfaces continue to exhibit interfacial area-minimizing statistics [55]. Indeed, systems that display macroscopic phase separation are invariably those with area-minimizing interfacial statistics! Therefore, in practice, the maximum number of coexisting phases that will be observed is simply $n_p^{\text{max}} = n_c + 1$.

In the event that an ensemble can be constructed in which any of the species pseudopotentials or the global quantity are fixed (corresponding to the semi-grand canonical ensemble or Gibbs ensemble in equilibrium, respectively), elements of ρ^{sys} are no longer fixed and the mean value of these elements must be solved for. At most, an additional n_c (the total number of elements of ρ^{sys}) number of unknowns can be generated through this hypothetical change of ensemble. If we denote the number of fixed potentials (which again consists of the species pseudopotentials and global quantity) as n_{fix} , the total number of degrees of freedom is now $n_{\text{dof}} = n_c - n_p + 1 - n_{\text{fix}}$. Thus, in equilibrium, fixing the pressure for a one-component system would result in $n_{\text{dof}} = 1 - n_p$, and hence it is practically impossible to observe two phase coexistence with non-zero phase fractions. If one fixes the pressure precisely at the

coexistence pressure, one will observe either of the two phases (with equal probability) but not both coexisting, as the presence of an interface is generally disfavored.

IV. REVISITING THE ONE-COMPONENT COEXISTENCE CRITERIA

Section II B makes clear that there are one-component systems where the coexistence theory in Refs. [17, 22, 38] does not immediately apply, as they considered systems where the species pseudopotential can be readily identified (in Ref. [17] u is the scalar potential g while in Ref. [22] u is the dynamic pressure $\mathcal{P}$). While these works successfully described macroscopic phase separation in a variety of active matter systems, there can be nonequilibrium systems where the effective body force has a form that prevents the immediate identification of u and consequently renders these systems outside the scope of the previously developed one-component coexistence theory. It was argued in Ref. [22] that the effective body force can always be integrated to define a dynamic pressure that is spatially constant in steady-states, $\mathcal{P} \equiv \int dz b^{\text{eff}}$, and that the bulk part of this dynamic pressure is always equal between coexisting phases. While one can always perform this integration, it will generally introduce nonlocal terms that cannot be well-approximated in a local gradient expansion. The utility of a dynamic pressure in a coexistence theory, where it acts as the species pseudopotential u , relies on $\mathcal{P}$ being a local function of ρ and its spatial gradients. We will now demonstrate that the species pseudopotential, which is a local function of ρ and its gradients, can always be obtained from the effective body force when $n_c = 1$. Furthermore, we provide the conditions for when a *local* dynamic pressure can be defined, i.e., when $u = \mathcal{P}$.

Consider the scalar ($n_c = 1$) version of the effective body force [Eq. (13)]. Substituting Eq. (13d) into Eq. (13c), differentiating and substituting the result into Eq. (13b), we arrive at a second-order ODE for $\mathcal{T}$ that solely contains the coefficients in the effective body-force:

$$2\mathcal{T}b^{(3,1)} = \frac{d}{d\rho} \left[\mathcal{T}b^{(3,2)} - \frac{d}{d\rho} (\mathcal{T}b^{(3,3)}) \right]. \quad (27)$$

This contrasts multicomponent systems where the equivalent condition is a system of PDEs that is not guaranteed to have a solution. Equation (27) can be solved for $\mathcal{T}$, allowing us to identify the one-component pseudopotential:

$$u^{\text{bulk}} = \int d\rho \mathcal{T}b^{(1,1)}, \quad (28a)$$

$$u^{(2,2)} = \mathcal{T}b^{(3,3)}, \quad (28b)$$

$$u^{(2,1)} = \frac{1}{2} \left[\mathcal{T}b^{(3,2)} - \frac{d}{d\rho} (\mathcal{T}b^{(3,3)}) \right]. \quad (28c)$$

Only when $\mathcal{T} = 1$ is the the dynamic pressure local with $u = \mathcal{P}$, requiring:

$$2b^{(3,1)} = \frac{d}{d\rho} b^{(3,2)} - \frac{d^2}{d\rho^2} b^{(3,3)}. \quad (29)$$

With an expression for u that is a local gradient expansion of the form considered in Refs. [17, 22, 38], one can subsequently apply the one-component coexistence theory developed in these works (which our theory in Section II B reduces to when $n_c = 1$ after including the above extension) to predict the phase diagram of these systems.

It may be counterintuitive that neither u nor $\mathcal{G}$ are necessarily mechanical quantities. Importantly, our coexistence criteria are always derived from the static mechanical balance of the system. The lack of a local, mechanical state function that is equal in coexisting phases simply means there are *non-local* effects in the dynamic pressure, $\mathcal{P} \equiv \int dz b^{\text{eff}}$, which must be spatially constant. Systems such as active Brownian particles [22] thus represent an exceptional case where this mechanical balance can be expressed as uniformity of a *local* dynamic pressure.

V. MECHANICS OF PASSIVE PAIRWISE INTERACTING SYSTEMS

All of our coexistence criteria follow from the species force densities. To demonstrate how to derive the form of the effective body force from microscopic considerations and that our theory recovers the known equilibrium criteria, we consider multicomponent passive systems with pairwise interactions. The static momentum balance for these systems is obtained through an Irving-Kirkwood [50] procedure with the z -component of the effective body force acting on species i taking the following *exact* form [53, 56]:

$$b_i^{\text{eff}}(z) = -k_B T \partial_z \rho_i(z) - \rho_i(z) \sum_j \int_V d\mathbf{x}' \rho_j(z') g_{ij}(z, z', \Delta x, \Delta y) F_{ij}(\Delta x, \Delta y, \Delta z). \quad (30)$$

The first term on the right-hand side arises from the single-body translational degrees of freedom of the particles. If expressed as a stress, this would be the “ideal gas” contribution to the stress. The second term arises from the pairwise particle interactions and, in principle, requires an integration over the entire system volume, V . The difference between the position we are integrating over and the position we seek to evaluate the body force at is represented by $\Delta x = x' - x$, $\Delta y = y' - y$, and $\Delta z = z' - z$. Here, $g_{ij}(z, z', \Delta x, \Delta y)$ is the pair distribution function which provides a measure of the likelihood of finding a particle of species j located at z' conditioned on a particle of species i is located at z . We note that the translational invariance in the x and y directions results in the pair distribution function only depending on Δx and Δy and hence the choice of x and y are arbitrary. $F_{ij}(\Delta x, \Delta y, \Delta z)$ is the z -component of the pairwise interaction force between particles i and j and solely depends on the relative positions. The integral in Eq. (30) thus represents the z -component of all interaction forces exerted on particles of species i located at z by all particles of species j .

The effective body force above is exact for pairwise interacting passive particles. Our task is now to formally expand

this expression up to third-order in spatial density gradients and explicitly identify the coefficients [see Eq. (8)] for this class of systems. We can then use the machinery developed in the previous Section to extract the multicomponent coexistence criteria and confirm that they are indeed identical to those obtained from bulk thermodynamics. The expansion of Eq. (30), formally performed in the SI [53, 57], involves a gradient expansion of the non-local densities [i.e., $\rho_j(z')$ appearing in Eq. (30)] and approximates the pair distribution functions of inhomogeneous systems using the pair distribution functions of homogeneous systems. The latter approximation is likely a source of error in our higher order expansion coefficients as there is no widely accepted microscopic theory for the pair distribution function of inhomogeneous fluids [58]. We note that we truncate the expansion (with respect to species densities) of the inhomogeneous pair distribution function at first-order, whereas we truncate the spatial expansions of the non-local species densities at third-order. Using our expansion, we obtain explicit forms for the coefficients of each b_i^{eff} in a passive pairwise interacting system:

$$b_{ij}^{(1,1)} = -k_B T \delta_{ij} - \rho_i \int d\mathbf{x}' \Delta z \left(F_{ij} g_{ij}^0 + \frac{1}{2} \sum_k^{n_c} F_{ik} \rho_k \frac{\partial g_{ik}^0}{\partial \rho_j} \right), \quad (31a)$$

$$b_{ijkl}^{(3,1)} \approx 0, \quad (31b)$$

$$b_{ijk}^{(3,2)} \approx \rho_i \int d\mathbf{x}' \frac{1}{4} (\Delta z)^3 \left(F_{ij} \frac{\partial g_{ij}^0}{\partial \rho_k} + F_{ik} \frac{\partial g_{ik}^0}{\partial \rho_j} \right), \quad (31c)$$

$$b_{ij}^{(3,3)} \approx \rho_i \int d\mathbf{x}' \frac{1}{6} (\Delta z)^3 \left(F_{ij} g_{ij}^0 + \frac{1}{2} \sum_k^{n_c} F_{ik} \rho_k \frac{\partial g_{ik}^0}{\partial \rho_j} \right), \quad (31d)$$

where $\rho_i \equiv \rho_i(z)$, $F_{ij} \equiv F_{ij}(\Delta x, \Delta y, \Delta z)$, and $g_{ij}^0 \equiv g_{ij}^0(\Delta x, \Delta y, \Delta z)$ is the pair distribution function of species i and j when the species densities are spatially uniform with values $\rho(z)$. We again emphasize that the nature of our approximation for our inhomogeneous pair distribution function likely introduces error in the third-order coefficients above.

The coefficients in Eq. (31) can be evaluated provided expressions for the pairwise interaction forces and a theory for the pair distribution function of homogeneous systems. While the precise values of these coefficients can vary dramatically for different systems, we recognize that *all passive systems* must have precisely the same coexistence criteria (see Section II A). These criteria must emerge from the specific *structure* of these coefficients. The nature of this structure can be best identified by noting that the body force coefficients are entirely consistent with the following effective body forces:

$$b_i^{\text{eff}} = -\rho_i \partial_z \mu_i, \quad (32a)$$

where:

$$\mu_i = \mu_i^{\text{bulk}} - \sum_j^{n_c} \sum_k^{n_c} \frac{1}{2} \frac{\partial \kappa_{ij}}{\partial \rho_k} \partial_z \rho_j \partial_z \rho_k - \sum_j^{n_c} \kappa_{ij} \partial_{zz}^2 \rho_j. \quad (32b)$$

This second-order expansion of the chemical potential is ob-

tained from $\mu_i = \delta \mathcal{F} / \delta \rho_i$ with:

$$\mathcal{F}[\rho(z)] = \int_V d\mathbf{x}' \left(f^{\text{bulk}} + \frac{1}{2} \sum_i^{n_c} \sum_j^{n_c} \kappa_{ij} \partial_z \rho_i \partial_z \rho_j \right). \quad (32c)$$

Here, κ_{ij} is symmetric with respect to the exchange of indices i and j (as any antisymmetric contributions are inconsequential). Furthermore, derivatives of the interfacial coefficient $\partial \kappa_{ij} / \partial \rho_k$ are symmetric under exchange of any pairs of the i, j , and k indices [51]. This variational form of the body force [Eq. (32a)] is consistent with the perspective of linear irreversible thermodynamics which posits that the direct force acting on particles of species i is simply $-\partial_z \mu_i$ [59]. Moreover, this form of the body force is entirely consistent with obtaining the thermodynamic pressure P upon summing all body forces with $\sum_i^{n_c} b_i^{\text{eff}} = -\partial_z P$ in accordance with both mechanics and the equilibrium Gibbs-Duhem relation [53].

