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Kinetic derivation of Cahn-Hilliard fluid modelsVincent Giovangigli *

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A compressible Cahn-Hilliard fluid model is derived from the kinetic theory of dense gas mixtures. The fluid model involves a van der Waals and Cahn-Hilliard gradient energy, a generalized Korteweg's tensor, a generalized Dunn and Serrin heat flux, and Cahn-Hilliard-type diffusive fluxes. Starting from the BBGKY hierarchy for gas mixtures, a Chapman-Enskog method is used—with a proper scaling of the generalized Boltzmann equations—as well as higher-order Taylor expansions of pair distribution functions. A Euler and van der Waals model is obtained at zeroth order, while the Cahn-Hilliard fluid model is obtained at first order, involving viscous, heat, and diffusive fluxes. The Cahn-Hilliard extra terms are associated with intermolecular forces and pair interaction potentials.

DOI: [10.1103/PhysRevE.104.054109](https://doi.org/10.1103/PhysRevE.104.054109)**I. INTRODUCTION**

Cahn-Hilliard models of fluid mixtures describe interphases—interfaces between phases—as regions with smooth variations of physical properties [1–3]. Such diffuse interface models generalize to fluid mixtures previous models developed for single-species fluids [2–5]. Diffuse interface models have been used successfully to describe spinodal decomposition, droplets dynamics, three-phase contact lines, surface diffusion, as well as transcritical flames [1–11].

For single-species fluids, the thermodynamics of diffuse interface models has been built by van der Waals [4] using a gradient-squared term in the free energy and the corresponding capillary tensor has been derived by Korteweg [12]. The proper heat flux has been obtained by Dunn and Serrin in the framework of rational thermodynamics [13]. These equations have alternatively been obtained from Hamiltonian considerations by Gavriluk and Shugrin [14] and deduced from the kinetic theory of dense gases by Giovangigli [15].

For fluid mixtures, Cahn and Hilliard [1] first used a mole fraction gradient-squared term in the free energy and later a density gradient to develop a thermodynamic formalism [16]. The Cahn-Hilliard equations have then been obtained in isothermal situations without convection phenomena [1] and later coupled with Navier-Stokes-type equations [17,18]. The general situation of nonisothermal Cahn-Hilliard fluids with Navier-Stokes-type equations has next been investigated using mainly thermodynamical considerations [2,19–23]. In this work, we first rederive the Cahn-Hilliard fluid equations from rational thermodynamics for completeness and to serve as a comparison with the kinetic theory derivation. The model obtained from rational thermodynamics that is in agreement with the kinetic derivation is found to differ from previous models of the literature [2,19–24]. The capillary force terms in diffusion fluxes and the capillary-diffusive contributions in the heat flux are found to differ. We establish, however,

that the resulting model *essentially agrees* with those obtained in Refs. [2,19,20,23,24], while some other models are found to be unphysical. Thermodynamic methods using entropy production rates are incidentally found to be ambiguous for diffuse interface models since there are various terms in the entropy production rate that involve products of several gradients as for single-species fluids [15].

Cahn-Hilliard fluid models also yield discontinuous interface models when the capillarity coefficients go to zero [2]. Such heterogeneous fluid limiting models may independently be obtained from rational thermodynamics as investigated by Kjelstrup and Bedeaux [25].

Aside from macroscopic thermodynamical arguments, it is important to investigate Cahn-Hilliard fluids *at the molecular level*. Statistical mechanics of equilibrium systems that are highly inhomogeneous on the scale of length of intermolecular forces has been used to investigate fluid interfaces [3,26–29]. The links between interface structure, stress tensor, surface tension, pair distribution functions, and intermolecular forces have been deepened and this has led to expressions for the interfacial energy, the capillary pressure tensor and the capillary coefficient [3,26–29].

Considering nonequilibrium systems, the kinetic theory of gases has been used in various contexts to investigate phase transitions as described in the review paper by Frezzotti and Barbante [30]. Liquid-vapor phase changes have notably been investigated by employing linearized Boltzmann equations with condensation-evaporation boundary conditions [31–33]. Vlasov-Enskog-type equations have also been used to investigate spatial aspects of phase transition [34–46]. Detailed molecular dynamics of Lennard-Jones fluids have further been performed by Frezzotti *et al.* [47] and compared to capillary fluid models with a general very good agreement. Concerning the derivation from the kinetic theory of diffuse interface models for single-species fluids, a notable achievement was that of Rocard who derived the capillary force acting locally in a fluid using a Taylor expansion of the pair distribution function [5,48]. Rocard recovered the Korteweg tensor and expressed the capillary coefficient in term of the interaction potential.

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Piechór also investigated the links between kinetic nonlocal stresses and Korteweg's tensor using an Enskog-Vlasov equation [38]. An elegant minimum BGK-Vlasov model has also been introduced by Takata and Noguchi [40] with non-ideal effects mediated through a nonlocal self-consistent force term and collisions acting as a thermal bath. A gradient-type energy has been obtained in the continuum limit as well as a single-species Cahn-Hilliard-type equation in an isothermal framework [40]. These results have then been generalized to the situation of nonisothermal fluids [46]. Still considering single-species fluids, a full derivation of nonisothermal capillary fluid equations from the kinetic theory of dense gases has been obtained by Giovangigli [15]. However, to the best of the author's knowledge, a complete derivation of Cahn-Hilliard fluid mixture models from the kinetic theory of dense gas mixtures is still missing is the object of this work. The resulting model will then be compared with those obtained from rational thermodynamics.

The kinetic theory of dense gas mixtures is based on generalized Boltzmann equations for the species one-particle distribution functions [49–51], generalizing the situation of single-species fluids [52–58]. Such Boltzmann equations are obtained from the two first BBGKY hierarchy equations and involve cluster expansions as well as Bogoliubov's functional property. A key point of such generalized Boltzmann equations, allowing the derivation of Cahn-Hilliard fluids, is that the collision terms involve species one-particle distribution functions evaluated *at different spatial positions*.

With the aim of deriving fluid macroscopic equations from the kinetic model, we introduce a new Enskog scaling for collision operators in the generalized Boltzmann equations. We next revisit and simplify the derivation of nonideal fluid equations—still without capillary effects—with viscous, heat, and diffusion fluxes as investigated by Cohen *et al.* [50]. The new scaling clarifies the analysis of fluid equations and directly yields that the zeroth-order one-particle distributions are Maxwellians. Assuming that repulsive potentials are hard, some collision integrals for dense gas mixtures are also simplified in such a way that the diffusive fluxes are directly expressed in terms of chemical potential gradients in agreement with thermodynamics. In comparison, linear system inversions have been used in previous work to transform fluxes expressed in terms of density gradients into fluxes expressed in terms of chemical potential gradients [50,51]. The corresponding matrices, however, may be singular in the situation of thermodynamic instabilities. The resulting macroscopic equations are found to be that of nonideal Navier-Stokes-Fourier-Fick fluids with density dependent transport coefficients [49–51], generalizing the results obtained for single-species fluids [52,54,56–58].

To recover diffuse interface models at the Euler level—the zeroth order of Enskog expansion—we introduce symmetrized zeroth-order species pair distribution functions. Higher-order Taylor expansions of pair distribution functions are then performed in the conservation equations. For the sake of simplicity, the kinetic derivation is performed in the situation where the capillary coefficients are independent of temperature. As a result, we obtain the Euler and van der Waals equations for fluid mixtures, extending previous results for single-species fluids [15]. The internal energy includes

density gradient terms, the pressure tensor involves a generalized Korteweg-type tensor and the heat flux includes a Dunn and Serrin-type contribution. The diffuse interface or capillary coefficients are also related to intermolecular forces and interaction potentials.

The Cahn-Hilliard fluid model is next obtained at the Navier-Stokes level—the first order of Enskog expansion—by using higher-order expansions of pair distribution functions in the conservation equations and in the linearized Boltzmann equations. The symmetrized pair distribution functions already used at the Euler level yield all relevant terms of the Cahn-Hilliard diffusion driving forces and conservation equations at first order. The alterations arising from the differences between the Bogoliubov pair distribution functions and the symmetrized pair distribution functions are also investigated and shown to be negligible in the regime investigated. The resulting Cahn-Hilliard fluid equations then coincide with the model derived from rational thermodynamics, that is, the energy density, the zeroth-order extra gradient terms in the pressure tensor and the heat flux coincide as well as the Cahn-Hilliard-type fluxes and the capillary-diffusive heat fluxes. The energy conservation equations and the species diffusion driving forces differ from that of previous work but the differences with some previous models are found to be unessential. Finally, the Gibbsian entropy is found to coincide with the zeroth-order kinetic entropy only in the absence of capillary terms.

The equations governing Cahn-Hilliard fluids are investigated in Sec. II using rational thermodynamics. The kinetic theory of dense gas mixtures and the generalized Boltzmann equations are described in Sec. III. The derivation of nonideal multicomponent fluid equations without capillary effects is presented in Sec. IV. The zeroth-order Euler and van der Waals equations are obtained in Sec. V and the first-order Cahn-Hilliard equations in Sec. VI. A discussion of the Cahn-Hilliard equations and their derivation is finally presented in Sec. VII.

II. CAHN-HILLIARD FLUIDS FROM RATIONAL THERMODYNAMICS

We first derive in this section the equations governing Cahn-Hilliard fluids from rational thermodynamics. These equations involve a generalized Cahn-Hilliard and van der Waals' energy [4], a Korteweg's tensor [12], a Dunn and Serrin's heat flux [13], Cahn-Hilliard-type diffusive fluxes, and a capillary-diffusive heat flux. We also address the ambiguity of rational thermodynamics—the thermodynamics of irreversible processes—for such *nonlinear* problems, with the apparition of various gradients' products terms in the rate of entropy production, leading to artificial alternatives for the expression of transport fluxes.

A. A Cahn-Hilliard-type free energy

The Cahn-Hilliard free energy per unit volume \mathcal{A} is written in the form

$$\mathcal{A} = \mathcal{A}^u + \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \bar{\chi}_{ij} \nabla \rho_i \cdot \nabla \rho_j, \quad (2.1)$$

where $\mathfrak{S} = \{1, \dots, n_s\}$ denotes the species indexing set, n_s the number of species, \mathcal{A}^u the bulk free energy per unit volume, ρ_i the partial density of the i th species, ∇ the usual differential operator, and $\bar{\alpha}_{ij}$, $i, j \in \mathfrak{S}$, the mass-based capillary coefficients that are symmetric $\bar{\alpha}_{ij} = \bar{\alpha}_{ji}$. The superscript “u” is used to denote standard or bulk phase thermodynamic properties that do not involve gradients, i.e., that are also valid for spatially uniform fluids. The free energy \mathcal{A}^u only depends on the partial densities ρ_1, \dots, ρ_n and the absolute temperature T whereas the gradient-squared term $\sum_{i,j \in \mathfrak{S}} \frac{1}{2} \bar{\alpha}_{ij} \nabla \rho_i \cdot \nabla \rho_j$ in \mathcal{A} represents an excess free energy of the interfacial region. Such gradient energies Eq. (2.1) have notably been considered by Cahn [16], Rowlinson and Widom [3], Falk [19], Alt and Pawlow [24], Verschueren [20], Liu *et al.* [23], and Heida *et al.* [21], and reduce to the van der Waals energy for single-species fluids [2–5]. Energies involving mass or mole fraction gradients are also easily rewritten in the general form Eq. (2.1) using properly chosen capillary coefficients $\bar{\alpha}_{ij}$.