Comparison of Eqs. (31) and (32) allows us to identify the following relations:

$$\frac{\partial \mu_i^{\text{bulk}}}{\partial \rho_j} = \frac{k_B T}{\rho_i} \delta_{ij} + \int d\mathbf{x}' (\Delta z) \left(F_{ij} g_{ij}^0 + \frac{1}{2} \sum_k^{n_c} F_{ik} \rho_k \frac{\partial g_{ik}^0}{\partial \rho_j} \right), \quad (33a)$$

$$\kappa_{ij} = - \int d\mathbf{x}' (\Delta z)^3 \frac{1}{6} \left(F_{ij} g_{ij}^0 + \frac{1}{2} \sum_k^{n_c} F_{ik} \rho_k \frac{\partial g_{ik}^0}{\partial \rho_j} \right), \quad (33b)$$

$$\frac{\partial \kappa_{ij}}{\partial \rho_k} = - \int d\mathbf{x}' (\Delta z)^3 \frac{1}{8} \left(F_{ij} \frac{\partial g_{ij}^0}{\partial \rho_k} + F_{ik} \frac{\partial g_{ik}^0}{\partial \rho_j} \right). \quad (33c)$$

We can compactly express the form of the body force coefficients of passive pairwise interacting systems as:

$$b_{ij}^{(1,1)} = -\rho_i \frac{\partial \mu_i^{\text{bulk}}}{\partial \rho_j}, \quad (34a)$$

$$b_{ijkl}^{(3,1)} = -\frac{1}{2} \rho_i \frac{\partial^2 \kappa_{ij}}{\partial \rho_k \partial \rho_l}, \quad (34b)$$

$$b_{ijk}^{(3,2)} = -2 \rho_i \frac{\partial \kappa_{ij}}{\partial \rho_k}, \quad (34c)$$

$$b_{ij}^{(3,3)} = -\rho_i \kappa_{ij}. \quad (34d)$$

Interestingly, comparison of Eqs. (31b) and (34b) indicates every component of the Hessian of every κ_{ij} must vanish. Truncating our expansion of the inhomogeneous pair distribution functions at first-order in derivatives with respect to the species densities appears to limit our theory to κ_{ij} coefficients that are constant or linear in the species densities.

While our theory cannot describe nonlinear κ_{ij} coefficients, the nature of our approximation does not appear to have impacted Eq. (33a). We recognize that $\partial \mu_i^{\text{bulk}} / \partial \rho_j$ comprises the Hessian matrix of the bulk free energy density with elements $H_{ij}^{\text{bulk}} = \partial \mu_i^{\text{bulk}} / \partial \rho_j = \partial^2 f^{\text{bulk}} / \partial \rho_i \partial \rho_j$. Equation (33a) thus offers *microscopic expressions* for bulk thermodynamic quantities. Intriguingly, our microscopic expressions for the Hessian (and κ_{ij}) directly involve the pairwise forces in addition to the structure, which is encoded through

g_{ij}^0 . This is in contrast to the more familiar microscopic expressions for these quantities, which simply include other measures of structure. In particular, the Hessian of the free energy can be obtained by examining the long wavelength behavior of elements of the multicomponent static structure factor tensor [60–62]. In the SI [53, 63], we verify the equivalency of the established expressions for the Hessian of the bulk free energy with our force-based expression [Eq. (33a)]. Additionally, we numerically verify that our (approximate) microscopic expression for κ_{ij} is indeed symmetric upon exchange of i and j for a model passive system.

With the structure of the body force coefficients identified, we are now poised to demonstrate the recovery of the equilibrium coexistence criteria. The effective body force is nearly in gradient form [see Eq. (32)] except for a factor of density outside the gradient, hence we immediately identify every element of the transformation tensor as $\mathcal{T}_{in} = -\delta_{in}(\rho_n)^{-1}$ and the species pseudopotentials as the chemical potentials with $u_i = \mu_i$. Substituting this into our identified system of PDEs [Eq. (13)], we indeed find that this satisfies our equations. We can further confirm that our body force coefficients in Eq. (31), which recover the equilibrium chemical potentials, also recover the thermodynamic pressure as the global quantity. We indeed find that $\mathcal{E} \sim \rho$ satisfies Eq. (18) and our global quantity is thus entirely consistent with the thermodynamic pressure and the equilibrium Gibbs-Duhem relation, $dP = \rho \cdot d\mu$. We can identify the forms of $\mathcal{G}^{\text{bulk}}$ (P^{bulk}) and $\mathcal{G}^{\text{int}}$ (P^{int}) as:

$$P^{\text{bulk}} = \sum_i^{n_c} \rho_i \mu_i^{\text{bulk}} - \int \mu_i^{\text{bulk}} d\rho_i, \quad (35a)$$

$$P^{\text{int}} = - \sum_i^{n_c} \sum_j^{n_c} \left[\sum_k^{n_c} \frac{1}{2} \left(\rho_i \frac{\partial \kappa_{ij}}{\partial \rho_k} - \kappa_{ij} \delta_{ik} \right) \partial_z \rho_j \partial_z \rho_k + \rho_i \kappa_{ij} \partial_{zz}^2 \rho_j \right]. \quad (35b)$$

As shown in the SI, the interfacial contribution to the pressure is a generalization of the one-component (and 1D) interfacial Korteweg stress [53, 64, 65]. We have also confirmed in the SI that our microscopic expression for the bulk thermodynamic pressure is indeed consistent with the generalization of the one-component virial theorem [51, 66].

VI. NONEQUILIBRIUM MODEL APPLICATION

To demonstrate the effectiveness of our theory, we introduce simple phenomenological nonequilibrium field theories as a testing platform. We can then compare the phase diagrams obtained by numerically solving for the complete spatial profiles of the species densities with those more simply obtained from our coexistence criteria.

Phenomenological continuum models for single-component density fields, such as Active Model B+ (AMB+) [14, 67–69], and multicomponent systems, such as the Nonreciprocal Cahn-Hilliard (NRCH) model [27, 28],

have been introduced to explore nonequilibrium nucleation, kinetics, and phase behavior. Here, we introduce Multicomponent Active Model B+ (MAMB+), which combines the more general structure of the interfacial terms in AMB+ (in comparison to the simpler Active Model B [14, 69]) with the multicomponent interactions of the NRCH model. In one dimension (this can be straightforwardly generalized), MAMB+ has the following dynamics for each of the n_c conserved scalar order-parameter fields, $\rho_i(z, t)$, at position z and time t [53]:

$$\partial_t \rho_i = -\partial_z J_i, \quad (36a)$$

$$J_i = \sum_j^{n_c} M_{ij} b_j^{\text{eff}}, \quad (36b)$$

$$b_j^{\text{eff}} = -\rho_j \left(\partial_z u_j^0 + \sum_k^{n_c} \eta_{jk}^N \partial_z \rho_k - \sum_k^{n_c} \sum_n^{n_c} \xi_{jkn}^A \partial_{zz}^2 \rho_k \partial_z \rho_n - \sum_k^{n_c} \sum_n^{n_c} \sum_m^{n_c} \theta_{jknm} \partial_z \rho_k \partial_z \rho_n \partial_z \rho_m \right), \quad (36c)$$

$$u_j^0 = \frac{\delta \mathcal{F}}{\delta \rho_j} + \tau_j^N - \sum_k^{n_c} \sum_n^{n_c} \lambda_{jkn} \partial_z \rho_k \partial_z \rho_n - \sum_k^{n_c} \pi_{jk}^{A'} \partial_{zz}^2 \rho_k, \quad (36d)$$

where J_i is, again, the density flux of species i in the z -direction. Here, we have proposed that J_i follows a linear transport relation in which a flux of species i is directly generated by the body force on species i and *indirectly* driven by the body forces on every other species. These fluxes and forces are coupled through a generally asymmetric mobility tensor with elements M_{ij} whose symmetric part is positive-definite. In addition to being Markovian, this form ensures that stationary states are force-free and fluxes act in the same direction as the effective body forces, $\sum_i^{n_c} J_i b_i^{\text{eff}} > 0$.

The proposed form of the body force consists of four distinct contributions. The first term resembles that of passive systems (recall $b_j^{\text{eff}} = -\rho_j \partial_z \mu_j$ for systems at equilibrium) with a key distinction that the defined species pseudopotentials cannot be obtained variationally. The next three terms are “non-gradient” that prevent the simple identification of the species pseudopotentials. Each η_{jk}^N captures first-order contributions to b_j^{eff} that cannot be integrated into the bulk portion of u_j^0 . The next two non-gradient contributions are third-order, the first coming from each ξ_{jkn}^A where $\xi_{jkn}^A = -\xi_{jnk}^A$. The final non-gradient contribution comes from each θ_{jknm} , which is symmetric under the exchange of the k , n , and m indices.

In the absence of the non-integrable body force terms, u_j^0 acts as the species pseudopotential which consists of four contributions. The first is variational, the functional derivative of a free energy $\mathcal{F}$ [see Eq. (32c)], which again is simply the chemical potential [see Eq. (32b)] of a passive system ($\mu_j \equiv \delta \mathcal{F} / \delta \rho_j$). The next three contributions are non-variational. τ_j^N captures contributions to u_j^0 that cannot be integrated into f^{bulk} while the next two terms capture second-order non-variational effects. For systems at equilibrium, the coefficients on the Laplacian and square-gradient terms are always related as both emerge from the functional differen-

tiation of the free energy. Here, each λ_{jkn} (which is symmetric under the exchange of k and n) breaks this relation. Finally, each $\pi_{jk}^{A'}$ captures broken symmetries (with respect to exchanging j and k and permuting the j , k , and n indices of the derivative $\partial\pi_{jk}^{A'}/\partial\rho_n$) that cannot be achieved at equilibrium.

In the SI [53], we demonstrate that the proposed form of MAMB+ captures all possible first and third-order gradient contributions to b_j^{eff} , and all possible bulk and second-order contributions to u_j^0 , while preserving clear limits in which gradient and passive dynamics are recovered. MAMB+ reduces to AMB+ [68, 69] when there is a single-component ($n_c = 1$). Introducing multiple chemical species provides additional avenues to achieve nonequilibrium systems in MAMB+. In AMB+, there is one parameter (analogous to our ξ) that breaks the gradient structure of b^{eff} , and one parameter (analogous to our λ) that breaks the variational structure of the would-be species pseudopotential, u^0 . For a single-component system in one spatial dimension and when ξ is a constant, λ can be redefined to include ξ such that the effective body force is always in gradient form. When $n_c > 1$ we can break the passive structure of the effective body forces and species pseudopotentials in more ways. Counting the number of unique, nonzero η_{jk}^N , ξ_{jkn}^A , and θ_{jknm} , we see that we have $\frac{n_c^4}{6} + n_c^3 + \frac{5}{6}n_c^2 - n_c$ terms that can break the gradient structure of the effective body forces. Performing the same counting for τ_j^N , λ_{jkn} , and $\pi_{jk}^{A'}$, we see that there are $\frac{1}{2}n_c^3 + n_c^2 + \frac{1}{2}n_c - 1$ terms that can break the variational structure of the species pseudopotentials. Additionally, contrasting the one-component case, MAMB+ is distinct from MAMB (defined as dynamics with every η_{jk}^N , ξ_{jkn}^A , and θ_{jknm} set to zero) in one spatial dimension with constant nonequilibrium coefficients if any ξ_{jkn}^A is nonzero. In Appendix E, we demonstrate that pairwise-interacting multicomponent systems will generally fall under the classification of MAMB+ unless a pathological relationship between their pair correlation functions is satisfied (which is the case in equilibrium). We then provide numerical evidence that this relationship is broken for a nonreciprocally-interacting system that phase-separates across a broad range of parameters [35], meaning the prediction of the phase diagram of this system requires the determination of a nontrivial (and possibly nonexistent) transformation tensor, $\mathcal{T}$, through Eq. (13).

For gradient dynamics, every η_{jk}^N , ξ_{jkn}^A , and θ_{jknm} are zero such that $\mathcal{T}_{ij} = -\rho_i^{-1}\delta_{ij}$ and $u_j = u_j^0$ solve Eq. (13) with $J_i = -\sum_j^{n_c} M_{ij}\rho_j\partial_z u_j$. Moreover, for passive systems, every τ_j^N , λ_{jkn} , and $\pi_{jk}^{A'}$ are zero, meaning the species pseudopotential is the chemical potential, $u_j^0 = \delta\mathcal{F}/\delta\rho_j$. In this limit, MAMB becomes Multicomponent Model B (MMB). Making any component of these nonequilibrium tensors nonzero breaks the passive structure, disallowing the definition of a global free energy.

For simplicity, we validate our theory using MAMB, where we can tune each τ_j^N , λ_{jkn} , and $\pi_{jk}^{A'}$ and only need to find $\mathcal{E}$ as the transformation tensor takes its passive form. We adopt

the following simple functional forms:

$$f^{\text{bulk}} = \sum_i^{n_c} \left(\frac{a_i}{2} \rho_i^2 + \frac{b_i}{4} \rho_i^4 + \frac{1}{2} \sum_j^{n_c} \chi_{ij}^S \rho_i \rho_j \right), \quad (37a)$$

$$\tau_i^N = \sum_j^{n_c} \chi_{ij}^A \rho_j, \quad (37b)$$

where f^{bulk} appears in the free energy functional [see Eq. (32c)], and χ_{ij}^S and χ_{ij}^A are symmetric and antisymmetric, respectively, upon exchange of i and j . We further assume that every a_i , b_i , χ_{ij}^S , χ_{ij}^A , λ_{jkn} , κ_{ij} , and $\pi_{ij}^{A'}$ are constant. It proves convenient to define $\bar{\kappa}_{ij} \equiv \kappa_{ij} + \pi_{ij}^{A'}$. Furthermore, we now focus on two-component systems with the two species denoted as A and B . To further simplify, we set $a_A = a_B = a$, $b_A = b_B = 1$, $\chi_{AA}^S = \chi_{BB}^S = 0$, $\chi_{AB}^S = \chi_{BA}^S = \chi$, $\chi_{AB}^A = -\chi_{BA}^A = \alpha$, and $\lambda_{Bkn} = 0 \ \forall k, n \in \{A, B\}$.

We derive $\mathcal{E}$ for the considered systems using the system of PDEs in Eq. (18), augmented with the derived compatibility conditions for a two-component system, as detailed in the SI [53]. First, we examine the coexistence criteria of the NRCH model, a subclass of MAMB where every λ_{jkn} is zero. Coexistence criteria have been recently proposed for this model when the parameters are constrained such that $\bar{\kappa}_{AB}(\chi - \alpha) = \bar{\kappa}_{BA}(\chi + \alpha)$ [29, 40, 41]. Interestingly, Frohoff *et al.* found that this choice of parameters allows the dynamics to be mapped to “spurious” gradient dynamics [70]. Here, we look to recover the corresponding coexistence criteria using the systematic formalism of our theory while extending the criteria to cases where $\bar{\kappa}_{AB}(\chi - \alpha) \neq \bar{\kappa}_{BA}(\chi + \alpha)$.

Using the procedure outlined in Section II B, $\mathcal{G}$ cannot be identified for arbitrary values of the remaining parameters. However, we can identify $\mathcal{E}^{\text{bulk}}$ and $\mathcal{E}^{\text{int}}$ (detailed in Appendix D):

$$\mathcal{E}^{\text{bulk}} = \left[\rho_A \ \frac{\chi + \alpha}{\chi - \alpha} \rho_B \right]^T, \quad (38a)$$

$$\mathcal{E}^{\text{int}} = \left[\rho_A \ \frac{\bar{\kappa}_{AB}}{\bar{\kappa}_{BA}} \rho_B \right]^T. \quad (38b)$$

If the coupling parameter ratio is satisfied, $\bar{\kappa}_{AB}(\chi - \alpha) = \bar{\kappa}_{BA}(\chi + \alpha)$, $\mathcal{E}^{\text{bulk}} = \mathcal{E}^{\text{int}}$ and the conditions in Eq. (20) are the exact coexistence criteria. It is in this restricted case that the coexistence criteria found using our theory reduce to those of Refs. [29, 40, 41] and the system has spurious gradient dynamics [41, 70]. If the coupling parameter ratio is not satisfied, $\bar{\kappa}_{AB}(\chi - \alpha) \neq \bar{\kappa}_{BA}(\chi + \alpha)$, the set of criteria corresponding to equality of $\mathcal{G}^{\text{bulk}}$ [Eq. (20b)] can be approximated by defining $\mathcal{G}^{\text{bulk}} \equiv \mathcal{E}^{\text{bulk}} \cdot \mathbf{u}^{\text{bulk}} - \int \mathbf{u}^{\text{bulk}} \cdot d\mathcal{E}^{\text{bulk}}$ and equating it across phases.

We now compare the phase diagrams predicted using our theory to those obtained from numerically determining the complete spatial profiles, $\rho_A^c(z)$ and $\rho_B^c(z)$. To obtain these profiles, we use the numerical scheme outlined in Refs. [53, 71–74]. Figure 3(a) and (b) displays the numerically determined coexistence densities for the NRCH model alongside those predicted using our theory. In Fig. 3(a), we find $\mathcal{E}^{\text{bulk}} = \mathcal{E}^{\text{int}}$ and hence we construct the predicted phase diagram using the exact criteria [Eq. (20)]. In Fig. 3(b), $\mathcal{E}^{\text{bulk}} \neq \mathcal{E}^{\text{int}}$ and

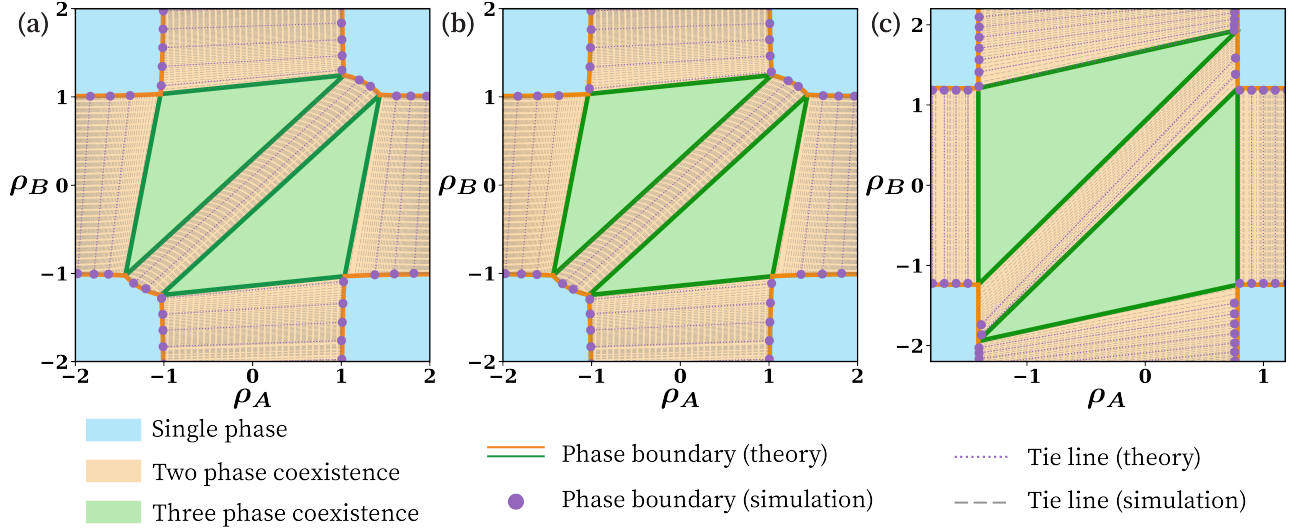


FIG. 3. Theoretical and numerical phase diagrams of the considered MAMB models. NRCH models with (a) $\bar{\kappa}_{AB}(\chi - \alpha) = \bar{\kappa}_{BA}(\chi + \alpha)$, where $\mathcal{E}^{\text{bulk}} = \mathcal{E}^{\text{int}}$ and (b) $\bar{\kappa}_{AB}(\chi - \alpha) \neq \bar{\kappa}_{BA}(\chi + \alpha)$, where $\mathcal{E}^{\text{bulk}} \neq \mathcal{E}^{\text{int}}$. For both (a) and (b) we set $a = -1$, $\chi = -0.5$, $\alpha = -0.2$, and $\bar{\kappa}_{AA} = \bar{\kappa}_{BB} = 1/(6\pi)$, with $\bar{\kappa}_{AB} = \bar{\kappa}_{BA} = 0$ for (a) and $\bar{\kappa}_{AB} = \bar{\kappa}_{BA} = 0.01/(6\pi)$ for (b). (c) A MAMB system which results in an $\mathcal{E}$ with nonlinear elements, achieved by introducing $\lambda_{AAA} = 0.01$, $\chi = -\alpha = -1$ with $a = -1.5$, $\bar{\kappa}_{AA} = \bar{\kappa}_{BB} = 1/8\pi$, and $\bar{\kappa}_{AB} = \bar{\kappa}_{BA} = \lambda_{AAB} = \lambda_{ABB} = \lambda_{ABA} = 0$.

we must approximate the criterion in Eq. (20b) by equating $\mathcal{G}^{\text{bulk}}$ (defined in terms of $\mathcal{E}^{\text{bulk}}$) across phases. We find excellent agreement between our theory and simulations, reproducing the two phase and three phase coexistence boundaries quantitatively for all parameters considered, including when $\bar{\kappa}_{AB}(\chi - \alpha) \neq \bar{\kappa}_{BA}(\chi + \alpha)$.