Denoting by \mathcal{S} the Gibbsian entropy per unit volume and \bar{g}_i the Gibbs function per unit mass of the i th species, we have the thermodynamic relation $d\mathcal{A}^u = -S^u dT + \sum_{i \in \mathfrak{S}} \bar{g}_i^u d\rho_i$. Differentiating Eq. (2.1), it is obtained that

$$\begin{aligned} d\mathcal{A} = & - \left(S^u - \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \partial_T \bar{\alpha}_{ij} \nabla \rho_i \cdot \nabla \rho_j \right) dT \\ & + \sum_{k \in \mathfrak{S}} \left(\bar{g}_k^u + \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \partial_{\rho_k} \bar{\alpha}_{ij} \nabla \rho_i \cdot \nabla \rho_j \right) d\rho_k \\ & + \sum_{i \in \mathfrak{S}} \bar{\gamma}_i \cdot d\nabla \rho_i, \end{aligned} \quad (2.2)$$

where d denotes the differentiation operator and where the mass-based vectors $\bar{\gamma}_i$, $i \in \mathfrak{S}$, are defined by

$$\bar{\gamma}_i = \sum_{j \in \mathfrak{S}} \bar{\alpha}_{ij} \nabla \rho_j, \quad i \in \mathfrak{S}. \quad (2.3)$$

Using the thermodynamic relations $\partial_T \mathcal{A} = -S$ and $\partial_{\rho_i} \mathcal{A} = \bar{g}_i$, $i \in \mathfrak{S}$, the identity Eq. (2.2) implies that the *Gibbsian* entropy \mathcal{S} and the species Gibbs functions par unit mass \bar{g}_k are given by

$$\begin{aligned} \mathcal{S} = & S^u - \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \partial_T \bar{\alpha}_{ij} \nabla \rho_i \cdot \nabla \rho_j, \\ \bar{g}_k = & \bar{g}_k^u + \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \partial_{\rho_k} \bar{\alpha}_{ij} \nabla \rho_i \cdot \nabla \rho_j. \end{aligned} \quad (2.4)$$

The mixture Gibbs function per unit volume \mathcal{G} is then found to be

$$\mathcal{G} = \mathcal{G}^u + \sum_{i,j,k \in \mathfrak{S}} \frac{1}{2} \rho_k \partial_{\rho_k} \bar{\alpha}_{ij} \nabla \rho_i \cdot \nabla \rho_j, \quad (2.5)$$

and the pressure $p = \mathcal{G} - \mathcal{A}$ reads

$$p = p^u + \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \left(\sum_{k \in \mathfrak{S}} \rho_k \partial_{\rho_k} \bar{\alpha}_{ij} - \bar{\alpha}_{ij} \right) \nabla \rho_i \cdot \nabla \rho_j. \quad (2.6)$$

The equality of the Gibbsian entropy \mathcal{S} with the bulk entropy S^u when capillarity coefficients are independent of

temperature is in agreement with van der Waals derivation in the situation of single-species fluids [3,4]. We also note that when capillarity coefficients only depend on temperature, as will be obtained from the kinetic theory, there are no capillary contributions in the species Gibbs functions $\bar{g}_k = \bar{g}_k^u$, $k \in \mathfrak{S}$. Denoting by \mathcal{E} the energy per unit volume and using the thermodynamic relation $\mathcal{E} = \mathcal{A} + T\mathcal{S}$, it is further obtained that

$$\mathcal{E} = \mathcal{E}^u + \sum_{i,j \in \mathfrak{S}} \frac{1}{2} (\bar{\alpha}_{ij} - T \partial_T \bar{\alpha}_{ij}) \nabla \rho_i \cdot \nabla \rho_j. \quad (2.7)$$

The generalized volumetric Gibbs relation is finally obtained in the form

$$Td\mathcal{S} = d\mathcal{E} - \sum_{i \in \mathfrak{S}} \bar{g}_i d\rho_i - \sum_{i \in \mathfrak{S}} \bar{\gamma}_i \cdot d\nabla \rho_i \quad (2.8)$$

and involves the extra gradient variables $\nabla \rho_i$, $i \in \mathfrak{S}$.

B. Entropy production and fluid equations

The conservation equations for the partial densities ρ_i , $i \in \mathfrak{S}$, are in the form

$$\partial_t \rho_i + \nabla \cdot (\rho_i \mathbf{v}) + \nabla \cdot \bar{\mathcal{F}}_i = 0, \quad i \in \mathfrak{S}, \quad (2.9)$$

where \mathbf{v} denotes the fluid velocity and $\bar{\mathcal{F}}_i$ the mass flux of the i th species. For the sake of simplicity, no chemical source terms have been considered in the species equations. The diffusive fluxes $\bar{\mathcal{F}}_i$, $i \in \mathfrak{S}$, satisfy the mass conservation constraints $\sum_{i \in \mathfrak{S}} \bar{\mathcal{F}}_i = 0$ so that summing the n_s species conservation Eqs. (2.9) yields the total mass conservation equation $\partial_t \rho + \nabla \cdot (\rho \mathbf{v}) = 0$.

The momentum conservation equation reads

$$\partial_t (\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) + \nabla \cdot \mathcal{P} = 0, \quad (2.10)$$

where \otimes is the tensor product between vectors and \mathcal{P} the total pressure tensor, and the total energy conservation equation is in the form

$$\partial_t (\mathcal{E} + \frac{1}{2} \rho |\mathbf{v}|^2) + \nabla \cdot [\mathbf{v} (\mathcal{E} + \frac{1}{2} \rho |\mathbf{v}|^2)] + \nabla \cdot (\mathcal{Q} + \mathcal{P} \cdot \mathbf{v}) = 0, \quad (2.11)$$

where \mathcal{Q} denotes the total heat flux. Multiplying the momentum conservation equation Eq. (2.10) by the velocity vector \mathbf{v} and subtracting the result from the total energy conservation Eq. (2.11) also yields a conservation equation for the internal energy \mathcal{E} as in standard fluids.

Combining the conservation equations and Gibbs relation Eq. (2.8), the following expression for the rate of entropy production Eq. (A7) may be obtained as detailed in

Appendix A:

$$\begin{aligned}
\partial_t \mathcal{S} + \nabla \cdot (\mathbf{v} \mathcal{S}) + \nabla \cdot \left[\frac{\mathcal{Q}}{T} - \sum_{i \in \mathfrak{S}} \frac{\bar{\mathbf{y}}_i}{T} (\rho_i \nabla \cdot \mathbf{v} + \nabla \cdot \bar{\mathcal{F}}_i) - \sum_{i \in \mathfrak{S}} \left(\frac{\bar{g}_i}{T} - \frac{\nabla \cdot \bar{\mathbf{y}}_i}{T} \right) \bar{\mathcal{F}}_i \right] \\
= -\frac{1}{T} \left[\mathcal{P} - p \mathbf{I} - \sum_{i \in \mathfrak{S}} (\nabla \rho_i \otimes \bar{\mathbf{y}}_i - \rho_i \nabla \cdot \bar{\mathbf{y}}_i \mathbf{I}) \right] : \nabla \mathbf{v} \\
- \left[\mathcal{Q} - \sum_{i \in \mathfrak{S}} \bar{\mathbf{y}}_i (\rho_i \nabla \cdot \mathbf{v} + \nabla \cdot \bar{\mathcal{F}}_i) + \sum_{i \in \mathfrak{S}} \nabla \cdot \bar{\mathbf{y}}_i \bar{\mathcal{F}}_i \right] \cdot \nabla \left(\frac{-1}{T} \right) \\
- \sum_{i \in \mathfrak{S}} \bar{\mathcal{F}}_i \cdot \left(\nabla \frac{\bar{g}_i}{T} - \frac{\nabla (\nabla \cdot \bar{\mathbf{y}}_i)}{T} \right), \tag{2.12}
\end{aligned}$$

where \mathbf{I} denotes the unit tensor. Proceeding as in the thermodynamics of irreversible processes [59] and using the Curie principle, we deduce from the expression of entropy production Eq. (2.12) that the pressure tensor and the total heat flux are in the form

$$\mathcal{P} = p \mathbf{I} + \sum_{i \in \mathfrak{S}} \nabla \rho_i \otimes \bar{\mathbf{y}}_i - \sum_{i \in \mathfrak{S}} \rho_i \nabla \cdot \bar{\mathbf{y}}_i \mathbf{I} + \mathcal{P}^d, \tag{2.13}$$

$$\mathcal{Q} = \sum_{i \in \mathfrak{S}} \bar{\mathbf{y}}_i \rho_i \nabla \cdot \mathbf{v} + \sum_{i \in \mathfrak{S}} \bar{\mathbf{y}}_i \nabla \cdot \bar{\mathcal{F}}_i - \sum_{i \in \mathfrak{S}} \nabla \cdot \bar{\mathbf{y}}_i \bar{\mathcal{F}}_i + \mathcal{Q}^d, \tag{2.14}$$

where \mathcal{P}^d is the viscous tensor and \mathcal{Q}^d the dissipative heat flux. The diffusion fluxes reduce to their dissipative part $\bar{\mathcal{F}}_i = \bar{\mathcal{F}}^d$, $i \in \mathfrak{S}$ and the vectors $\bar{\mathbf{y}}_i$, $i \in \mathfrak{S}$, are given by Eq. (2.3). We also deduce that the dissipative fluxes \mathcal{P}^d , $\bar{\mathcal{F}}_i$, $i \in \mathfrak{S}$, and \mathcal{Q}^d are in the form

$$\mathcal{P}^d = -\mathbf{v} \nabla \cdot \mathbf{v} \mathbf{I} - \eta \left(\nabla \mathbf{v} + \nabla \mathbf{v}^t - \frac{2}{3} \nabla \cdot \mathbf{v} \mathbf{I} \right), \tag{2.15}$$

$$\bar{\mathcal{F}}_i = - \sum_{j \in \mathfrak{S}} L_{ij} \left[\nabla \left(\frac{\bar{g}_j}{T} \right) - \frac{\nabla \nabla \cdot \bar{\mathbf{y}}_j}{T} \right] - L_{ie} \nabla \left(\frac{-1}{T} \right), \tag{2.16}$$

$$\mathcal{Q}^d = - \sum_{i \in \mathfrak{S}} L_{ei} \left[\nabla \left(\frac{\bar{g}_i}{T} \right) - \frac{\nabla \nabla \cdot \bar{\mathbf{y}}_i}{T} \right] - L_{ee} \nabla \left(\frac{-1}{T} \right), \tag{2.17}$$

where \mathbf{v} denotes the volume viscosity, η the shear viscosity and L_{ij} , $i, j \in \mathfrak{S} \cup \{e\}$, the mass and heat transport coefficients. The matrix of mass and heat transport coefficients L defined by $L = (L_{ij})_{i,j \in \mathfrak{S} \cup \{e\}}$ is symmetric positive semidefinite with a nullspace spanned by the vector $(1, \dots, 1, 0)^t$ as for ordinary fluids [59,60]. The fluxes $\bar{\mathcal{F}}_i = \bar{\mathcal{F}}_i^d$, $i \in \mathfrak{S}$, and \mathcal{Q}^d are obtained with Eqs. (2.16) and (2.17) in their *thermodynamic form* [59–61] and the link with the usual form is discussed in Sec. IV D.

In the following, we will denote for convenience by \mathcal{P}^{KO} the Korteweg-type tensor, i.e., the zeroth-order gradient part of the pressure tensor \mathcal{P} , and by \mathcal{Q}^{DS} the Dunn and Serrin-

type heat flux, i.e., the zeroth-order gradient part of the total heat flux \mathcal{Q} , given by

$$\begin{aligned}
\mathcal{P}^{\text{KO}} &= \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \left(\sum_{k \in \mathfrak{S}} \rho_k \partial_{\rho_k} \bar{\mathcal{X}}_{ij} - \bar{\mathcal{X}}_{ij} \right) \nabla \rho_i \cdot \nabla \rho_j \mathbf{I} \\
&+ \sum_{i,j \in \mathfrak{S}} \bar{\mathcal{X}}_{ij} \nabla \rho_i \otimes \nabla \rho_j - \sum_{i,j \in \mathfrak{S}} \rho_i \nabla \cdot (\bar{\mathcal{X}}_{ij} \nabla \rho_j) \mathbf{I}, \tag{2.18}
\end{aligned}$$

$$\mathcal{Q}^{\text{DS}} = \sum_{i,j \in \mathfrak{S}} \bar{\mathcal{X}}_{ij} \rho_i \nabla \rho_j \nabla \cdot \mathbf{v}. \tag{2.19}$$

We will also denote by \mathcal{Q}^{CD} the extra *capillary-diffusive* first-order term given by

$$\mathcal{Q}^{\text{CD}} = - \sum_{i \in \mathfrak{S}} \nabla \cdot \bar{\mathbf{y}}_i \bar{\mathcal{F}}_i + \sum_{i \in \mathfrak{S}} \bar{\mathbf{y}}_i \nabla \cdot \bar{\mathcal{F}}_i. \tag{2.20}$$

These fluxes \mathcal{P}^{KO} , \mathcal{Q}^{DS} , and \mathcal{Q}^{CD} will have to be recovered from the kinetic theory as well as the expression of the dissipative fluxes. Some simplifications may further be obtained in the situation of free energies expressed in terms of mass or mole fraction gradients as discussed in Appendix B.