We can understand the high accuracy of the approximate criterion used in Fig. 3(b) by computing $\Delta^{\alpha\beta}\mathcal{G}^{\text{bulk}}$ [Eq. (25)]:

$$\Delta^{\alpha\beta}\mathcal{G}^{\text{bulk}} = \left(\frac{\chi + \alpha}{\chi - \alpha} - \frac{\bar{\kappa}_{AB}}{\bar{\kappa}_{BA}} \right) \int_{\rho_B^\alpha}^{\rho_B^\beta} [u_B^{\text{bulk}}(\rho^c) - u_B^{\text{coexist}}] d\rho_B^c \quad (39)$$

As shown in the SI [53], we find $\Delta^{\alpha\beta}\mathcal{G}^{\text{bulk}} \approx 0$ and hence equating $\mathcal{G}^{\text{bulk}}$ across phases works well as approximate criteria, as evidenced by the high accuracy of the predicted phase diagram in Fig. 3(b). Additionally, we provide further analysis of the path-dependence of our approximate coexistence criteria in the SI [53].

To further explore the robustness of our theory, we now explore systems in which the elements of the Maxwell construction vector contain nonlinear terms, contrasting with passive systems and systems following NRCH dynamics. We find that this is achieved by adjusting the model parameters to the following: $\chi = -\alpha$, $\lambda_{AAA} \neq 0$, $\bar{\kappa}_{AA} = \bar{\kappa}_{BB} \neq 0$, and the remaining elements of $\bar{\kappa}_{jk}$ λ_{jkn} set to zero. For these dynamics, we find the following generalized Maxwell construction vector:

$$\mathcal{E} = \left[\exp\left(\frac{2\lambda_{AAA}}{\bar{\kappa}_{AA}} \rho_A\right) \ 0 \right]^T, \quad (40)$$

which allows us to fully define $\mathcal{G}$. Using the coexistence criteria derived from this Maxwell construction vector, we con-

struct the phase diagram for this system using the exact criteria [Eq. (20)], shown in Fig. 3(c). The agreement between the theoretically predicted phase boundaries and those obtained numerically is once again excellent. Notably, the only system in Fig. 3 where an effective free energy can be defined is Fig. 3(a). It is clear that the theory developed in Section II B enables one to precisely determine the phase diagram solely using the derived state functions and coexistence criteria despite the absence of an effective free energy.

We note that the phase diagrams corresponding to the examined NRCH systems [Figs. 3(a) and (b)] have an inversion symmetry with respect to the two density fields ($\rho \rightarrow -\rho$). This symmetry is embedded in the species body forces corresponding to the NRCH model which is also invariant under $\rho \rightarrow -\rho$. This inversion symmetry with respect to the density fields is broken for the phase diagram of the MAMB system considered in Fig. 3(c) and is indeed consistent with the considered MAMB body force which does not impose this symmetry on the species density fields.

VII. DISCUSSION AND CONCLUSION

We have presented a theory for multicomponent coexistence rooted in mechanics that is applicable to both equilibrium and nonequilibrium systems. This theory outlines a procedure for converting the coupled species static mechanical balances into equality of bulk state functions that we term species “pseudopotentials”. Importantly, this step was previously missing from the one-component coexistence theory in Refs. [17, 22, 38], where the existence of a pseudopotential was assumed. At equilibrium, we have verified that these state functions are simply the species chemical potentials. More

generally, these species pseudopotentials can then be used to determine additional criteria in the form of either a generalized Maxwell construction or equality of a global quantity which becomes the pressure at equilibrium. Sometimes, the coexistence criteria can also be expressed as a generalized common tangent construction on a suitably defined bulk free energy. However, even when this is the case, oftentimes the pseudopotentials cannot be derived from an effective free energy functional. Crucially, while all coexisting phases at equilibrium satisfy equality of species chemical potentials and pressure regardless of the system details, this is not the case out of equilibrium. The functional forms of the species pseudopotentials and the global quantity directly follow from the details of the species mechanics, which, in general, cannot be determined variationally for nonequilibrium systems. To validate that our theory indeed reproduces the phase boundaries of nonequilibrium systems, we introduce the phenomenological Multicomponent Active Model B+ (MAMB+). By explicitly determining the full spatial profiles for several model systems (including some under the umbrella of the Nonreciprocal Cahn-Hilliard model), we numerically determined the phase boundaries and found excellent quantitative agreement with our theory.

Our mechanical theory rests on the determination of mechanical equations of state in the form of the effective body force coefficients. In passive systems, when the coexistence criteria are *always* equality of the species chemical potentials and pressure, a number of experimental and computational techniques have been developed to obtain the functional form of these equations of state. Experimental determination of the activity coefficients that characterize the non-ideal contributions to the chemical potential has a rich and long history for multicomponent fluids [75]. Moreover, several particle-based simulation techniques exist for probing these equations of state [76, 77]. The success of the synergy between theory, experiment, and computation in our understanding of multicomponent *equilibrium* phase behavior is evident in a number of disparate contexts. The development of theoretical, computational, and experimental approaches for determining the mechanical body force coefficients will be needed if a similar level of success is to be found *out of equilibrium*.

There are a number of theoretical tools for determining the body force coefficients required in our theory for nonequilibrium multicomponent coexistence, including the formal expansion of the exact form of the body force as determined through the Irving-Kirkwood procedure. Whether these theories can be validated or informed through experimental or computational investigations will be important for the practical implementation of this coexistence theory. One route to determining the coefficients may come through dynamical measurements. To that end, an indirect method to experimentally or computationally determine these mechanical coefficients may come through measuring the *flux* generated by sufficiently small values of $\mathbf{b}^{\text{eff}}$. By keeping the force small such that the functional form of $\mathbf{b}^{\text{eff}}$ is not altered, we expect the species fluxes to follow the constitutive relation $\mathbf{J} = \mathbf{M} \cdot \mathbf{b}^{\text{eff}} + \mathcal{O}([\mathbf{b}^{\text{eff}}]^3)$, where terms that are nonlinear in the driving force are $\mathcal{O}([\mathbf{b}^{\text{eff}}]^3)$. Using this constitutive relation,

we anticipate that the information encoded in dynamical measurements of the species fluxes will be useful in determining the required body force coefficients. One potential avenue to determine these coefficients is to perhaps leverage recent machine learning approaches for learning hydrodynamic equations of motion [78–80].

There remain a number of theoretical avenues to pursue. While our theory outlines a procedure for the determination of phase boundaries solely in terms of bulk equations of state, *solutions* for the species pseudopotentials and global quantity are not guaranteed. In the event that these functions cannot be determined analytically or numerically, the coexistence criteria cannot be cast as equality of state functions between phases. In some limiting cases when the species pseudopotentials can be found but the global quantity cannot be identified, approximate criteria can still be found in the form of a generalized Maxwell construction. Within our framework, there may be nonequilibrium systems that display macroscopic coexistence but with phase boundaries that cannot be determined from bulk equations of state alone, as shown in the SI [53]. Our theory does not yield bulk criteria that apply to every nonequilibrium coexistence scenario, and instead should be interpreted as a framework, applicable to every nonequilibrium system, that allows one to determine if bulk coexistence criteria exist and, if so, what they are. Understanding the nature of the class of nonequilibrium systems (perhaps using the structure of MAMB+) that elude our framework is the subject of ongoing work.

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Appendix A: Derivation of Criteria for Multicomponent Coexistence

1. Transformation Tensor

We look to derive the transformation tensor, $\mathcal{T}$, that can convert the per-species effective body forces into per-species pseudopotentials. We first explicitly write out the summations over the species for the expansion of $\mathbf{b}^{\text{eff}}$ [see Eq. (8)]:

$$b_i^{\text{eff}}(z) \approx b_i^{(1)} + b_i^{(3)}, \quad (\text{A1a})$$

where:

$$b_i^{(1)} = \sum_j^{n_c} b_{ij}^{(1,1)} \partial_z \rho_j, \quad (\text{A1b})$$

$$b_i^{(3)} = - \sum_j^{n_c} \sum_k^{n_c} \sum_l^{n_c} b_{ijkl}^{(3,1)} \partial_z \rho_j \partial_z \rho_k \partial_z \rho_l - \sum_j^{n_c} \sum_k^{n_c} b_{ijk}^{(3,2)} \partial_{zz}^2 \rho_j \partial_z \rho_k - \sum_j^{n_c} b_{ij}^{(3,3)} \partial_{zzz}^3 \rho_j. \quad (\text{A1c})$$

Notably, only the contributions to $b_{ijk}^{(3,1)}$ that are symmetric upon exchange of the j , k , and l indices will remain after triple contraction into a symmetric rank 3 tensor with components $\partial_z \rho_j \partial_z \rho_k \partial_z \rho_l$. We define $\mathbf{b}^{(3,1)}$ to satisfy this symmetry. Proceeding similarly for $\mathbf{u}$ [see Eq. (10)]:

$$u_n \approx u_n^{\text{bulk}} + u_n^{\text{int}}, \quad (\text{A2a})$$

where:

$$u_n^{\text{int}} = - \sum_j^{n_c} \sum_k^{n_c} u_{njk}^{(2,1)} \partial_z \rho_j \partial_z \rho_k - \sum_j^{n_c} u_{nj}^{(2,2)} \partial_{zz}^2 \rho_j. \quad (\text{A2b})$$

Here, we note that only the symmetric contributions to $u_{njk}^{(2,1)}$ upon exchange of j and k will contribute to the pseudopotential of species n , as these indices are contracted into a symmetric matrix with components $\partial_z \rho_j \partial_z \rho_k$. While the contraction with a symmetric tensor will ensure that any antisymmetric contributions to $u_{njk}^{(2,1)}$ will vanish, we nevertheless define $\mathbf{u}^{(2,1)}$ to satisfy this symmetry in order to reduce the number of unknown coefficients.

The transformation tensor, $\mathcal{T}$, and species pseudopotentials, $\mathbf{u}$, are defined to satisfy the relationship:

$$\sum_i^{n_c} \mathcal{T}_{ni} b_i^{\text{eff}} = \partial_z u_n. \quad (\text{A3})$$

We now aim to identify when this ansatz holds, and if so, what the components of $\mathcal{T}$ and $\mathbf{u}$ are.

Differentiating u_n in the z -direction we have:

$$\begin{aligned} \partial_z u_n = & \sum_j^{n_c} \frac{\partial u_n^{\text{bulk}}}{\partial \rho_j} \partial_z \rho_j - \sum_j^{n_c} \sum_k^{n_c} \sum_l^{n_c} \frac{\partial u_{njk}^{(2,1)}}{\partial \rho_l} \partial_z \rho_j \partial_z \rho_k \partial_z \rho_l \\ & - \sum_j^{n_c} \sum_k^{n_c} \left(\frac{\partial u_{nj}^{(2,2)}}{\partial \rho_k} + 2u_{njk}^{(2,1)} \right) \partial_{zz}^2 \rho_j \partial_z \rho_k \\ & - \sum_j^{n_c} u_{nj}^{(2,2)} \partial_{zzz}^3 \rho_j, \end{aligned} \quad (\text{A4})$$

where we again note that only the contributions to $\partial u_{njk}^{(2,1)} / \partial \rho_l$ that are symmetric upon the exchange of indices j , k and l will contribute to $\partial_z u_n$. Substituting the forms of b_i^{eff} and $\partial_z u_n$ into Eq. (A3), we identify the following relations that must

hold for $\mathcal{T}$ and $\mathbf{u}$ to satisfy Eq. (A3):

$$\sum_i^{n_c} \mathcal{T}_{ni} b_{ij}^{(1,1)} = \frac{\partial u_n^{\text{bulk}}}{\partial \rho_j} \quad \forall n, j \in \mathcal{C}, \quad (\text{A5a})$$

$$\sum_i^{n_c} \mathcal{T}_{ni} b_{ijkl}^{(3,1)} = \left[\frac{\partial u_{njk}^{(2,1)}}{\partial \rho_l} \right]^{S_{jkl}} \quad \forall n, j, k, l \in \mathcal{C}, \quad (\text{A5b})$$

$$\sum_i^{n_c} \mathcal{T}_{ni} b_{ijk}^{(3,2)} = \frac{\partial u_{nj}^{(2,2)}}{\partial \rho_k} + 2u_{njk}^{(2,1)} \quad \forall n, j, k \in \mathcal{C}, \quad (\text{A5c})$$

$$\sum_i^{n_c} \frac{\partial}{\partial \rho_k} \left(\mathcal{T}_{ni} b_{ij}^{(3,3)} \right) = \frac{\partial u_{nj}^{(2,2)}}{\partial \rho_k} \quad \forall n, j, k \in \mathcal{C}, \quad (\text{A5d})$$

where the superscript S_{jkl} denotes the symmetry of permuting the indices j , k , l . For example, $[A_{ijkl}]^{S_{jkl}} \equiv \frac{1}{6}(A_{ijkl} + A_{ijlk} + A_{ikjl} + A_{iklj} + A_{iljk} + A_{ilkj})$. From the system of partial different equations presented in Eq. (A5), we see that there are $n_c^2 + 2n_c^3 + \frac{1}{6}n_c^2(n_c + 1)(n_c + 2)$ equations for $n_c + 2n_c^2 + \frac{1}{2}n_c^2(n_c + 1)$ variables (elements of both the transformation tensor and species pseudopotentials) and hence this system of PDEs is overdetermined.

We look to combine Eq. (A5) to find equations for the elements $\mathcal{T}_{ni}$ solely in terms of the known body force coefficients, i.e., eliminating the species pseudopotential coefficients from Eq. (A5). However, one must ensure the commutativity of partial differentiation with respect to the species densities, something that is generally not guaranteed. Given forms for the coefficients in the effective body forces, one can generally differentiate Eq. (A5) to obtain compatibility conditions (equations that must be satisfied to ensure the commutativity of partial differentiation). This process, known as completion to involution [52], depends on the form of the effective body forces and the number of species, and hence we cannot perform it generally. Here, we only demonstrate how to eliminate the species pseudopotential coefficients from the equations in Eq. (A5), noting that any solution to the following combined equations can be subsequently checked to see if partial differentiation is commutative.

We first examine Eq. (A5a), where differentiation with respect to ρ_k results in $\partial^2 u_n^{\text{bulk}} / \partial \rho_k \partial \rho_j$ which must be symmetric with respect to exchange of indices j and k . This symmetry allows us to identify the first relation that $\mathcal{T}_{ni}$ must satisfy:

$$\begin{aligned} \sum_i^{n_c} \left[\frac{\partial \mathcal{T}_{ni} b_{ij}^{(1,1)}}{\partial \rho_k} - \frac{\partial \mathcal{T}_{ni} b_{ik}^{(1,1)}}{\partial \rho_j} \right. \\ \left. + \mathcal{T}_{ni} \frac{\partial b_{ij}^{(1,1)}}{\partial \rho_k} - \mathcal{T}_{ni} \frac{\partial b_{ik}^{(1,1)}}{\partial \rho_j} \right] = 0 \quad \forall n, j, k \in \mathcal{C}. \end{aligned} \quad (\text{A6})$$

Next, we note $u_{njk}^{(2,1)} = u_{njk}^{(2,1)} \quad \forall n, j, k \in \mathcal{C}$ and hence:

$$\begin{aligned} \sum_i^{n_c} \left[\mathcal{T}_{ni} b_{ijk}^{(3,2)} - \mathcal{T}_{ni} b_{ikj}^{(3,2)} - \frac{\partial \mathcal{T}_{ni} b_{ij}^{(3,3)}}{\partial \rho_k} + \frac{\partial \mathcal{T}_{ni} b_{ik}^{(3,3)}}{\partial \rho_j} \right. \\ \left. - \mathcal{T}_{ni} \frac{\partial b_{ij}^{(3,3)}}{\partial \rho_k} + \mathcal{T}_{ni} \frac{\partial b_{ik}^{(3,3)}}{\partial \rho_j} \right] = 0 \quad \forall n, j, k \in \mathcal{C}. \end{aligned} \quad (\text{A7})$$

Lastly, we find an additional condition by differentiating Eqs. (A5c) and (A5d) and subsequently combining the resulting relations with Eq. (A5b) to obtain:

$$\sum_i^{n_c} \left[6\mathcal{T}_{ni}b_{ijkl}^{(3,1)} - \frac{\partial}{\partial \rho_l}(\mathcal{T}_{ni}b_{ijk}^{(3,2)}) - \frac{\partial}{\partial \rho_k}(\mathcal{T}_{ni}b_{ijl}^{(3,2)}) - \frac{\partial}{\partial \rho_j}(\mathcal{T}_{ni}b_{ilk}^{(3,2)}) + 2\frac{\partial^2}{\partial \rho_k \partial \rho_l}(\mathcal{T}_{ni}b_{ij}^{(3,3)}) + \frac{\partial^2}{\partial \rho_k \partial \rho_j}(\mathcal{T}_{ni}b_{il}^{(3,3)}) \right] = 0 \quad \forall n, j, k, l \in \mathcal{C}. \quad (\text{A8})$$

We emphasize that the system of partial differential equations in Eqs. (A6), (A7), and (A8) does not contain all of the compatibility conditions necessary to ensure the commutativity of partial differentiation. As an example of the process used to ensure this commutativity, we perform the procedure for the system of PDEs for $\mathcal{E}$ and $\mathcal{G}$ (described in the next Section) when $n_c = 2$ in the SI [53].

2. Maxwell Construction Vector

We look to derive the Maxwell construction vector $\mathcal{E}$ that defines the generalized multicomponent Gibbs-Duhem relation. Explicitly writing the summations over the species densities, the expansion of the global quantity, $\mathcal{G}$, reads:

$$\mathcal{G} \approx \mathcal{G}^{\text{bulk}} + \mathcal{G}^{\text{int}}, \quad (\text{A9a})$$

where:

$$\mathcal{G}^{\text{int}} = - \sum_j^{n_c} \sum_k^{n_c} \mathcal{G}_{jk}^{(2,1)} \partial_z \rho_j \partial_z \rho_k - \sum_j^{n_c} \mathcal{G}_j^{(2,2)} \partial_{zz}^2 \rho_j. \quad (\text{A9b})$$

Here, we again note that only contributions to $\mathcal{G}_{jk}^{(2,1)}$ that are symmetric upon the exchange of the j and k indices will remain after contraction into the symmetric matrix with components $\partial_z \rho_j \partial_z \rho_k$.

The Maxwell construction vector and the global quantity are defined to satisfy the generalized multicomponent Gibbs-Duhem relation:

$$\sum_i^{n_c} \mathcal{E}_i du_i = d\mathcal{G}. \quad (\text{A10})$$

The explicit expansion of the species pseudopotentials, $\mathbf{u}$, can be found in Eq. (A2). We now aim to identify when the generalized Gibbs-Duhem relation holds, and when the relation does hold, what $\mathcal{G}$ and the components of $\mathcal{E}$ are.