The mass and heat transport coefficients L_{ij} , $i, j \in \mathfrak{S} \cup \{e\}$, may also be rescaled in the form

$$\begin{aligned}
\mathcal{L}_{ij} &= \frac{L_{ij}}{T \rho_i \rho_j}, \quad i, j \in \mathfrak{S}, \quad \mathcal{L}_{ei} = \mathcal{L}_{ie} = \frac{\hat{L}_{ie}}{T \rho_i} \quad i \in \mathfrak{S}, \\
\mathcal{L}_{ee} &= \frac{\hat{L}_{ee}}{T^2}, \tag{2.21}
\end{aligned}$$

and we define for convenience the force term \mathbf{X}_i as the opposite of the force on the i th species per unit volume

$$\mathbf{X}_i = \rho_i T \left(\nabla \left(\frac{\bar{g}_i}{T} \right) - \frac{\nabla \nabla \cdot \bar{\mathbf{y}}_i}{T} \right), \quad i \in \mathfrak{S}. \tag{2.22}$$

This force term may be split as $\mathbf{X}_i = \mathbf{X}_i^{\text{th}} + \mathbf{X}_i^{\text{ch}}$ where \mathbf{X}_i^{th} and \mathbf{X}_i^{ch} are the opposite of the thermodynamic force and the capillary force of the i th species per unit volume

$$\mathbf{X}_i^{\text{th}} = \rho_i T \nabla \left(\frac{\bar{g}_i}{T} \right), \quad \mathbf{X}_i^{\text{ch}} = -\rho_i \nabla \nabla \cdot \bar{\mathbf{y}}_i, \quad i \in \mathfrak{S}. \tag{2.23}$$

The thermodynamic force per unit mass on the i th species is also given by $-T \nabla (\bar{g}_i/T)$ [59] and the capillary force per unit mass by $\nabla \nabla \cdot \bar{\mathbf{y}}_i$. Defining then the species diffusion velocities

$\mathcal{V}_i, i \in \mathfrak{S}$, by [56,57]

$$\mathcal{V}_i = \frac{\mathcal{F}_i}{\rho_i}, \quad i \in \mathfrak{S}, \quad (2.24)$$

we may rewrite the species diffusion velocities and the heat flux in the form

$$\mathcal{V}_i = - \sum_{j \in \mathfrak{S}} \mathcal{L}_{ij} \mathcal{X}_j - \mathcal{L}_{ie} \nabla \log T, \quad (2.25)$$

$$\mathcal{Q}^d = - \sum_{i \in \mathfrak{S}} \mathcal{L}_{ei} \mathcal{X}_i - \mathcal{L}_{ee} \nabla T. \quad (2.26)$$

One may also introduce the diffusion driving forces $\mathbf{d}_i = \mathcal{X}_i/nk_B T$, $i \in \mathfrak{S}$, where n is the total number density and k_B the Boltzmann constant. The diffusion velocities are easily rewritten in terms of such diffusion driving forces that may also be split between the thermodynamic diffusion driving force $\mathbf{d}_i^{\text{th}} = \mathcal{X}_i^{\text{th}}/nk_B T$ and the Cahn-Hilliard diffusion driving force $\mathbf{d}_i^{\text{ch}} = \mathcal{X}_i^{\text{ch}}/nk_B T$. Finally, to relate the thermodynamic form of dissipative flux Eqs. (2.16), (2.17) or Eqs. (2.25), (2.26) to more traditional forms, it is necessary to subtract a temperature gradient from the thermodynamic force terms $\mathcal{X}_i^{\text{th}}, i \in \mathfrak{S}$. This generally involves pressure-based thermodynamic functions that explode at mechanical unstable states [9] as addressed in Sec. IVE 2.

C. Ambiguity of rational thermodynamics

An important difficulty associated with rational thermodynamics when applied to phase field models is the presence in the rate of entropy production of quantities involving *products of several gradients*. More specifically, in Eq. (2.12) of entropy production, all terms in the form

$$\rho_i \nabla \cdot \mathbf{v} \bar{\mathbf{y}}_i \cdot \nabla \left(\frac{-1}{T} \right), \quad i \in \mathfrak{S}, \quad (2.27)$$

involve both temperature and velocity gradients. Considering these terms as *temperature gradient terms* one recovers the Korteweg-type tensor \mathcal{P}^{KO} and Dunn and Serrin-type heat flux \mathcal{Q}^{DS} . However, using $\nabla \cdot \mathbf{v} = \nabla \mathbf{v} : \mathbf{I}$, these gradients' product terms Eq. (2.27) may also be considered as *velocity derivative terms*. This then leads to an alternative form of entropy production as well as to *unphysical transport fluxes* as already established in the situation of a single-species fluid [15].

Similarly, various terms may be regrouped differently in the expression of the entropy production rate, as notably $\bar{\mathcal{F}}_i \cdot \nabla (\nabla \cdot \bar{\mathbf{y}}_i)/T$, $i \in \mathfrak{S}$. More specifically, the variant entropy production rate Eq. (A6) has been used in the literature [2,20,23] as well as the other variant Eq. (A8) in Refs. [19,24]. The resulting flux expressions only differ in the first-order capillary flux \mathcal{Q}^{CD} and in the force terms $\mathcal{X}_i, i \in \mathfrak{S}$, all the other terms being unchanged. The first variant Eq. (A6) leads to the flux

$$\mathcal{Q}^{\text{CD}} = \sum_{i \in \mathfrak{S}} \bar{\mathbf{y}}_i \cdot \nabla \cdot \bar{\mathcal{F}}_i, \quad (2.28)$$

with the terms $-\sum_{i \in \mathfrak{S}} \nabla \cdot \bar{\mathbf{y}}_i \bar{\mathcal{F}}_i$ missing, and to the force terms

$$\mathcal{X}'_i = \rho_i T \left(\nabla \frac{\bar{g}_i}{T} - \nabla \cdot \frac{\bar{\mathbf{y}}_i}{T} \right) = \rho_i T \nabla \left(\frac{\bar{g}_i}{T} - \frac{\nabla \cdot \bar{\mathbf{y}}_i}{T} \right), \quad i \in \mathfrak{S}, \quad (2.29)$$

with the factor $1/T$ inside the gradient operator. The other variant Eq. (A8) leads to the heat flux

$$\mathcal{Q}^{\text{CD}} = 0, \quad (2.30)$$

with both terms $-\sum_{i \in \mathfrak{S}} \nabla \cdot \bar{\mathbf{y}}_i \bar{\mathcal{F}}_i$ and $\sum_{i \in \mathfrak{S}} \bar{\mathbf{y}}_i \cdot \nabla \cdot \bar{\mathcal{F}}_i$ missing, and to the force terms

$$\mathcal{X}''_i = \rho_i T \left(\nabla \frac{\bar{g}_i}{T} - \nabla \nabla \cdot \frac{\bar{\mathbf{y}}_i}{T} \right) = \rho_i T \nabla \left(\frac{\bar{g}_i}{T} - \nabla \cdot \frac{\bar{\mathbf{y}}_i}{T} \right), \quad i \in \mathfrak{S}, \quad (2.31)$$

with the factor $1/T$ inside the gradient and divergence operators. Even though these fluxes differ from the results obtained from the kinetic theory, we will see in Sec. VII A that these models *essentially agree* since temperature variations and diffusive fluxes are modest in interphase fronts.

Finally, the other variant Eq. (A9) leads to the flux

$$\mathcal{Q}^{\text{CD}} = - \sum_{i \in \mathfrak{S}} \bar{g}_i \bar{\mathcal{F}}_i - \sum_{i \in \mathfrak{S}} \nabla \cdot \bar{\mathbf{y}}_i \bar{\mathcal{F}}_i + \sum_{i \in \mathfrak{S}} \bar{\mathbf{y}}_i \cdot \nabla \cdot \bar{\mathcal{F}}_i, \quad (2.32)$$

that contains the unphysical term $-\sum_{i \in \mathfrak{S}} \bar{g}_i \bar{\mathcal{F}}_i$. Even in the absence of capillarity terms, the heat flux $\mathcal{Q} = \mathcal{Q}^d - \sum_{i \in \mathfrak{S}} \bar{g}_i \bar{\mathcal{F}}_i$ is in contradiction with classical models of fluid mixtures [59,60,62–64].

Rational thermodynamics, that is usually a faithful tool for linearlike problems, is here unable to determine *unambiguously* the proper transport fluxes. For such nonlinear problems, there is a failure of rational thermodynamics in the sense that simple algebraic reorderings of the entropy production rate seem to lead to different physical fluxes and thus to different physics. This is why *only finer physical theories*, like the kinetic theory of dense gas mixtures, may determine unambiguously the proper fluxes and equations.

D. Equilibrium interfaces

The structure of equilibrium phase interfaces at zero velocity may be obtained by extremalizing the entropy \mathcal{S} for given amounts of species mass $\rho_k, k \in \mathfrak{S}$, and energy \mathcal{E} [9,65].

Using the method of Lagrange multipliers, the infinitesimal variation of interfacial entropy reads

$$\delta \int \left(\mathcal{S} - \alpha_e \mathcal{E} - \sum_{k \in \mathfrak{S}} \alpha_k \rho_k \right) dx = 0, \quad (2.33)$$

where $\alpha_k, k \in \mathfrak{S}$, and α_e are Lagrange multipliers and δ is the variational symbol. Using Gibbs relation Eq. (2.8) and a few integration by parts, it is obtained from Eq. (2.33) that

$$\int \left\{ \left(\frac{1}{T} - \alpha_e \right) \delta \mathcal{E} + \sum_{k \in \mathfrak{S}} \left(- \frac{\bar{g}_k}{T} + \nabla \cdot \frac{\bar{\mathbf{y}}_k}{T} - \alpha_k \right) \delta \rho_k \right\} dx = 0. \quad (2.34)$$

Since the variations $\delta\mathcal{E}$ and $\delta\rho_k$, $k \in \mathfrak{S}$, are arbitrary in Eq. (2.34), we conclude that

$$\frac{1}{T} - \alpha_e = 0, \quad (2.35)$$

$$-\frac{\bar{g}_k}{T} + \nabla \cdot \frac{\bar{\mathcal{Y}}_k}{T} - \alpha_k = 0, \quad k \in \mathfrak{S}. \quad (2.36)$$

The interface is thus isothermal and the generalized chemical potentials $\bar{g}_k - \nabla \cdot \bar{\mathcal{Y}}_k$ are also constant through the interface. Taking the gradient of these relations, we thus obtain that $\nabla T = 0$ and that the force terms Eq. (2.22) vanish $\mathbf{X}_k = 0$, $k \in \mathfrak{S}$. As a consequence, the heat flux \mathcal{Q} as well as the species mass fluxes \mathcal{F}_k , $k \in \mathfrak{S}$, vanish through the interface that may also be convected at any velocity.

Assuming then that capillarity coefficients $\bar{\alpha}_{ij}$, $i, j \in \mathfrak{S}$, are constant for the sake of simplicity, multiplying Eq. (2.36) by $\nabla\rho_k$, summing over $k \in \mathfrak{S}$, and keeping in mind that the interface is isothermal, we obtain that $\nabla\mathcal{A}^u - \sum_{k \in \mathfrak{S}} \nabla\rho_k \nabla \cdot \bar{\mathcal{Y}}_k + T \sum_{k \in \mathfrak{S}} \nabla\rho_k \alpha_k = 0$. Multiplying Eq. (2.36) by ρ_k , summing over $k \in \mathfrak{S}$, we also deduce that $\mathcal{G}^u - \sum_{k \in \mathfrak{S}} \rho_k \nabla \cdot \bar{\mathcal{Y}}_k + T \sum_{k \in \mathfrak{S}} \rho_k \alpha_k = 0$. Taking the gradient of this identity and subtracting the former relation then yields that $\nabla p^u - \sum_{k \in \mathfrak{S}} \rho_k \nabla \nabla \cdot \bar{\mathcal{Y}}_k = 0$ that is the mechanical equilibrium condition. Such a structure of equilibrium fronts shows that, in an interphase, typically a vaporization front, density gradients may be very large, but we may assume that temperature variations as well as diffusion fluxes remain modest in a macroscopic regime. Considering also two phases at equilibrium denoted with the superscript \sharp and \flat , and letting the gradients go to zero far from the interface, we obtain the classical equilibrium conditions $T^\sharp = T^\flat$, $\bar{g}_k^\sharp = \bar{g}_k^\flat$, $k \in \mathfrak{S}$, and $p^\sharp = p^\flat$ between the phases.

In the situation of single-species fluids, we may further investigate the structure of a one-dimensional vaporization front [3,4,6]. Denoting by l and g the indices of the liquid and its vapor at equilibrium, the equilibrium relations yields $T_l = T_g$, $p_l = p_g$, and $\bar{g}_l = \bar{g}_g$. Denoting by z the normal coordinate, the isothermal interface is such that $\frac{1}{2}\varkappa(d\rho/dz)^2 = \mathcal{A} - \mathcal{A}_g - \bar{g}_g(\rho - \rho_g)$. The function $\mathcal{A} - \mathcal{A}_g - \bar{g}_g(\rho - \rho_g)$ is the difference between \mathcal{A} and its bi-tangent line, since $\mathcal{A}_l = \mathcal{A}_g - \bar{g}_g(\rho_l - \rho_g)$ from the equality of pressures and since $\partial_\rho \mathcal{A} = \bar{g}$ at constant temperature. Approximating the excess function $\mathcal{A} - \mathcal{A}_g - \bar{g}_g(\rho - \rho_g)$ as $\bar{\mathcal{A}}(\rho - \rho_l)^2(\rho - \rho_g)^2$, where $\bar{\mathcal{A}}$ is a constant, the density is found in the form $\rho(z) = \frac{1}{2}(\rho_l + \rho_g) + \frac{1}{2}(\rho_l - \rho_g) \tanh(z/2\bar{z})$ with the characteristic length $\bar{z} = (\varkappa/2\bar{\mathcal{A}})^{1/2}/(\rho_l - \rho_g)$.

E. Terminology

The traditional terminology used for fluids involving gradient terms in free energies is not without criticisms. The word *capillary* is traditionally used to denote the extra gradient terms in the energy, the pressure tensor, and the heat or mass fluxes. Historically, this terminology is associated with fluid rising in thin tubes or capillaries. However, there are not necessary thin tubes in a given fluid and discontinuous multiphase models also imply the rise of liquids in thin tubes provided Laplace's law is used and three point boundary conditions are applied at contact lines. In other words, the rise of fluids in

thin tubes is due to curvature effects, Laplace's law, and to the interaction with tube walls [3], instead of being a property of the bulk fluid.

A much better terminology is that of *diffuse interface*. The higher-order derivative terms indeed lead to transition zones between phases where thermodynamic and fluid properties are smooth, thereby the terminology *diffuse*. Such terms are also mainly important in thin transition zones between phases and thus the vocable *interface* is also an excellent denomination. The gradient energy terms, that are due to potential interaction between particles, are also present in a supercritical fluid where in principle, strictly speaking, there are no interfaces, but where one may still find sharp transition zones [9].

Another very good terminology is that of *cohesive fluids*. All the gradient terms are indeed due to cohesive forces that are also independent of the state of the fluid. This terminology is often used with *cohesion* of a fluid or *cohesive forces* and could also be used for such capillary or diffuse interface fluids. The only possible ambiguity is that attractive terms in van der Waals-type equations are also sometimes termed cohesion coefficients. In this work, we will equivalently use *capillary*, *diffuse interface*, or *cohesive*.

III. A DENSE GAS MIXTURE KINETIC MODEL

A kinetic theory describing moderately dense gas mixtures is summarized in this section as well as the corresponding macroscopic fluid equations [50].

A. The BBGKY hierarchy

We consider a dense gas mixture and the associated BBGKY hierarchy—also termed the YBG hierarchy [3]—governing multiple-particle distribution functions [50]. It is assumed, for the sake of simplicity, that there are no external forces acting on the particles, that the species are monatomic, and that no chemical reactions are involved between the species. The two first equations of the BBGKY hierarchy for fluid mixtures are then in the form

$$\partial_t f_i + \mathbf{c}_i \cdot \nabla_{\mathbf{r}_i} f_i = \sum_{j \in \mathfrak{S}} \int \theta_{ij} f_{ij} d\mathbf{x}_j, \quad (3.1)$$

$$\begin{aligned} \partial_t f_{ij} + \mathbf{c}_i \cdot \nabla_{\mathbf{r}_i} f_{ij} + \mathbf{c}_j \cdot \nabla_{\mathbf{r}_j} f_{ij} - \theta_{ij} f_{ij} \\ = \sum_{k \in \mathfrak{S}} \int (\theta_{ik} + \theta_{jk}) f_{ijk} d\mathbf{x}_k, \end{aligned} \quad (3.2)$$

where ∂_t denotes the time derivative operator, f_i the one-particle distribution of the i th species, \mathbf{r}_i the spatial position of a particle of the i th species, \mathbf{c}_i the velocity of a particle of the i th species, f_{ij} the pair distribution of the (i, j) th pair of species, f_{ijk} the triplet distribution of the (i, j, k) th triplet of species, $\nabla_{\mathbf{r}_i}$ the derivative operator with respect to the spatial coordinate \mathbf{r}_i , and $\nabla_{\mathbf{c}_i}$ the derivative operator with respect to the velocity \mathbf{c}_i . We also denote for short by \mathbf{x}_i the pair of vectors $\mathbf{x}_i = (\mathbf{r}_i, \mathbf{c}_i)$ and by $d\mathbf{x}_i$ the volume element $d\mathbf{r}_i d\mathbf{c}_i$. The differential operator θ_{ij} is given by

$$\theta_{ij} = \frac{1}{m_i} \nabla_{\mathbf{r}_i} \varphi_{ij} \cdot \nabla_{\mathbf{c}_i} + \frac{1}{m_j} \nabla_{\mathbf{r}_j} \varphi_{ij} \cdot \nabla_{\mathbf{c}_j}, \quad (3.3)$$

where m_i denotes the mass of a particle of the i th species and φ_{ij} the interaction potential between particles of the i th and j th species that only depends on the interparticle distance $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$ and we denote by $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ the difference between the particle spatial positions. Strictly speaking, we should denote differently the spatial positions of two colliding particles when $i = j$, but these subtleties will be left implicit for the sake of notational simplicity [50]. We will also sometimes denote by \mathbf{r} a common coordinate for all distributions f_i , $i \in \mathfrak{S}$. The traditional distribution functions are $f_i = f_i(\mathbf{x}_i, t) = f_i(\mathbf{r}_i, \mathbf{c}_i, t)$, the particle pair distribution functions are $f_{ij} = f_{ij}(\mathbf{x}_i, \mathbf{x}_j, t)$ and satisfy the symmetry relations $f_{ij}(\mathbf{x}_i, \mathbf{x}_j, t) = f_{ji}(\mathbf{x}_j, \mathbf{x}_i, t)$. The triplet particle distribution functions f_{ijk} similarly depend on $(\mathbf{x}_i, \mathbf{x}_j, \mathbf{x}_k, t)$ but triple collision effects are not taken into account in this work. For a single gas, the equations of the BBGKY hierarchy have been derived independently by Bogoliubov [66], Born and Green [67], Kirkwood [68], and introduced by Yvon [69], and we refer to the literature [50,51,56,57,70] for more details.

The aim of this work being the derivation of macroscopic equations governing Cahn-Hilliard-type fluids, we only use in this work a simplified kinetic theory of moderately dense gas mixtures. In particular internal states, triple collisions or chemical reactions are not taken into account and we will also simplify some of the collision integrals associated with dense gases. We refer to the literature for various difficulties associated with dense gases like bound states, divergences with quadruple collisions in three dimensions, long time tails for time correlation functions [52,54,56–58] as well as for internal states and chemical reactions [62–64].

B. Macroscopic equations

The gas number density of the i th species n_i is given by

$$n_i(\mathbf{r}_i, t) = \int f_i(\mathbf{r}_i, \mathbf{c}_i, t) d\mathbf{c}_i, \quad (3.4)$$

the total number density n by $n(\mathbf{r}, t) = \sum_{i \in \mathfrak{S}} n_i(\mathbf{r}, t)$, and the pair number densities n_{ij} read

$$n_{ij}(\mathbf{r}_i, \mathbf{r}_j, t) = \int f_{ij}(\mathbf{r}_i, \mathbf{c}_i, \mathbf{r}_j, \mathbf{c}_j, t) d\mathbf{c}_i d\mathbf{c}_j. \quad (3.5)$$

The partial density of the i th species ρ_i is given by $\rho_i = m_i n_i$, the total mass density by $\rho(\mathbf{r}, t) = \sum_{i \in \mathfrak{S}} \rho_i(\mathbf{r}, t)$ and the gas velocity \mathbf{v} is defined by

$$\rho(\mathbf{r}, t) \mathbf{v}(\mathbf{r}, t) = \sum_{i \in \mathfrak{S}} \int m_i \mathbf{c}_i f_i(\mathbf{r}, \mathbf{c}_i, t) d\mathbf{c}_i, \quad (3.6)$$

where the distributions are evaluated at a common location $\mathbf{r} = \mathbf{r}_i$, $i \in \mathfrak{S}$.

The internal energy per unit volume of the fluid is decomposed into

$$\mathcal{E} = \mathcal{E}^K + \mathcal{E}^P, \quad (3.7)$$

where \mathcal{E}^K is the kinetic part and originates from the peculiar motion of the particles whereas \mathcal{E}^P is the potential part due to

the species pair interaction potentials [50,56,57]. The kinetic part \mathcal{E}^K and the potential part \mathcal{E}^P may be written

$$\mathcal{E}^K(\mathbf{r}, t) = \sum_{i \in \mathfrak{S}} \int \frac{1}{2} m_i |\mathbf{c}_i - \mathbf{v}|^2 f_i(\mathbf{r}, \mathbf{c}_i, t) d\mathbf{c}_i, \quad (3.8)$$

$$\mathcal{E}^P(\mathbf{r}, t) = \sum_{i, j \in \mathfrak{S}} \int \frac{1}{2} \varphi_{ij}(r_{ij}) n_{ij}(\mathbf{r}, \mathbf{r} + \mathbf{r}_{ij}, t) d\mathbf{r}_{ij}, \quad (3.9)$$

where we have used $d\mathbf{x}_j = d\mathbf{r}_j d\mathbf{c}_j = d\mathbf{r}_{ij} d\mathbf{c}_j$.

The general macroscopic equations in unclosed form may further be obtained by taking appropriate moments of Eqs. (3.1) and (3.2) as detailed in Appendix C. The mass conservation equation is derived by integrating Eq. (3.1) with respect to \mathbf{c}_i and reads

$$\partial_t \rho_i + \nabla \cdot (\rho_i \mathbf{v}) + \nabla \cdot \overline{\mathcal{F}}_i = 0, \quad (3.10)$$

where the mass diffusion flux of the i th species $\overline{\mathcal{F}}_i$ is given by

$$\overline{\mathcal{F}}_i = \int m_i (\mathbf{c}_i - \mathbf{v}) f_i d\mathbf{c}_i. \quad (3.11)$$

The momentum equation, obtained by multiplying Eq. (3.1) by $m_i \mathbf{c}_i$, integrating with respect to \mathbf{c}_i , and summing over $i \in \mathfrak{S}$, is in the form

$$\partial_t (\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) + \nabla \cdot \mathcal{P} = 0, \quad (3.12)$$

and the total pressure tensor \mathcal{P} is decomposed into

$$\mathcal{P} = \mathcal{P}^K + \mathcal{P}^P. \quad (3.13)$$

The tensor \mathcal{P}^K is the traditional kinetic part

$$\mathcal{P}^K(\mathbf{r}, t) = \sum_{i \in \mathfrak{S}} \int m_i (\mathbf{c}_i - \mathbf{v}) \otimes (\mathbf{c}_i - \mathbf{v}) f_i(\mathbf{r}, \mathbf{c}_i, t) d\mathbf{c}_i, \quad (3.14)$$

whereas \mathcal{P}^P is the potential part

$$\begin{aligned} \mathcal{P}^P(\mathbf{r}, t) = & - \sum_{i, j \in \mathfrak{S}} \frac{1}{2} \int \frac{\varphi'_{ij}(r_{ij})}{r_{ij}} \mathbf{r}_{ij} \otimes \mathbf{r}_{ij} \\ & \times n_{ij}[\mathbf{r} - (1 - \alpha)\mathbf{r}_{ij}, \mathbf{r} + \alpha\mathbf{r}_{ij}, t] d\alpha d\mathbf{r}_{ij}, \end{aligned} \quad (3.15)$$

and the scalar α must be integrated over (0,1). The potential part of the pressure tensor $\mathcal{P}^P(\mathbf{r}, t)$ has been obtained in a form similar to that of single-species fluids [57] that is more convenient than the expressions presented by Cohen *et al.* [50]. The tensor \mathcal{P}^K corresponds to the transfer of momentum due to the flow of particles and \mathcal{P}^P to the transfer of momentum among particles due to intermolecular forces between species pairs [56,57].