Differentiating $\mathcal{G}$ in the z -direction we have:

$$\begin{aligned} \partial_z \mathcal{G} = & \sum_j^{n_c} \frac{\partial \mathcal{G}^{\text{bulk}}}{\partial \rho_j} \partial_z \rho_j - \sum_j^{n_c} \sum_k^{n_c} \sum_l^{n_c} \frac{\partial \mathcal{G}_{jk}^{(2,1)}}{\partial \rho_l} \partial_z \rho_j \partial_z \rho_k \partial_z \rho_l \\ & - \sum_j^{n_c} \sum_k^{n_c} \left(\frac{\partial \mathcal{G}_j^{(2,2)}}{\partial \rho_k} + 2\mathcal{G}_{jk}^{(2,1)} \right) \partial_{zz}^2 \rho_j \partial_z \rho_k \\ & - \sum_j^{n_c} \mathcal{G}_j^{(2,2)} \partial_{zzz}^3 \rho_j, \quad (\text{A11}) \end{aligned}$$

where we again note that only the contributions to $\partial \mathcal{G}_{jk}^{(2,1)} / \partial \rho_l$ that are symmetric upon the exchange of the indices j, k and l will remain after contraction into the symmetric matrix with components $\partial_z \rho_j \partial_z \rho_k \partial_z \rho_l$. Substituting $\partial_z u_i$ [Eq. (A4)] and $\partial_z \mathcal{G}$ [Eq. (A11)] into Eq. (A10), we identify the following relations that must be satisfied for Eq. (A10) to hold:

$$\sum_i^{n_c} \mathcal{E}_i \frac{\partial u_i^{\text{bulk}}}{\partial \rho_j} = \frac{\partial \mathcal{G}^{\text{bulk}}}{\partial \rho_j} \quad \forall j \in \mathcal{C}, \quad (\text{A12a})$$

$$\sum_i^{n_c} \frac{\partial}{\partial \rho_k} (\mathcal{E}_i u_{ij}^{(2,2)}) = \frac{\partial \mathcal{G}_j^{(2,2)}}{\partial \rho_k} \quad \forall j, k \in \mathcal{C}, \quad (\text{A12b})$$

$$\sum_i^{n_c} \mathcal{E}_i \left(2u_{ijk}^{(2,1)} + \frac{\partial u_{ij}^{(2,2)}}{\partial \rho_k} \right) = 2\mathcal{G}_{jk}^{(2,1)} + \frac{\partial \mathcal{G}_j^{(2,2)}}{\partial \rho_k} \quad \forall j, k \in \mathcal{C}, \quad (\text{A12c})$$

$$\sum_i^{n_c} \mathcal{E}_i \left[\frac{\partial u_{ijk}^{(2,1)}}{\partial \rho_l} \right]^{S_{jkl}} = \left[\frac{\partial \mathcal{G}_{jk}^{(2,1)}}{\partial \rho_l} \right]^{S_{jkl}} \quad \forall j, k, l \in \mathcal{C}. \quad (\text{A12d})$$

From the system of PDEs in Eq. (A12), we see that there are $n_c + 2n_c^2 + \frac{1}{6}n_c(n_c + 1)(n_c + 2)$ equations for $1 + 2n_c + \frac{1}{2}n_c(n_c + 1)$ variables (elements of both the Maxwell construction vector and the global quantity) and hence this system of PDEs is overdetermined.

We look to express Eq. (A12) solely in terms of the known coefficients of the species pseudopotentials, i.e. eliminating the coefficients in $\mathcal{G}$ from the equations by differentiating and combining the relations presented in Eq. (A12). As was the case for $\mathcal{T}$, an $\mathcal{E}$ that satisfies this system of PDEs is not guaranteed to respect the commutativity of partial differentiation. Here, we demonstrate how to eliminate the coefficients in $\mathcal{G}$ from the equations in Eq. (A12) for any number of species. Solutions to these equations can subsequently be checked to see if they respect the commutativity of partial differentiation. In the SI [53], we explicitly differentiate (prolong) the system of PDEs in Eq. (A12) when $n_c = 2$ to obtain the compatibility conditions that ensure partial differentiation with respect to the species densities is commutative (involutive).

We first identify the relationships required to determine the bulk contribution to the Maxwell construction vector from Eq. (A12a). Notably, the Hessian of $\mathcal{G}^{\text{bulk}}$ must be symmetric, $\partial^2 \mathcal{G}^{\text{bulk}} / \partial \rho_j \partial \rho_k = \partial^2 \mathcal{G}^{\text{bulk}} / \partial \rho_k \partial \rho_j$, yielding the relationship:

$$\sum_i^{n_c} \left[E_{ij} \frac{\partial u_i^{\text{bulk}}}{\partial \rho_k} - E_{ik} \frac{\partial u_i^{\text{bulk}}}{\partial \rho_j} \right] = 0 \quad \forall j, k \in \mathcal{C}, \quad (\text{A13})$$

where $E_{ij} \equiv \partial \mathcal{E}_i / \partial \rho_j$. Additionally, $\mathcal{G}_{jk}^{(2,1)}$ must be symmetric with respect to exchanging j and k :

$$\sum_i^{n_c} \left[u_{ij}^{(2,2)} E_{ik} - u_{ik}^{(2,2)} E_{ij} \right] = 0 \quad \forall j, k \in \mathcal{C}. \quad (\text{A14})$$

Lastly, we find a set of equations by differentiating Eqs. (A12b) and (A12c) and combining them with

Eq. (A12d):

$$\sum_i^{n_c} \left[2E_{il}u_{ijk}^{(2,1)} + 2E_{ik}u_{ijl}^{(2,1)} + 2E_{ij}u_{ilk}^{(2,1)} - \frac{\partial}{\partial \rho_l}(E_{ik}u_{ij}^{(2,2)}) - \frac{\partial}{\partial \rho_k}(E_{il}u_{ij}^{(2,2)}) - \frac{\partial}{\partial \rho_j}(E_{ik}u_{il}^{(2,2)}) \right] = 0 \quad \forall j, k, l \in \mathcal{C}. \quad (\text{A15})$$

Appendix B: Impact of Additive and Multiplicative Constants on Coexistence Criteria

Here, we show that both $\mathcal{T}$ and $\mathcal{E}$ only need to be determined up to certain multiplicative/additive constants. From Eq. (12), it is clear that introducing a global multiplicative constant c into the transformation tensor, $\mathcal{T} \rightarrow c\mathcal{T}$, does not affect the coexistence criteria as the species pseudopotentials may be suitably redefined, $\mathbf{u} \rightarrow c\mathbf{u}$. Moreover, contracting the transformation tensor with a diagonal matrix of constants only acts to rescale the species pseudopotentials, leaving the conditions of spatially uniform species pseudopotentials unchanged. To see this, we express the transformation tensor as $\mathcal{T} = \mathbf{A} \cdot \tilde{\mathcal{T}}$, i.e., as the product of a diagonal matrix of constants, $\mathbf{A}$, contracted into a bare transformation tensor, $\tilde{\mathcal{T}}$. Substituting this into Eq. (12) and multiplying each side by the inverse of $\mathbf{A}$, $\mathbf{A}^{-1}$, we find $\tilde{\mathcal{T}} \cdot \mathbf{b}^{\text{eff}} = \mathbf{A}^{-1} \cdot \partial_z \mathbf{u}$. As $\mathbf{A}$ (and consequently its inverse) is constant and diagonal, we see that we can define rescaled pseudopotentials, $\mathbf{A}^{-1} \cdot \partial_z \mathbf{u} = \partial_z \tilde{\mathbf{u}}$, such that $\tilde{\mathcal{T}} \cdot \mathbf{b}^{\text{eff}} = \partial_z \tilde{\mathbf{u}}$. We then see that using the bare transformation tensor, $\tilde{\mathcal{T}}$, and the transformation tensor contracted with a diagonal matrix of constants, $\mathcal{T}$, result in the same species pseudopotentials up to a multiplicative factor, and hence $\mathbf{u} = \mathbf{u}^{\text{coexist}}$ and $\tilde{\mathbf{u}} = \tilde{\mathbf{u}}^{\text{coexist}}$ are equivalent steady-state conditions. This has the effect that one may always introduce an arbitrary multiplicative constant into the species pseudopotentials without affecting the coexistence criteria.

It is also clear from the generalized Maxwell construction [Eq. (21)] that additive constants to the elements of $\mathcal{E}$ are inconsequential. Additionally, re-scaling each element of $\mathcal{E}$ by a constant also does not impact Eq. (21). As a result, the coexistence criteria resulting from $\mathcal{E}$ and $a\mathcal{E} + \mathbf{c}$ (where a is a constant and $\mathbf{c}$ is a vector of constants whose elements need not be identical) will yield identical results.

Appendix C: Existence of Effective Free Energy

In this Appendix, we derive the conditions for the pseudopotentials to be the functional derivative of an effective free energy functional:

$$\mathbf{u} = \frac{\delta \mathcal{W}}{\delta \mathcal{E}}, \quad (\text{C1a})$$

where

$$\mathcal{W}[\rho(z)] = \int_V d\mathbf{r} \left(w^{\text{bulk}} + \frac{1}{2} \mathbf{w}^{(2,1)} : \partial_z \rho \partial_z \rho \right). \quad (\text{C1b})$$

Here, w^{bulk} is the bulk effective free energy and $\mathbf{w}^{(2,1)}$ is a symmetric matrix parameterizing interfacial contributions to the effective free energy. Given that each component of $\mathcal{E}$ is an entirely local state function of $\mathbf{X}$, the chain rule for functional differentiation yields a simple, equivalent form of $\mathbf{u} = \delta \mathcal{W} / \delta \mathcal{E}$:

$$\mathbf{u} = \frac{\delta \mathcal{W}}{\delta \rho} \cdot \mathbf{E}^{-1}, \quad (\text{C1c})$$

which will be the more straightforward form to work with. Both Eqs. (C1a) and (C1c) require $\mathcal{E}$ to exist and every component to be nonconstant. Moreover, Eq. (C1c) requires $\mathbf{E}$ to be invertible, which is slightly more restrictive than every component of $\mathcal{E}$ being nonconstant.

To proceed, we contract Eq. (C1c) with $\mathbf{E}$ to obtain $\mathbf{u} \cdot \mathbf{E} = \delta \mathcal{W} / \delta \rho$. Evaluating the functional derivative of $\mathcal{W}$ explicitly writing summations, we have:

$$\sum_i^{n_c} u_i E_{ij} = \frac{\partial w^{\text{bulk}}}{\partial \rho_j} - \sum_k^{n_c} w_{jk}^{(2,1)} \partial_{zz}^2 \rho_k - \sum_k^{n_c} \sum_l^{n_c} \left[\frac{\partial w_{jk}^{(2,1)}}{\partial \rho_l} - \frac{1}{2} \frac{\partial w_{kl}^{(2,1)}}{\partial \rho_j} \right]^{S_{kl}} \partial_z \rho_k \partial_z \rho_l \quad \forall j \in \mathcal{C}, \quad (\text{C2})$$

where the S_{kl} superscript extracts the symmetric (with respect to exchanging k and l) portion of a matrix. Substituting the expansion for each u_i [Eq. (A2)] and matching terms, we find:

$$\sum_i^{n_c} u_i^{\text{bulk}} E_{ij} = \frac{\partial w^{\text{bulk}}}{\partial \rho_j}, \quad (\text{C3a})$$

$$\sum_i^{n_c} u_{ik}^{(2,2)} E_{ij} = w_{jk}^{(2,1)}, \quad (\text{C3b})$$

$$2 \sum_i^{n_c} u_{ikl}^{(2,1)} E_{ij} = \frac{\partial w_{jk}^{(2,1)}}{\partial \rho_l} + \frac{\partial w_{jl}^{(2,1)}}{\partial \rho_k} - \frac{\partial w_{kl}^{(2,1)}}{\partial \rho_j}. \quad (\text{C3c})$$

Substituting these definitions into Eq. (C1b) and mandating translational invariance of the effective free energy functional (i.e., $\delta \mathcal{W} = 0$ for the transformation $z \rightarrow z + \delta z$, where δz is a constant), we recover the generalized Gibbs-Duhem relation, just as one can recover the equilibrium Gibbs-Duhem relation by mandating translational invariance of an equilibrium free energy functional [81–83]. It is then apparent that the generalized Gibbs-Duhem relation holds if the effective free energy exists. However, it is not clear if the converse is true (with the condition that $\mathbf{E}$ must be invertible).