The conservation equation for internal energy \mathcal{E} is next derived in several steps and may also be combined with the kinetic energy conservation equation to derive the total energy conservation equation. One first multiply Eq. (3.1) by $\frac{1}{2} m_i |\mathbf{c}_i - \mathbf{v}|^2$, integrate with respect to \mathbf{c}_i , and sum over $i \in \mathfrak{S}$, to obtain a balance equation for the kinetic part \mathcal{E}^K of the internal energy. The balance equation for the potential part of the energy \mathcal{E}^P is then obtained by multiplying the two-particle distribution function Eq. (3.2) by the potential energy $\frac{1}{2} \varphi_{ij}(r_{ij})$, integrating with respect to \mathbf{c}_i , \mathbf{c}_j , and $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$, and summing over $i, j \in \mathfrak{S}$. After lengthy calculations, the

governing equation for $\mathcal{E} = \mathcal{E}^K + \mathcal{E}^P$ is found in the form

$$\partial_t \mathcal{E} + \nabla \cdot (\mathbf{v} \mathcal{E}) + \nabla \cdot \mathcal{Q} = -\mathcal{P} : \nabla \mathbf{v}, \quad (3.16)$$

where the total heat flux is decomposed into

$$\mathcal{Q} = \mathcal{Q}^K + \mathcal{Q}_1^P + \mathcal{Q}_2^P. \quad (3.17)$$

The kinetic part \mathcal{Q}^K is in the form

$$\mathcal{Q}^K(\mathbf{r}, t) = \sum_{i \in \mathfrak{S}} \frac{1}{2} \int m_i |\mathbf{c}_i - \mathbf{v}|^2 (\mathbf{c}_i - \mathbf{v}) f_i(\mathbf{r}, \mathbf{c}_i, t) d\mathbf{c}_i, \quad (3.18)$$

the potential parts \mathcal{Q}_1^P and \mathcal{Q}_2^P are given by

$$\begin{aligned} \mathcal{Q}_1^P(\mathbf{r}, t) &= \sum_{i, j \in \mathfrak{S}} \frac{1}{2} \int \varphi_{ij}(r_{ij}) (\mathbf{c}_i - \mathbf{v}) f_{ij}(\mathbf{r}, \mathbf{c}_i, \mathbf{r} + \mathbf{r}_{ij}, \mathbf{c}_j, t) \\ &\quad \times d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j, \end{aligned} \quad (3.19)$$

$$\begin{aligned} \mathcal{Q}_2^P(\mathbf{r}, t) &= - \sum_{i, j \in \mathfrak{S}} \frac{1}{4} \int \frac{\varphi'_{ij}(r_{ij})}{r_{ij}} \mathbf{r}_{ij} \mathbf{r}_{ij} \cdot (\mathbf{c}_i - \mathbf{v} + \mathbf{c}_j - \mathbf{v}) \\ &\quad \times f_{ij}(\mathbf{r} - (1 - \alpha)\mathbf{r}_{ij}, \mathbf{c}_i, \mathbf{r} + \alpha\mathbf{r}_{ij}, \mathbf{c}_j, t) \\ &\quad \times d\alpha d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j, \end{aligned} \quad (3.20)$$

and the scalar α must be integrated over $(0,1)$. The potential parts of the heat flux \mathcal{Q}_2^P is written here in a form similar to that of single-species fluids [57] that is more convenient than the expression presented by Cohen *et al.* [50]. The heat flow vector \mathcal{Q}^K is similar to that of a dilute gas and represents the transfer of thermal energy due to the flow of particles. The first potential part \mathcal{Q}_1^P represents the flow of potential energy carried by the particles and \mathcal{Q}_2^P represents the flux of energy associated with long range forces between species pairs and thermal agitation. The scalar product of \mathcal{Q}_2^P with a normal vector to a surface element represents the work per unit time done on all species particles on one side, that move with their peculiar motion, by all species particles on the other side, and both fluxes \mathcal{Q}_1^P and \mathcal{Q}_2^P only depend on the species peculiar velocities $\mathbf{c}_i - \mathbf{v}$ and $\mathbf{c}_j - \mathbf{v}$.

C. Generalized Boltzmann equations

The kinetic theory of dense gas mixtures involves generalized Boltzmann equations governing the species one-particle distribution functions f_i , $i \in \mathfrak{S}$. These equations are obtained by expanding multiple distribution functions with clusters of independent particles and using Bogoliubov's method [49–51], in a similar way as for single-species fluids [52,54,56–58].

Neglecting the contributions arising from triple distributions or more [54,57], the pair distribution functions f_{ij} are first written in the form $f_{ij} = \mathfrak{S}_{ij} f_i f_j$ where the streaming operators \mathfrak{S}_{ij} read

$$\mathfrak{S}_{ij} = \exp(-t\mathfrak{H}_{ij}) \exp(t\mathfrak{H}_i) \exp(t\mathfrak{H}_j), \quad (3.21)$$

with $\mathfrak{H}_i = \mathbf{c}_i \cdot \nabla_{\mathbf{r}_i}$ denoting the Hamiltonian operator of the i th particle alone and

$$\mathfrak{H}_{ij} = \mathbf{c}_i \cdot \nabla_{\mathbf{r}_i} + \mathbf{c}_j \cdot \nabla_{\mathbf{r}_j} - \theta_{ij},$$

the Hamiltonian operator of the (i, j) th pair of particles. The streaming operators $\exp(t\mathfrak{H}_s)$ form Abelian one parameter

groups of operators and correspond to the streaming of systems of s independent particle under the influence of the Hamiltonian \mathfrak{H}_s . It has been assumed that the initial distribution is a product of uncorrelated distributions $f_{ij}(\mathbf{x}_i, \mathbf{x}_j, 0) = f_i(\mathbf{x}_i, 0) f_j(\mathbf{x}_j, 0)$. A fundamental assumption in the model is that the operators $\mathfrak{S}_{ij}(\mathbf{x}_i, \mathbf{x}_j, t)$ have finite limits as t is large with respect to the collision time

$$\tau_{ij}(\mathbf{r}_i, \mathbf{c}_i, \mathbf{r}_j, \mathbf{c}_j) = \lim_{t \rightarrow \infty} \mathfrak{S}_{ij}(\mathbf{r}_i, \mathbf{c}_i, \mathbf{r}_j, \mathbf{c}_j, t), \quad (3.22)$$

so that the pair distribution functions are finally in the form

$$f_{ij} = \tau_{ij} f_i f_j, \quad i, j \in \mathfrak{S}, \quad (3.23)$$

and we refer for more details to Bennett and Curtiss [49], Cohen *et al.* [50], and Braun *et al.* [51] as well as to Choh and Uhlenbeck [52], Ferziger and Kaper [57], Dorfman and van Beijeren [58], and García-Colín *et al.* [54] for the single-species situation.

The generalized Boltzmann equations governing one-particle distribution functions f_i , $i \in \mathfrak{S}$, are then in the form

$$\partial_t f_i + \mathbf{c}_i \cdot \nabla_{\mathbf{r}_i} f_i = \mathcal{J}_i(f), \quad (3.24)$$

where $f = (f_i)_{i \in \mathfrak{S}}$ and the i th collision operator \mathcal{J}_i reads

$$\mathcal{J}_i(f) = \sum_{j \in \mathfrak{S}} \int \theta_{ij} \tau_{ij} f_i(\mathbf{r}_i, \mathbf{c}_i, t) f_j(\mathbf{r}_j, \mathbf{c}_j, t) d\mathbf{x}_j. \quad (3.25)$$

A key point in these operators is that the one-particle species distribution functions are taken at different positions \mathbf{r}_i and \mathbf{r}_j .

The action of the operators τ_{ij} is notably discussed in Refs. [52–54,57,58,71] and we let for convenience

$$\mathbf{r}'_i = \tau_{ij} \mathbf{r}_i, \quad \mathbf{r}'_j = \tau_{ij} \mathbf{r}_j, \quad (3.26)$$

$$\mathbf{c}'_i = \tau_{ij} \mathbf{c}_i, \quad \mathbf{c}'_j = \tau_{ij} \mathbf{c}_j. \quad (3.27)$$

From the conservation of momentum during a collision we have

$$m_i \mathbf{c}_i + m_j \mathbf{c}_j = m_i \mathbf{c}'_i + m_j \mathbf{c}'_j, \quad (3.28)$$

and from the conservation of energy

$$\frac{1}{2} m_i |\mathbf{c}_i|^2 + \frac{1}{2} m_j |\mathbf{c}_j|^2 + \varphi_{ij}(r_{ij}) = \frac{1}{2} m_i |\mathbf{c}'_i|^2 + \frac{1}{2} m_j |\mathbf{c}'_j|^2. \quad (3.29)$$

From the relation $f_{ij} = \tau_{ij} f_i f_j$ we further obtain the Bogoliubov distribution [56,66]

$$f_{ij}(\mathbf{r}_i, \mathbf{c}_i, \mathbf{r}_j, \mathbf{c}_j, t) = f_i(\mathbf{r}'_i, \mathbf{c}'_i, t) f_j(\mathbf{r}'_j, \mathbf{c}'_j, t), \quad (3.30)$$

and we define $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ and $\mathbf{r}'_{ij} = \mathbf{r}'_j - \mathbf{r}'_i$. In addition, when r_{ij} is large, there is no interaction between the particles, in such a way that τ_{ij} reduces to the identity operator and the pair distribution function $f_{ij}(\mathbf{x}_i, \mathbf{x}_j, t)$ is then the product of two independent distributions $f_i(\mathbf{x}_i, t) f_j(\mathbf{x}_j, t)$.

Decomposing f_{ij} in the form

$$\begin{aligned} f_{ij} &= f_i(\mathbf{r}_i, \mathbf{c}'_i, t) f_j(\mathbf{r}_i, \mathbf{c}'_j, t) + [f_i(\mathbf{r}'_i, \mathbf{c}'_i, t) f_j(\mathbf{r}'_j, \mathbf{c}'_j, t) \\ &\quad - f_i(\mathbf{r}_i, \mathbf{c}'_i, t) f_j(\mathbf{r}_i, \mathbf{c}'_j, t)], \end{aligned} \quad (3.31)$$

we may accordingly split the operator $\mathcal{J}_i(f)$ into

$$\mathcal{J}_i(f) = \mathcal{J}_i^{(0)}(f) + \mathcal{J}_i^{(1)}(f), \quad (3.32)$$

where

$$\mathcal{J}_i^{(0)}(f) = \sum_{j \in \mathfrak{S}} \int \theta_{ij} f_i(\mathbf{r}_i, \mathbf{c}'_i, t) f_j(\mathbf{r}_i, \mathbf{c}'_j, t) d\mathbf{x}_j, \quad (3.33)$$

$$\begin{aligned} \mathcal{J}_i^{(1)}(f) = \sum_{j \in \mathfrak{S}} \int & \theta_{ij} [f_i(\mathbf{r}'_i, \mathbf{c}'_i, t) f_j(\mathbf{r}'_i, \mathbf{c}'_j, t) \\ & - f_i(\mathbf{r}_i, \mathbf{c}'_i, t) f_j(\mathbf{r}_i, \mathbf{c}'_j, t)] d\mathbf{x}_j. \end{aligned} \quad (3.34)$$

The generalized Boltzmann equations may finally be written in the form

$$\partial_t f_i + \mathbf{c}_i \cdot \nabla_{\mathbf{r}_i} f_i = \mathcal{J}_i^{(0)}(f) + \mathcal{J}_i^{(1)}(f), \quad (3.35)$$

and Bogoliubov has established that the operators $\mathcal{J}_i^{(0)}(f)$ coincide with Boltzmann operators [57,66]. One may also note that the operator $\mathcal{J}_i^{(0)}$ only involves the particular distributions $f_i(\mathbf{r}_i, \mathbf{c}'_i, t) f_j(\mathbf{r}_i, \mathbf{c}'_j, t)$, whereas the terms $\mathcal{J}_i^{(1)}(f)$ may be interpreted as *nonlocal perturbations* arising from the difference of spatial positions during collisions.

D. Differential expressions for $\mathcal{J}_i^{(1)}$

We rewrite in this section the perturbed collision operators $\mathcal{J}_i^{(1)}$, $i \in \mathfrak{S}$, as sums of integro-differential operators for future use. To this aim, we first describe the traditional splitting of \mathbf{r}'_i and \mathbf{r}'_j using the invariance of centers of mass during collisions [50,57]. The center of mass \mathbf{r}_{ij}^m during a collision between particles of the i th and j th species may be written

$$\mathbf{r}_{ij}^m = \mu_i \mathbf{r}_i + \mu_j \mathbf{r}_j,$$

where μ_i and μ_j are the mass ratios for the (i, j) th pair

$$\mu_i = \frac{m_i}{m_i + m_j}, \quad \mu_j = \frac{m_j}{m_i + m_j}. \quad (3.36)$$

From the invariance of \mathbf{r}_{ij}^m in a collision we have $\tau_{ij} \mathbf{r}_{ij}^m = \mathbf{r}_{ij}^m$ and from $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ we also have $\mathbf{r}_{ij}^m = \mathbf{r}_i + \mu_j \mathbf{r}_{ij}$. After some algebra, it is obtained that

$$\mathbf{r}'_i = \mathbf{r}_i + \mu_j \mathbf{r}_{ij} - \mu_j \mathbf{r}'_{ij}, \quad (3.37)$$

$$\mathbf{r}'_j = \mathbf{r}_i + \mu_j \mathbf{r}_{ij} + \mu_i \mathbf{r}'_{ij}, \quad (3.38)$$

where $\mathbf{r}'_{ij} = \mathbf{r}'_j - \mathbf{r}'_i$. To split $\mathcal{J}_i^{(1)}$, $i \in \mathfrak{S}$, we then write that

$$\delta \mathbf{r}_i = \mathbf{r}'_i - \mathbf{r}_i = \mathbf{r}'_i - \mathbf{r}_{ij}^m + \mathbf{r}_{ij}^m - \mathbf{r}_i, \quad (3.39)$$

$$\delta \mathbf{r}_j = \mathbf{r}'_j - \mathbf{r}_i = \mathbf{r}'_j - \mathbf{r}_{ij}^m + \mathbf{r}_{ij}^m - \mathbf{r}_i, \quad (3.40)$$

and use that $\mathbf{r}_{ij}^m - \mathbf{r}_i = \mu_j \mathbf{r}_{ij}$ whereas $\mathbf{r}'_i - \mathbf{r}_{ij}^m = -\mu_j \mathbf{r}'_{ij}$ and $\mathbf{r}'_j - \mathbf{r}_{ij}^m = \mu_i \mathbf{r}'_{ij}$.

From Eq. (3.34) of $\mathcal{J}_i^{(1)}(f)$ as well as Eqs. (3.39) and (3.40), we obtain

$$\mathcal{J}_i^{(1)}(f) = \mathcal{J}_i^{(1),s}(f) + \mathcal{J}_i^{(1),a}(f), \quad (3.41)$$

where

$$\begin{aligned} \mathcal{J}_i^{(1),a}(f) = \sum_{j \in \mathfrak{S}} \int & \theta_{ij} [f_i(\mathbf{r}'_i, \mathbf{c}'_i, t) f_j(\mathbf{r}'_j, \mathbf{c}'_j, t) \\ & - f_i(\mathbf{r}_{ij}^m, \mathbf{c}'_i, t) f_j(\mathbf{r}_{ij}^m, \mathbf{c}'_j, t)] d\mathbf{x}_j, \end{aligned} \quad (3.42)$$

$$\begin{aligned} \mathcal{J}_i^{(1),s}(f) = \sum_{j \in \mathfrak{S}} \int & \theta_{ij} [f_i(\mathbf{r}_{ij}^m, \mathbf{c}'_i, t) f_j(\mathbf{r}_{ij}^m, \mathbf{c}'_j, t) \\ & - f_i(\mathbf{r}_i, \mathbf{c}'_i, t) f_j(\mathbf{r}_i, \mathbf{c}'_j, t)] d\mathbf{x}_j. \end{aligned} \quad (3.43)$$

The operators $\mathcal{J}_i^{(1),a}$ measure the collision effects with respect to the centers of mass, whereas the operators $\mathcal{J}_i^{(1),s}$ measure the shift between the local coordinates and the centers of mass.

Letting for convenience

$$f_{ij}^{\text{cl}}(\mathbf{r}, \mathbf{c}_i, \mathbf{c}_j, t) = f_i(\mathbf{r}, \mathbf{c}'_i, t) f_j(\mathbf{r}, \mathbf{c}'_j, t), \quad (3.44)$$

and using that $\mathbf{r}_{ij}^m - \mathbf{r}_i = \mu_j \mathbf{r}_{ij}$, we obtain after some calculus that

$$\begin{aligned} \mathcal{J}_i^{(1),s}(f) = \sum_{j \in \mathfrak{S}} \mu_j \int & \theta_{ij} \partial_{\mathbf{r}} f_{ij}^{\text{cl}} [\alpha \mathbf{r}_{ij}^m + (1 - \alpha) \mathbf{r}_i, \mathbf{c}_i, \mathbf{c}_j, t] \\ & \cdot \mathbf{r}_{ij} d\alpha d\mathbf{x}_j. \end{aligned} \quad (3.45)$$

Similarly, since $\mathbf{r}'_i - \mathbf{r}_{ij}^m = -\mu_j \mathbf{r}'_{ij}$ and $\mathbf{r}'_j - \mathbf{r}_{ij}^m = \mu_i \mathbf{r}'_{ij}$, we have

$$\mathcal{J}_i^{(1),a}(f) = - \sum_{j \in \mathfrak{S}} \mu_{ij} \int \theta_{ij} \Xi_{ij}(\alpha, \mathbf{r}_{ij}^m, \mathbf{r}'_{ij}, \mathbf{c}'_i, \mathbf{c}'_j, t) \cdot \mathbf{r}'_{ij} d\alpha d\mathbf{x}_j, \quad (3.46)$$

where

$$\begin{aligned} \Xi_{ij}(\alpha, \mathbf{r}_{ij}^m, \mathbf{r}'_{ij}, \mathbf{c}'_i, \mathbf{c}'_j, t) & \\ & = \frac{1}{m_i} \partial_{\mathbf{r}} f_i(\mathbf{r}_{ij}^m - \alpha \mu_j \mathbf{r}'_{ij}, \mathbf{c}'_i, t) f_j(\mathbf{r}_{ij}^m + \alpha \mu_i \mathbf{r}'_{ij}, \mathbf{c}'_j, t) \\ & - f_i(\mathbf{r}_{ij}^m - \alpha \mu_j \mathbf{r}'_{ij}, \mathbf{c}'_i, t) \frac{1}{m_j} \partial_{\mathbf{r}} f_j(\mathbf{r}_{ij}^m + \alpha \mu_i \mathbf{r}'_{ij}, \mathbf{c}'_j, t). \end{aligned}$$

The perturbed collision operator $\mathcal{J}_i^{(1)}(f)$ may thus be written as the sum of two integro-differential operators $\mathcal{J}_i^{(1),a}$ and $\mathcal{J}_i^{(1),s}$.

The transformed coordinates \mathbf{r}'_i and \mathbf{r}'_j , and the transformed velocities \mathbf{c}'_i and \mathbf{c}'_j , are often used in kinetic developments concerning dense gases because they cannot be expressed simply in terms of \mathbf{r}_i , \mathbf{r}_j , \mathbf{c}_i and \mathbf{c}_j . Only the terms arising from the center of mass \mathbf{r}_{ij}^m and associated with $\mathcal{J}_i^{(1),s}$ appear to be convenient to manipulate.

E. Kinetic entropy

A kinetic entropy for dense gas mixtures has been introduced by Cohen *et al.* [50] and reads

$$\begin{aligned} S^{\text{K}} = - \sum_{i \in \mathfrak{S}} k_{\text{B}} \int & f_i [\log(h_{\text{p}}^3 f_i / m_i^3) - 1] d\mathbf{c}_i \\ & - \frac{1}{2} \sum_{i, j \in \mathfrak{S}} k_{\text{B}} \int \{ f_{ij} [\log(f_{ij} / f_i f_j) - 1] + f_i f_j \} \\ & \times d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j, \end{aligned} \quad (3.47)$$

where h_{p} is the Planck constant. In the situation of single-species fluids, similar entropies have been introduced in a pioneering work by Stratonovich [72] and investigated by Nettleton and Green [73], and the entropy Eq. (3.47) has also been used by Klimontovich [74].

An important point about such kinetic entropies is that, contrarily to the case of dilute fluids, there is no known H theorem for spatially nonuniform systems governed by the generalized Boltzmann Eqs. (3.24). An H-theorem has only been established for single-species fluids in the special situation of *spatially homogeneous* fluids by Klimontovich [74]. The entropies of systems of particles for the BBGKY hierarchy have also been investigated by Martynov who established that there are entropy exchanges between the different levels of approximations [75] and by Singer who discussed different truncations of Kirkwood-type for the BBGKY hierarchy [76].

IV. NONIDEAL MULTICOMPONENT FLUIDS WITH NORMAL DIFFUSION

We investigate in this section the equation governing nonideal multicomponent fluids with normal diffusive processes, i.e., *without diffuse interface terms*. To this aim, we introduce a proper scaling for the generalized Boltzmann Eqs. (3.35) and use the Chapman-Enskog method. This new scaling clarifies the apparition of nonzero contributions from the collision terms \mathcal{J}_i in the fluid equations. It also directly yields that equilibrium distributions are Maxwellian distributions at zeroth order and will allow the derivation of Cahn-Hilliard fluid equations. This derivation of nonideal fluid governing equations only uses first-order Taylor expansions of pair distribution functions in the fluxes. The resulting nonideal thermodynamic properties will be denoted with the superscript u to be consistent with Sec. II. We also simplify some of the collision integrals for dense gas mixtures, typically assuming that repulsive potentials between pair of particles are hard. As a result, the diffusive fluxes are directly expressed in terms of chemical potential gradients, as expected from thermodynamics, without linear system inversions as in previous work [50,51]. We also avoid the use of pressure-based thermodynamic functions—like the species enthalpies or entropies—for expressing the diffusion fluxes [50,51], since such thermodynamic functions may explode at unstable thermodynamic states [9].

A. A new Enskog scaling

The generalized Boltzmann Eqs. (3.35) are written in the form

$$\partial_t f_i + \mathbf{c}_i \cdot \nabla_{\mathbf{r}_i} f_i = \frac{1}{\epsilon} \mathcal{J}_i^{(0)}(f) + \mathcal{J}_i^{(1)}(f), \quad (4.1)$$

where ϵ is the formal parameter associated with Enskog expansion. The distributions f_i , $i \in \mathfrak{S}$, are correspondingly expanded in the form

$$f_i = f_i^{(0)} [1 + \epsilon \phi_i^{(1)} + \mathcal{O}(\epsilon^2)], \quad (4.2)$$

where $\phi_i^{(1)}$ is the perturbed distribution for the i th species in the Navier-Stokes regime.

The traditional scaling of the collision operators \mathcal{J}_i used in previous work has been in the form \mathcal{J}_i/ϵ instead of $\mathcal{J}_i^{(0)}/\epsilon$. This leads to conceptual difficulties since there are invariably nonzero gradient terms arising from \mathcal{J}_i in the Euler and Navier-Stokes equations [52,54,56–58]. Since these terms arise from $\mathcal{J}_i^{(1)}$, the new scaling leads to a clearer derivation. Moreover, with the traditional scaling, it is necessary to *assume* at zeroth order that the distributions are

Maxwellians [50,56,57], whereas it will be simply derived by using Eq. (4.1). Finally, we do not use a distinguished limit where the Enskog parameter is taken to be equal to a typical rescaled macroscopic gradient [52,54,56–58]. This will notably allow the derivation of Cahn-Hilliard-type equations where typically first-order derivatives are mixed with third-order derivatives.

B. The Euler regime

We investigate in this section the zeroth order or Euler regime and the corresponding kinetic equations are

$$\mathcal{J}_i^{(0)}(f^{(0)}) = 0, \quad i \in \mathfrak{S}, \quad (4.3)$$

where $f^{(0)} = (f_i^{(0)})_{i \in \mathfrak{S}}$. Keeping in mind that the operators $\mathcal{J}_i^{(0)}$ coincide with the Boltzmann collision operators [57,66], and using Boltzmann H theorem, we obtain that the distributions $f_i^{(0)}$ are local Maxwellians

$$f_i^{(0)} = n_i \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \exp \left(- \frac{m_i |\mathbf{c}_i - \mathbf{v}|^2}{2k_B T} \right), \quad i \in \mathfrak{S}, \quad (4.4)$$

where n_i denotes the number density of the i th species, m_i the mass of the particles of the i th species, \mathbf{v} the local fluid velocity and T the local fluid temperature. The temperature T ensures that the local value of the internal energy density \mathcal{E} is recovered with $f^{(0)} = (f_i^{(0)})_{i \in \mathfrak{S}}$, including its potential part [50,51,54,57].

The zeroth-order pair distributions $f_{ij}^{(0)}$ are then evaluated from Eq. (3.44) and are in the form [50,54,55,57]

$$f_{ij}^{(0),cl} = f_i^{(0)}(\mathbf{r}_i, \mathbf{c}'_i, t) f_j^{(0)}(\mathbf{r}_i, \mathbf{c}'_j, t),$$

with both distributions $f_i^{(0)}$ and $f_j^{(0)}$ evaluated at $\mathbf{r} = \mathbf{r}_i = \mathbf{r}_j$ as suggested by the kernel of $\mathcal{J}^{(0)} = (\mathcal{J}_i^{(0)})_{i \in \mathfrak{S}}$ [50,52,54,57]. From the conservation of momentum Eq. (3.28) and energy Eq. (3.29) these zeroth-order distribution $f_{ij}^{(0),cl}$ may be rewritten as

$$f_{ij}^{(0),cl} = f_i^{(0)}(\mathbf{r}_i, \mathbf{c}_i, t) f_j^{(0)}(\mathbf{r}_i, \mathbf{c}_j, t) g_{ij}(\mathbf{r}_i, \mathbf{r}_{ij}), \quad (4.5)$$

where $g_{ij}(\mathbf{r}_i, \mathbf{r}_{ij})$ denotes the equilibrium correlation function

$$g_{ij}(\mathbf{r}_i, \mathbf{r}_{ij}) = \exp \left(- \frac{\varphi_{ij}(r_{ij})}{k_B T(\mathbf{r}_i)} \right), \quad (4.6)$$

evaluated at temperature $T(\mathbf{r}_i)$.