We first consider the bulk equation [Eq. (C3a)], finding $u_i^{\text{bulk}} = \partial w^{\text{bulk}} / \partial \mathcal{E}_i$. For the Hessian of w^{bulk} to be symmetric, we must have:

$$\sum_i^{n_c} \left[E_{ij} \frac{\partial u_i^{\text{bulk}}}{\partial \rho_k} - E_{ik} \frac{\partial u_i^{\text{bulk}}}{\partial \rho_j} \right] = 0 \quad \forall j, k \in \mathcal{C}, \quad (\text{C4})$$

which is identical to Eq. (A13). As $\partial_\rho \mathcal{G}^{\text{bulk}} = \mathcal{E} \cdot \partial_\rho \mathbf{u}^{\text{bulk}}$ from the generalized Gibbs-Duhem relation [Eq. (A10)] and consequently Eq. (A12a), Eq. (C3a) implies $\mathcal{G}^{\text{bulk}} = \mathcal{E} \cdot \mathbf{u}^{\text{bulk}} -$

w^{bulk} . This confirms that our coexistence criteria are indeed consistent with a common tangent construction on w^{bulk} with respect to $\mathcal{E}$ [Eq. (23)].

We next consider the interfacial equations [Eqs. (C3b) and (C3c)]. Noting $w_{jk}^{(2,1)} = w_{kj}^{(2,1)}$, we find a relationship identical to Eq. (A14)

$$\sum_i^{n_c} \left[u_{ij}^{(2,2)} E_{ik} - u_{ik}^{(2,2)} E_{ij} \right] = 0 \quad \forall j, k \in \mathcal{C}. \quad (\text{C5})$$

To find our last relationship, we substitute Eq. (C3b) into Eq. (C3c):

$$2 \sum_i^{n_c} u_{ikl}^{(2,1)} E_{ij} = \frac{\partial}{\partial \rho_l} \left(u_{ik}^{(2,2)} E_{ij} \right) + \frac{\partial}{\partial \rho_k} \left(u_{il}^{(2,2)} E_{ij} \right) - \frac{\partial}{\partial \rho_j} \left(u_{il}^{(2,2)} E_{ik} \right). \quad (\text{C6})$$

As $u_{ikl}^{(2,1)} = u_{ilk}^{(2,1)} \quad \forall i, k, l \in \mathcal{C}$, we have $n_c^2(n_c + 1)/2$ equations in Eq. (C6). Notably, summing over unique triplets of j , k , and l we find $n_c(n_c + 1)(n_c + 2)/6$ equations identical to Eq. (A15):

$$\sum_i^{n_c} \left[2E_{il}u_{ijk}^{(2,1)} + 2E_{ik}u_{ijl}^{(2,1)} + 2E_{ij}u_{ilk}^{(2,1)} - \frac{\partial}{\partial \rho_l} (E_{ik}u_{ij}^{(2,2)}) - \frac{\partial}{\partial \rho_k} (E_{il}u_{ij}^{(2,2)}) - \frac{\partial}{\partial \rho_j} (E_{ik}u_{il}^{(2,2)}) \right] = 0 \quad \forall j, k, l \in \mathcal{C}. \quad (\text{C7})$$

We again recover that the existence of an effective free energy implies the generalized Gibbs-Duhem, however we see that the converse is not true. Equation (C6) contains $(n_c^3 - n_c)/3$ more equations than Eq. (C7), meaning there are more conditions that need to be satisfied for an effective free energy [Eq. (C1)] to exist than the generalized Gibbs-Duhem relation [Eq. (A10)] except for in single-component systems where $\mathcal{W}$ can always be defined (as was shown in Ref. [17]). In fact, as the number of components increases, one can have an exact coexistence theory with a well-defined generalized Gibbs-Duhem relation and the existence of an effective free energy is increasing less likely. It is therefore clear that the perspective taken in Section IIB is applicable to a much broader class of systems than a perspective that relies on effective free energies.

Appendix D: Partial Solutions for the Maxwell Construction Vector

While a solution to the generalized Gibbs-Duhem relation [Eq. (15) and correspondingly Eq. (18)] ensures the system has exact coexistence criteria, in many cases this solution does not exist. In these scenarios, one may be able to solve for bulk and interfacial Maxwell construction vectors: $\mathcal{E}^{\text{bulk}}$ (derived from $\mathcal{G}^{\text{bulk}}$ and $\mathbf{u}^{\text{bulk}}$) and $\mathcal{E}^{\text{int}}$ (derived from $\mathcal{G}^{\text{int}}$ and $\mathbf{u}^{\text{int}}$), respectively. This decomposition is achieved by separating the terms in the generalized Gibbs-Duhem relation [Eq. (15)]:

$$\mathcal{E}^{\text{bulk}} \cdot d\mathbf{u}^{\text{bulk}} = d\mathcal{G}^{\text{bulk}}, \quad (\text{D1a})$$

$$\mathcal{E}^{\text{int}} \cdot d\mathbf{u}^{\text{int}} = d\mathcal{G}^{\text{int}}. \quad (\text{D1b})$$

We now identify the equations in Eq. (18) as bulk or interfacial. The bulk relation for Eq. (D1a) is:

$$\mathcal{E}^{\text{bulk}} \cdot \partial_\rho \mathbf{u}^{\text{bulk}} = \partial_\rho \mathcal{G}^{\text{bulk}}, \quad (\text{D2})$$

while the interfacial relations for Eq. (D1b) are:

$$\partial_\rho (\mathcal{E}^{\text{int}} \cdot \mathbf{u}^{(2,2)}) = \partial_\rho \mathcal{G}^{(2,2)}, \quad (\text{D3a})$$

$$\mathcal{E}^{\text{int}} \cdot (2\mathbf{u}^{(2,1)} + \partial_\rho \mathbf{u}^{(2,2)}) = 2\mathcal{G}^{(2,1)} + \partial_\rho \mathcal{G}^{(2,2)}, \quad (\text{D3b})$$

$$\mathcal{E}^{\text{int}} \cdot [\partial_\rho \mathbf{u}^{(2,1)}]^S = [\partial_\rho \mathcal{G}^{(2,1)}]^{S'}, \quad (\text{D3c})$$

as derived in Appendix A 2.

Equation (D2) does not guarantee that the Hessian of $\mathcal{G}^{\text{bulk}}$ is symmetric, however, one can obtain the equation that ensures this for a two-component system by differentiating Eq. (D2) as shown in the SI [53]. This is necessary for the Maxwell construction integral in Eq. (22) [or alternatively Eq. (21)] to be path-independent, and is hence a consequence of the $\mathcal{E}$ solution satisfying the bulk relations. We now show that Eq. (D3) ensures the weighted-area construction with $\mathbf{E} = \mathbf{E}^{\text{int}} \equiv \partial_\rho \mathcal{E}^{\text{int}}$ vanishes when evaluated along the path of the interfacial profile between the coexisting phases, ρ^c . The interfacial generalized Gibbs-Duhem relation [Eq. (D1b)] can be expressed as $\partial_z \mathcal{G}^{\text{int}} = \partial_z (\mathcal{E}^{\text{int}} \cdot \mathbf{u}^{\text{int}}) - \mathbf{u}^{\text{int}} \cdot \mathbf{E}^{\text{int}} \cdot \partial_z \rho$. Clearly, $\mathbf{u}^{\text{int}} \cdot \mathbf{E}^{\text{int}} \cdot \partial_z \rho$ must be the z -derivative of a contribution to $\mathcal{G}^{\text{int}}$. Spatially integrating this quantity across the interfacial profile is thus equal to the difference in a contribution to $\mathcal{G}^{\text{int}}$ across phases, which vanishes by definition in the coexisting phases. Therefore, the weighted-area construction [Eq. (22)] with $\mathbf{E} = \mathbf{E}^{\text{int}}$ is guaranteed to vanish when evaluated along $\rho^c(z)$:

$$\int_{z^\alpha}^{z^\beta} \left(\mathbf{u}^{\text{bulk}}(\rho^c) - \mathbf{u}^{\text{coexist}} \right) \cdot \mathbf{E}^{\text{int}}(\rho^c) \cdot \partial_z \rho^c dz = 0, \quad (\text{D4})$$

for all $\alpha, \beta \in \mathcal{P}$. When both the bulk and interfacial $\mathcal{E}$ are identical [i.e., solutions satisfy all relations in Eq. (18)], the integral vanishes along any path $\rho(z)$, i.e., not just along $\rho^c(z)$. In this case, Eq. (D4) is equal to the difference in $\mathcal{G}^{\text{bulk}}$ between the coexisting phases and hence $\mathcal{G}^{\text{bulk}}$ is equal in the phases.

When $\mathcal{E}^{\text{bulk}} \neq \mathcal{E}^{\text{int}}$, $\mathcal{E}^{\text{int}}$ can be used in an approximate Maxwell construction. The weighted Maxwell construction in Eq. (D4) remains universally zero when evaluated along the interfacial profile but loses path-independence, and is therefore generally nonzero along other integration paths. Upon selecting an integration path [e.g., $(\rho'_A, \rho'_B) : (0, 0) \rightarrow (\rho_A, 0) \rightarrow (\rho_A, \rho_B)$], the weighted-area construction (using $\mathcal{E} = \mathcal{E}^{\text{int}}$) can be performed to *approximate* the coexistence criteria. As demonstrated in the SI [53], this approximation provides reasonable estimates of the coexistence binodal for specific integration paths.