The nonideal multicomponent Euler fluid equations are then obtained at zeroth order [50,52,54,56–58]. To derive these equations, the most convenient method is to use the Maxwellian distributions Eq. (4.4), the pair correlation functions Eq. (4.5), and the macroscopic equations of Sec. III B with first-order Taylor expansions of pair distribution functions. This method is equivalent to directly take moments of the kinetic equations and use the differential expressions of the perturbed collision operators to evaluate $\mathcal{J}_i^{(1)}(f^{(0)})$. The multicomponent Euler equations are obtained in the form [50]

$$\partial_t \rho_i + \nabla \cdot (\rho_i \mathbf{v}) = 0, \quad i \in \mathfrak{S}, \quad (4.7)$$

$$\partial_t (\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) + \nabla p^u = 0, \quad (4.8)$$

$$\partial_t \mathcal{E}^u + \nabla \cdot (\mathbf{v} \mathcal{E}^u) + p^u \nabla \cdot \mathbf{v} = 0, \quad (4.9)$$

where the internal energy \mathcal{E}^u and the pressure p^u are detailed in the next section. The zeroth-order pressure tensor thus reduces to $\mathcal{P}^{(0)} = p^u \mathbf{I}$ and the zeroth-order mass and heat diffusion fluxes vanish $\overline{\mathcal{F}}_i^{(0)} = 0$, $i \in \mathfrak{S}$, and $\mathcal{Q}^{(0)} = 0$.

C. Thermodynamic properties

Using the one and two-particle distribution functions Eqs. (4.4) and (4.5), and the macroscopic equations of Eq. (3.2), the pressure is found in the form

$$p^u = \sum_{i \in \mathfrak{S}} n_i k_B T - \sum_{i, j \in \mathfrak{S}} \frac{1}{6} n_i n_j \int \phi'_{ij}(r_{ij}) r_{ij} g_{ij}(r_{ij}) d\mathbf{r}_{ij}. \quad (4.10)$$

Integrating by parts the integrals in Eq. (4.10), it is obtained that

$$\begin{aligned} & \frac{1}{6} \int \phi'_{ij}(r_{ij}) r_{ij} g_{ij}(\mathbf{r}_i, r_{ij}) d\mathbf{r}_{ij} \\ &= \frac{2\pi}{3} \int \phi'_{ij}(r_{ij}) r_{ij}^3 g_{ij}(\mathbf{r}_i, r_{ij}) dr_{ij} \\ &= 2\pi k_B T \int \mathfrak{f}_{ij} r_{ij}^2 dr_{ij} = \frac{1}{2} k_B T \int \mathfrak{f}_{ij} d\mathbf{r}_{ij}, \end{aligned}$$

where \mathfrak{f}_{ij} denote the (i, j) th species pair Mayer function

$$\mathfrak{f}_{ij}(\mathbf{r}_i, \mathbf{r}_{ij}) = \exp\left(-\frac{\phi_{ij}(r_{ij})}{k_B T(\mathbf{r}_i)}\right) - 1. \quad (4.11)$$

Denoting by β_{ij} the (i, j) th species pair second virial coefficients

$$\beta_{ij} = \int \mathfrak{f}_{ij} d\mathbf{r}_{ij}, \quad (4.12)$$

the pressure is then in the form [50]

$$p^u = \sum_{i \in \mathfrak{S}} n_i k_B T - \sum_{i, j \in \mathfrak{S}} \frac{1}{2} n_i n_j \beta_{ij} k_B T. \quad (4.13)$$

The internal energy is derived with a similar procedure and reads

$$\mathcal{E}^u = \frac{3}{2} \sum_{i \in \mathfrak{S}} n_i k_B T + \frac{1}{2} \sum_{i, j \in \mathfrak{S}} n_i n_j \int \phi_{ij}(r_{ij}) g_{ij}(r_{ij}) d\mathbf{r}_{ij}, \quad (4.14)$$

so that [50]

$$\mathcal{E}^u = \frac{3}{2} \sum_{i \in \mathfrak{S}} n_i k_B T + \frac{1}{2} \sum_{i, j \in \mathfrak{S}} n_i n_j \beta'_{ij} (k_B T)^2, \quad (4.15)$$

where $\beta'_{ij} = d\beta_{ij}/d(k_B T)$.

The fluid entropy is obtained by evaluating the kinetic entropy Eq. (3.47) with Maxwellian distributions Eq. (4.4) and the pair distribution functions Eq. (4.5). After some algebra, it is found that the volumetric entropy \mathcal{S}^u is in the form [50]

$$\mathcal{S}^u = - \sum_{i \in \mathfrak{S}} k_B n_i \left(\log(n_i \Lambda_i^3) - \frac{5}{2} \right) + \sum_{i, j \in \mathfrak{S}} \frac{1}{2} k_B n_i n_j (\beta_{ij} + k_B T \beta'_{ij}), \quad (4.16)$$

where Λ_i is the De Broglie thermal wavelength $\Lambda_i = h_p(2\pi m_i k_B T)^{-1/2}$ of the i th species. This entropy has been

shown to be second-order accurate by Cohen *et al.* [50], that is, one may establish that formally $\int \mathcal{S}^k dc_i - \mathcal{S}^u = \mathcal{O}(\epsilon^2)$.

The corresponding species Gibbs functions per molecule are next obtained in the form

$$g_i^u = k_B T \log(n_i \Lambda_i^3) - \sum_{j \in \mathfrak{S}} k_B T n_j \beta_{ij}, \quad (4.17)$$

and play an important role in diffusive processes. The mixture Gibbs function \mathcal{G}^u is then given by $\mathcal{G}^u = \sum_{k \in \mathfrak{S}} n_k g_k^u$. Cohen *et al.* [50] have also established that the volumetric Gibbs relation $d\mathcal{S}^u = d\mathcal{E}^u - \sum_{k \in \mathfrak{S}} g_k^u dn_k$ holds at second order.

Another interesting property of the species Gibbs functions g_i^u , $i \in \mathfrak{S}$, is that they are naturally pressure based, that is, the derivative of $g^u = \mathcal{G}^u/n$ with respect to the mole fraction of the i th species $x_i = n_i/n$ at fixed temperature, pressure, and other mole fractions coincides with g_i^u [77]. These species Gibbs functions g_i^u , $i \in \mathfrak{S}$, notably remain finite at states of mechanical instability when $\partial_n p^u = 0$. On the contrary, various traditional *pressure-based* thermodynamic functions like species enthalpies, entropies, or specific heats explode at unstable thermodynamic state where $\partial_n p^u = 0$, that is, when $\sum_{i, j \in \mathfrak{S}} n_i n_j \beta_{ij} = n$ [9]. Such exploding thermodynamic functions have notably been used by Cohen *et al.* [50] and Braun *et al.* [51] to express the mass and heat fluxes, so that such expressions are only valid when thermodynamic stability holds.

D. Linearized equations

At first order, taking into account the operator decomposition Eq. (3.32), the linearized equations governing the perturbed distribution functions $\phi^{(1)} = (\phi_i^{(1)})_{i \in \mathfrak{S}}$ are in the form

$$\mathcal{I}_i(\phi^{(1)}) = \psi_i^{(1)}, \quad i \in \mathfrak{S}, \quad (4.18)$$

where the i th linearized operator \mathcal{I}_i reads

$$\begin{aligned} \mathcal{I}_i(\phi^{(1)}) &= - \frac{1}{f_i^{(0)}} \sum_{j \in \mathfrak{S}} \int \theta_{ij} f_i^{(0)}(\mathbf{r}_i, \mathbf{c}'_i, t) f_j^{(0)}(\mathbf{r}_i, \mathbf{c}'_j, t) \\ &\quad \times [\phi_i^{(1)}(\mathbf{r}_i, \mathbf{c}'_i, t) + \phi_j^{(1)}(\mathbf{r}_i, \mathbf{c}'_j, t)] d\mathbf{x}_j, \end{aligned} \quad (4.19)$$

and the right-hand sides ψ_i are

$$\begin{aligned} \psi_i^{(1)} &= - (\partial_t \log f_i^{(0)} + \mathbf{c}_i \cdot \nabla_{\mathbf{r}_i} \log f_i^{(0)}) \\ &\quad + \frac{1}{f_i^{(0)}} \mathcal{J}_i^{(1)}(f^{(0)}), \quad i \in \mathfrak{S}. \end{aligned} \quad (4.20)$$

A fundamental property is now that the linearized operators \mathcal{I}_i coincide with Boltzmann linearized collision operators [57,66].

The right-hand sides $\psi^{(1)} = (\psi_i^{(1)})_{i \in \mathfrak{S}}$ are evaluated in Appendix D and may be written

$$\psi_i^{(1)} = -\psi_i^\eta : \nabla \mathbf{v} - \psi_i^\kappa \nabla \cdot \mathbf{v} - \sum_{j \in \mathfrak{S}} \psi_i^{D_j} \cdot \mathbf{X}_j^{\text{th}} - \psi_i^\lambda \cdot \nabla \left(\frac{-1}{k_B T} \right), \quad (4.21)$$

where ψ_i^η are symmetric traceless second-order tensors, ψ_i^κ are scalars, and $\psi_i^{D_j}$, $j \in \mathfrak{S}$, ψ_i^λ , are vectors. The quantity \mathbf{X}_i^{th} denotes the normal force term of the i th species arising solely

from thermodynamics, i.e., without capillary effects,

$$\mathbf{X}_i^{\text{th}} = n_i k_B T \nabla \left(\frac{g_i^{\text{u}}}{k_B T} \right) = \rho_i T \nabla \left(\frac{\bar{g}_i^{\text{u}}}{T} \right), \quad (4.22)$$

where g_i^{u} is the Gibbs function of the i th species per particle and $\bar{g}_i^{\text{u}} = g_i^{\text{u}}/m_i$ the Gibbs function per unit mass. This force term \mathbf{X}_i^{th} is the thermodynamic part of the total force term \mathbf{X}_i obtained in Eq. (2.22). This force term \mathbf{X}_i^{th} is also directly related to the thermodynamic diffusion driving force $\mathbf{X}_i^{\text{th}} = n k_B T \mathbf{d}_i^{\text{th}}$, $i \in \mathfrak{S}$. As detailed in Appendix D, the functions ψ_i^η , ψ_i^κ , $\psi_i^{D_j}$, $j \in \mathfrak{S}$, and $\psi_i^{\hat{\lambda}}$, are given by

$$\begin{aligned} \psi_i^\eta &= \frac{m_i}{k_B T} \left[(\mathbf{c}_i - \mathbf{v}) \otimes (\mathbf{c}_i - \mathbf{v}) - \frac{1}{3} |\mathbf{c}_i - \mathbf{v}|^2 \mathbf{I} \right] \\ &\times \left(1 - \sum_{j \in \mathfrak{S}} \frac{n_j m_j \beta_{ij}}{m_i + m_j} \right) + \sum_{j \in \mathfrak{S}} \mu_{ij} n_j \bar{\alpha}_{ij}^\eta, \end{aligned} \quad (4.23)$$

$$\begin{aligned} \psi_i^\kappa &= - \left(\frac{3}{2} - \frac{m_i |\mathbf{c}_i - \mathbf{v}|^2}{2 k_B T} \right) \left[\frac{2}{3} \left(1 - \sum_{j \in \mathfrak{S}} \frac{n_j m_j \beta_{ij}}{m_i + m_j} \right) \right. \\ &\left. + \frac{1}{T \partial_T \mathcal{E}^u} \left(\sum_{l \in \mathfrak{S}} n_l \partial_{n_l} \mathcal{E}^u - \mathcal{E}^u - p^u \right) \right] \\ &+ \sum_{j \in \mathfrak{S}} \mu_{ij} n_j \bar{\alpha}_{ij}^\kappa, \end{aligned} \quad (4.25)$$

$$\psi_i^{D_j} = \frac{1}{n_i k_B T} (\delta_{ij} - y_i) (\mathbf{c}_i - \mathbf{v}), \quad (4.26)$$

$$\begin{aligned} \psi_i^{\hat{\lambda}} &= -(\mathbf{c}_i - \mathbf{v}) \left(\frac{3}{2} k_B T - \frac{m_i |\mathbf{c}_i - \mathbf{v}|^2}{2} \right) \\ &\times \left(1 - \sum_{j \in \mathfrak{S}} \frac{n_j m_j \beta_{ij}}{m_i + m_j} \right) \\ &+ (\mathbf{c}_i - \mathbf{v}) \left[\frac{3}{2} k_B T + \sum_{j \in \mathfrak{S}} \frac{n_j m_i}{m_i + m_j} \beta'_{ij} (k_B T)^2 \right. \\ &\left. - \frac{m_i}{\rho} (\mathcal{E}^u + p^u) \right] + \sum_{j \in \mathfrak{S}} \mu_{ij} n_j \bar{\alpha}_{ij}^{\hat{\lambda}}, \end{aligned} \quad (4.28)$$

where $\mu_{ij} = m_i m_j / (m_i + m_j)$ denotes the reduced mass of the (i, j) th pair of particles, $y_i = \rho_i / \rho$ denotes the mass fraction of the i th species and $\bar{\alpha}_{ij}^\eta$, $\bar{\alpha}_{ij}^\kappa$ and $\bar{\alpha}_{ij}^{\hat{\lambda}}$ are collision integrals associated with dense gas mixtures. Some collision integrals associated with dense gases $\bar{\alpha}_{ij}^{D_j}$, $i, j \in \mathfrak{S}$, have been simplified by assuming that interaction potentials between pairs of particles are hard Eq. (D11) as detailed in Appendix D. The first-order Eqs. (4.18)–(4.21) are essentially similar to classical first-order relations obtained for dilute gases, except that there are extra gradient terms arising from the perturbed collision operators $\mathcal{J}_i^{(1)}$ and that the force terms \mathbf{X}_i^{th} , $i \in \mathfrak{S}$, involve chemical potential gradients.