Lastly, again in scenarios where $\mathcal{E}^{\text{bulk}} \neq \mathcal{E}^{\text{int}}$, approximate criteria can be formulated using $\mathcal{E}^{\text{bulk}}$ as well by defining $\mathcal{G}^{\text{bulk}} \equiv \mathcal{E}^{\text{bulk}} \cdot \mathbf{u}^{\text{bulk}} - \int \mathbf{u}^{\text{bulk}} \cdot d\mathcal{E}^{\text{bulk}}$. Noting Eq. (22) is always zero when evaluated along ρ^c , we re-express it and use the definition of $\mathcal{G}^{\text{bulk}}$ to identify $\Delta^{\alpha\beta} \mathcal{G}^{\text{bulk}} \equiv \mathcal{G}^\alpha - \mathcal{G}^\beta$:

$$\Delta^{\alpha\beta} \mathcal{G}^{\text{bulk}} = \int_{z^\alpha}^{z^\beta} [\mathbf{u}^{\text{bulk}}(\rho^c) - \mathbf{u}^{\text{coexist}}] \cdot (\mathbf{E}^{\text{bulk}}(\rho^c) - \mathbf{E}^{\text{int}}(\rho^c)) \cdot \partial_z \rho^c dz, \quad (\text{D5})$$

and hence $\Delta^{\alpha\beta} \mathcal{G}^{\text{bulk}} = 0$ when $\mathcal{E}^{\text{bulk}} = \mathcal{E}^{\text{int}}$. We may then set $\mathcal{G}^{\text{bulk}}$ equal across phases as approximate criteria, with the criteria becoming exact when the integrals in Eq. (D5) vanish. This is the case for the NRCH model in Fig. 3(b), where:

$$\Delta^{\alpha\beta} \mathcal{G}^{\text{bulk}} = \left(\frac{\chi + \alpha}{\chi - \alpha} - \frac{\bar{\kappa}_{AB}}{\bar{\kappa}_{BA}} \right) \int_{z^\alpha}^{z^\beta} \left[u_B^{\text{bulk}}(\rho^c) - u_B^{\text{coexist}} \right] \partial_z \rho_B^c dz \approx 0, \quad (\text{D6})$$

as shown in the SI [53]. We are then able to predict the co-existence densities in Fig. 3(b) by setting $\mathcal{G}^{\text{bulk}}$ equal across phases, providing a quantitatively excellent approximation.

Appendix E: Conditions for Pairwise Interacting Systems to be MAMB+

From the body-force coefficients in Eq. (31), direct comparison with the MAMB+ definition [Eq. (36)] allows these coefficients to be expressed in terms of the corresponding MAMB+ parameters:

$$\frac{\partial u_i^{0,\text{bulk}}}{\partial \rho_j} + \eta_{ij}^N = k_B T \delta_{ij} \frac{1}{\rho_i} + \int d\mathbf{x}' \Delta z \left(F_{ij} g_{ij}^0 + \frac{1}{2} \sum_k^{n_c} F_{ik} \rho_k \frac{\partial g_{ik}^0}{\partial \rho_j} \right), \quad (\text{E1a})$$

$$\kappa_{ij} + \pi_{ij}^{A'} = - \int d\mathbf{x}' \frac{1}{6} (\Delta z)^3 \left(F_{ij} g_{ij}^0 + \frac{1}{2} \sum_k^{n_c} F_{ik} \rho_k \frac{\partial g_{ik}^0}{\partial \rho_j} \right), \quad (\text{E1b})$$

$$2 \frac{\partial \kappa_{ij}}{\partial \rho_k} + \frac{\partial \pi_{ij}^{A'}}{\partial \rho_k} + 2 \lambda_{ijk} + \xi_{ijk}^A = - \int d\mathbf{x}' \frac{1}{4} (\Delta z)^3 \left(F_{ij} \frac{\partial g_{ij}^0}{\partial \rho_k} + F_{ik} \frac{\partial g_{ik}^0}{\partial \rho_j} \right), \quad (\text{E1c})$$

$$\theta_{ijk} = 0. \quad (\text{E1d})$$

A pairwise interacting system qualifies as MAMB+—rather than simply MAMB—if any η_{ij}^N or ξ_{ijk}^A is nonzero. Below, we identify the conditions under which these coefficients acquire nonzero values.

For η_{ij}^N to be nonzero, $b_{ij}^{(1,1)}/\rho_i$ must be nonintegrable (i.e., it cannot be expressed as $\partial u_i^{0,\text{bulk}}/\partial \rho_j$) for a pair of components i and j . This is case when $\partial(b_{ij}^{(1,1)}/\rho_i)/\partial \rho_k \neq$

$\partial(b_{ik}^{(1,1)}/\rho_i)/\partial \rho_j$ for any component $k \neq j$. In particular, we identify the symmetric contribution as:

$$2 \frac{\partial^2 u_i^{0,\text{bulk}}}{\partial \rho_j \partial \rho_k} = \frac{\partial}{\partial \rho_k} \left(\frac{b_{ij}^{(1,1)}}{\rho_i} \right) + \frac{\partial}{\partial \rho_j} \left(\frac{b_{ik}^{(1,1)}}{\rho_i} \right), \quad (\text{E2a})$$

and the skew-symmetric contribution as:

$$2 \frac{\partial \eta_{ij}}{\partial \rho_k} = -2 \frac{\partial \eta_{ik}}{\partial \rho_j} = \frac{\partial}{\partial \rho_k} \left(\frac{b_{ij}^{(1,1)}}{\rho_i} \right) - \frac{\partial}{\partial \rho_j} \left(\frac{b_{ik}^{(1,1)}}{\rho_i} \right). \quad (\text{E2b})$$

This yields the first set of conditions whose violation (nonzero value) indicates that the system is MAMB+ rather than MAMB:

$$\frac{\partial \eta_{ij}}{\partial \rho_k} = - \frac{\partial \eta_{ik}}{\partial \rho_j} = \frac{1}{4} \int d\mathbf{x}' \Delta z \left(F_{ij} \frac{\partial g_{ij}^0}{\partial \rho_k} - F_{ik} \frac{\partial g_{ik}^0}{\partial \rho_j} \right). \quad (\text{E3})$$

Similarly, ξ_{ijk}^A is nonzero if the expression found by differentiating Eq. (E1b) and subtracting it from Eq. (E1c) is not symmetric under $j \leftrightarrow k$. The second set of conditions whose violation signifies the system is MAMB+ are thus:

$$\xi_{ijk}^A = -\xi_{ikj}^A = \frac{1}{24} \int d\mathbf{x}' \Delta z^3 \left(F_{ik} \frac{\partial g_{ik}^0}{\partial \rho_j} - F_{ij} \frac{\partial g_{ij}^0}{\partial \rho_k} \right). \quad (\text{E4})$$

We will now demonstrate that the system in Ref. [35], a nonreciprocally-interacting two-component system that phase-separates across a broad range of parameters, falls under MAMB+. In this system, there are two components L and G that experience a pairwise force with z -component:

$$F_{LL}(r, \varphi) = F(r, \varphi; \epsilon_{LL}) \quad (\text{E5a})$$

$$F_{GG}(r, \varphi) = F(r, \varphi; \epsilon_{GG}) \quad (\text{E5b})$$

$$F_{LG}(r, \varphi) = F(r, \varphi; \epsilon_{LG}) \times (1 - \Theta(r - 2^{1/6} \sigma) \alpha), \quad (\text{E5c})$$

$$F_{GL}(r, \varphi) = F(r, \varphi; \epsilon_{LG}) \times (1 + \Theta(r - 2^{1/6} \sigma) \alpha), \quad (\text{E5d})$$

where $\Theta(x)$ is the Heaviside step function, σ is the length-scale of the interactions, α is the nonreciprocity (denoted Δ in Ref. [35]), φ is the polar angle, and:

$$F(r, \varphi; \epsilon_{ij}) = \frac{24\epsilon_{ij}}{r} \left[2 \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \Theta(2.5\sigma - r) \cos \varphi. \quad (\text{E5e})$$

is the z -component of a Lennard-Jones force. Figure 4 shows the values of $\partial_G \eta_{LL} = -\partial_L \eta_{LG}$ (where $\partial_G \equiv \partial/\partial \rho_G$ and $\partial_L \equiv \partial/\partial \rho_L$), $\partial_G \eta_{GL} = -\partial_L \eta_{GG}$, $\xi_{LLG}^A = -\xi_{LGL}^A$, and $\xi_{GLG}^A = -\xi_{GGL}^A$ as a function of α . It is clear that in equilibrium ($\alpha = 0$), each η_{ij}^N and ξ_{ijk}^A are zero; however, they become nonzero upon departing from equilibrium ($\alpha \neq 0$). Although the presence of these terms identifies the system as MAMB+, it nevertheless continues to phase-separate [84], as shown in the phase diagram of Ref. [35]. This indicates that transforming from effective body forces to species pseudopotentials is nontrivial in this system—if it is possible at all—and, more generally, that multicomponent phase-separating systems should be expected to fall into the MAMB+ class unless specific symmetry or interaction conditions are met.

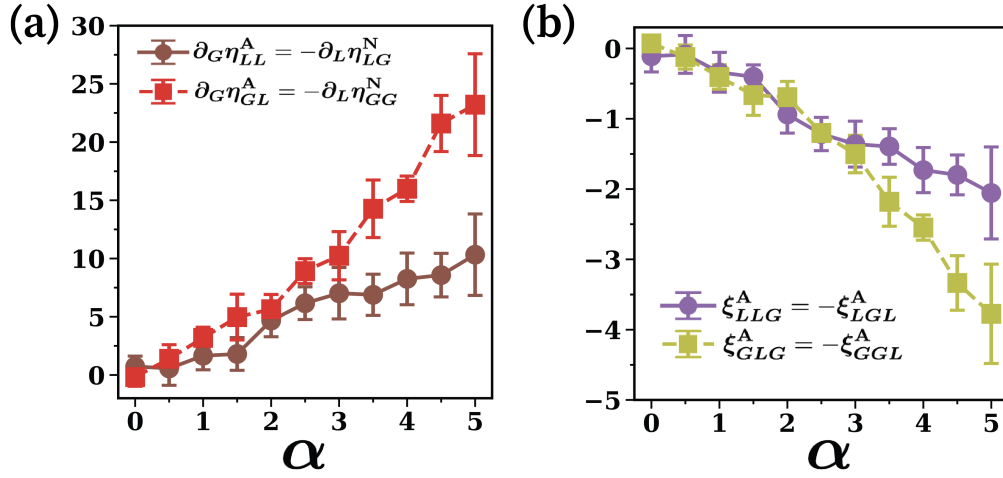


FIG. 4. Values of (a) $\partial_G \eta_{LL}^A = -\partial_L \eta_{LG}^N$ and $\partial_G \eta_{GL}^A = -\partial_L \eta_{GG}^N$ determined using Eq. (E3) and (b) $\xi_{LLG}^A = -\xi_{LGL}^A$ and $\xi_{GLG}^A = -\xi_{GGL}^A$ determined using Eq. (E4), both shown as a function of nonreciprocity α . The system is homogeneous and contains volume fractions $\phi_L = \rho_L \nu = 0.15$ and $\phi_G = \rho_G \nu = 0.05$ of species L and G where $\nu = \sqrt{2}\pi\sigma^3/6$ is the particle volume. The Lennard-Jones energy scales were chosen to be $\epsilon_{LL} = 0.5k_B T$, $\epsilon_{GG} = 0.6k_B T$, and $\epsilon_{LG} = 0.4k_B T$ and the system dynamics were integrated according to overdamped Langevin dynamics with translational white noise that satisfies the fluctuation-dissipation theorem (the details can be found in the SI [53]).

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