The distributions $\phi_i^{(1)}$ are then uniquely determined by imposing Enskog-type constraints so that the true value of the local macroscopic variables n_i , \mathbf{v} , and T , or equivalently \mathcal{E} , are determined by the distributions $f_i^{(0)}$ alone [54,57]. These

constraints, summarized in Appendix E, have been shown to reduce to [50,54,78]

$$\int f_i^{(0)} \phi_i^{(1)} d\mathbf{c}_i = 0, \quad (4.29)$$

$$\sum_{i \in \mathfrak{S}} \int m_i (\mathbf{c}_i - \mathbf{v}) f_i^{(0)} \phi_i^{(1)} d\mathbf{c}_i = 0, \quad (4.30)$$

$$\sum_{i \in \mathfrak{S}} \int \frac{1}{2} m_i |\mathbf{c}_i - \mathbf{v}|^2 f_i^{(0)} \phi_i^{(1)} d\mathbf{c}_i = 0. \quad (4.31)$$

In particular, the potential and gradient parts are eliminated in the constraints [50]. By linearity and isotropy of the collision operator, we may decompose $\phi_i^{(1)}$ in the form

$$\phi_i = -\phi_i^\eta : \nabla \mathbf{v} - \phi_i^\kappa \nabla \cdot \mathbf{v} - \sum_{j \in \mathfrak{S}} \phi_i^{D_j} \cdot \mathbf{X}_j^{\text{th}} - \phi_i^{\hat{\lambda}} \cdot \nabla \left(\frac{-1}{k_B T} \right), \quad (4.32)$$

where ϕ_i^η are traceless second-order symmetric tensor, ϕ_i^κ are scalars, $\phi_i^{D_j}$, $j \in \mathfrak{S}$, and $\phi_i^{\hat{\lambda}}$, are vectors.

Each unknown $\phi^\mu = (\phi_i^\mu)_{i \in \mathfrak{S}}$ for $\mu \in \{\eta, \kappa, D_j, \hat{\lambda}\}$ then satisfies a system of tensorial integral equations $\mathcal{I}_i(\phi^\mu) = \psi_i^\mu$, $i \in \mathfrak{S}$, and the $\phi^\mu = (\phi_i^\mu)_{i \in \mathfrak{S}}$ have the following structure [50]

$$\phi_i^\eta = \varphi_i^\eta (|\mathbf{c}_i - \mathbf{v}|^2) \left[(\mathbf{c}_i - \mathbf{v}) \otimes (\mathbf{c}_i - \mathbf{v}) - \frac{1}{3} |\mathbf{c}_i - \mathbf{v}|^2 \mathbf{I} \right],$$

$$\phi_i^\kappa = \varphi_i^\kappa (|\mathbf{c}_i - \mathbf{v}|^2),$$

$$\phi_i^{D_j} = \varphi_i^{D_j} (|\mathbf{c}_i - \mathbf{v}|^2) (\mathbf{c}_i - \mathbf{v}), \quad j \in \mathfrak{S},$$

$$\phi_i^{\hat{\lambda}} = \varphi_i^{\hat{\lambda}} (|\mathbf{c}_i - \mathbf{v}|^2) (\mathbf{c}_i - \mathbf{v}),$$

where φ_i^η , φ_i^κ , $\varphi_i^{D_j}$ and $\varphi_i^{\hat{\lambda}}$ are scalar isotropic functions of the velocities, i.e., that only depend on $|\mathbf{c}_i - \mathbf{v}|^2$. The tensorial distributions $\phi^\mu = (\phi_i^\mu)_{i \in \mathfrak{S}}$ further satisfy the induced constraints derived from Eqs. (4.29)–(4.31) according to their tensorial rank

$$\int f_i^{(0)} \phi_i^\kappa d\mathbf{c}_i = 0, \quad i \in \mathfrak{S},$$

$$\sum_{i \in \mathfrak{S}} \int \frac{1}{2} m_i |\mathbf{c}_i - \mathbf{v}|^2 f_i^{(0)} \phi_i^\kappa d\mathbf{c}_i = 0, \quad (4.33)$$

$$\sum_{i \in \mathfrak{S}} \int m_i (\mathbf{c}_i - \mathbf{v}) f_i^{(0)} \phi_i^{D_j} d\mathbf{c}_i = 0, \quad j \in \mathfrak{S}, \quad (4.34)$$

$$\sum_{i \in \mathfrak{S}} \int m_i (\mathbf{c}_i - \mathbf{v}) f_i^{(0)} \phi_i^{\hat{\lambda}} d\mathbf{c}_i = 0. \quad (4.35)$$

E. The Navier-Stokes-Fourier-Fick regime

1. Dissipative fluxes for all thermodynamic states

The resulting macroscopic equations at first order of Enskog expansion are of Navier-Stokes-Fourier-Fick-type [50]. The situation of single-species fluids, that only involves the fluid and energy equations, has been discussed in Refs. [52,54,56–58].

By substituting the expansion Eq. (4.32) into the expression of the diffusion fluxes Eq. (3.11), pressure tensors Eqs. (3.14), (3.15), and heat fluxes Eqs. (3.19), (3.20), it is

obtained after some algebra that

$$\mathcal{P} = p^u \mathbf{I} + \mathcal{P}^d, \quad \overline{\mathcal{F}}_i = \overline{\mathcal{F}}_i^d, \quad \mathcal{Q} = \mathcal{Q}^d, \quad (4.36)$$

where

$$\mathcal{P}^d = -\mathbf{v} \nabla \cdot \mathbf{v} \mathbf{I} - \eta \left(\nabla \mathbf{v} + \nabla \mathbf{v}^t - \frac{2}{3} \nabla \cdot \mathbf{v} \mathbf{I} \right), \quad (4.37)$$

$$\overline{\mathcal{F}}_i^d = - \sum_{j \in \mathfrak{S}} L_{ij} \nabla \left(\frac{\overline{g}_j^u}{T} \right) - L_{ie} \nabla \left(\frac{-1}{T} \right), \quad (4.38)$$

$$\mathcal{Q}^d = - \sum_{i \in \mathfrak{S}} L_{ei} \nabla \left(\frac{\overline{g}_i^u}{T} \right) - L_{ee} \nabla \left(\frac{-1}{T} \right), \quad (4.39)$$

and \mathbf{v} denotes the volume viscosity, η the shear viscosity, L_{ij} , $i, j \in \mathfrak{S} \cup \{e\}$ the mass and heat transport coefficients, and \overline{g}_i^u the Gibbs function per unit mass of the i th species. This thermodynamic form Eqs. (4.38) and (4.39) for the diffusion and heat fluxes is then fully compatible with rational thermodynamics [59,61].

Focusing in more details on mass fluxes $\overline{\mathcal{F}}_i = \int m_i (\mathbf{c}_i - \mathbf{v}) f_i^{(0)} \phi_i^{(1)} d\mathbf{c}_i$, $i \in \mathfrak{S}$, using the expression of the right-hand sides of Eq. (4.26), and using standard kinetic theory techniques, it is obtained that

$$\mathcal{V}_i = - \sum_{j \in \mathfrak{S}} \frac{1}{3} k_B T [\phi^{D_i}, \phi^{D_j}] \mathbf{X}_j^{\text{th}} - \frac{1}{3} k_B T [\phi^{D_i}, \phi^{\hat{\lambda}}] \nabla \left(\frac{-1}{k_B T} \right), \quad (4.40)$$

where for any $\xi = (\xi_i)_{i \in \mathfrak{S}}$ and $\zeta = (\zeta_i)_{i \in \mathfrak{S}}$, with ξ_i and ζ_i functions of \mathbf{c}_i , the bracket $\llbracket \xi, \zeta \rrbracket$ reads

$$\llbracket \xi, \zeta \rrbracket = \langle \langle f^{(0)} \xi, \mathcal{I} \zeta \rangle \rangle = \langle \langle f^{(0)} \mathcal{I} \xi, \zeta \rangle \rangle, \quad (4.41)$$

with $\mathcal{I} \zeta = [\mathcal{I}_i(\zeta)]_{i \in \mathfrak{S}}$, $f^{(0)} \xi = (f_i^{(0)} \xi_i)_{i \in \mathfrak{S}}$, and the scalar product $\langle \langle \xi, \zeta \rangle \rangle$ is given by

$$\langle \langle \xi, \zeta \rangle \rangle = \sum_{i \in \mathfrak{S}} \int \xi_i \odot \zeta_i d\mathbf{c}_i, \quad (4.42)$$

with \odot denoting the tensor maximum contraction symbol. Equations (4.38) are then directly obtained upon letting

$$L_{ij} = \frac{1}{3} \rho_i \rho_j k_B T^2 [\phi^{D_i}, \phi^{D_j}], \quad i, j \in \mathfrak{S}, \quad (4.43)$$

$$L_{ie} = \frac{1}{3} \rho_i T [\phi^{D_i}, \phi^{\hat{\lambda}}], \quad i \in \mathfrak{S}. \quad (4.44)$$

The resulting expressions for transport coefficients in dense gases are generally highly complex and we refer to the literature for more details [50]. The symmetry relations have notably been investigated by Ernst [79], including triple collisions.

The coefficients $L = (L_{ij})_{i, j \in \mathfrak{S} \cup \{e\}}$ are usually termed phenomenological coefficients in the thermodynamic literature but are not anymore phenomenological when obtained from the kinetic theory of dense gases and the link with the traditional transport coefficients is addressed in the next section.

2. Dissipative fluxes with thermodynamic stability

We discuss in this section the link between the matrix L and the traditional fluid mixture transport coefficients. To define the standard diffusion coefficients, it is necessary to subtract a temperature gradient from the forces \mathbf{X}_i^{th} , $i \in \mathfrak{S}$, and this procedure traditionally involves pressure-based thermodynamic

property. The traditional transport coefficients thus require the mechanical stability condition $\partial_\rho p < 0$.

In the situation of mechanical stability, the map $(T, \rho, y_1, \dots, y_{n_s}) \mapsto (T, p, y_1, \dots, y_{n_s})$ is locally invertible and one may introduce thermodynamic properties as functions of $(T, p, y_1, \dots, y_{n_s})$. For any thermodynamic function $\overline{\mathcal{A}}^u(T, \rho, y_1, \dots, y_{n_s})$ we may then define the pressure-based thermodynamic property

$$\widetilde{\mathcal{A}}^u(T, p, y_1, \dots, y_{n_s}) = \overline{\mathcal{A}}^u(T, \rho, y_1, \dots, y_{n_s}),$$

and the pressure-based Gibbs relation is in the form

$$d\widetilde{g}^u = \widetilde{v}^u dp^u - \widetilde{s}^u dT + \sum_{k \in \mathfrak{S}} \widetilde{g}_k^u dy_k. \quad (4.45)$$

Letting then for any thermodynamic property \mathcal{A}^u

$$\widetilde{\mathcal{A}}_k^u = \partial_{y_k} \widetilde{\mathcal{A}}^u(T, p, y_1, \dots, y_{n_s}),$$

we recover from Eq. (4.45) that the Gibbs functions \widetilde{g}_k^u , $k \in \mathfrak{S}$, are naturally pressure-based $\widetilde{g}_k^u = \overline{g}_k$, $k \in \mathfrak{S}$. We also obtain from Eq. (4.45) after some calculus

$$d \left(\frac{\widetilde{g}_k^u}{T} \right) = \frac{\widetilde{v}_k^u}{T} dp - \frac{\widetilde{h}_k^u}{T^2} dT + \sum_{l \in \mathfrak{S}} \frac{\partial y_l \widetilde{g}_k^u}{T} dy_l,$$

where $\widetilde{h}_k^u = \partial_{y_k} h^u(T, p, y_1, \dots, y_{n_s})$ is the enthalpy of the k th species, $h^u = e^u + p^u/\rho$ the mixture enthalpy per unit mass and $\rho h^u = \mathcal{H}^u = \mathcal{E}^u + p^u$. The classical diffusion driving forces \mathbf{d}_i^{cl} , $i \in \mathfrak{S}$, are then obtained by subtracting from the thermodynamic diffusion driving forces $\mathbf{d}_i^{\text{th}} = \mathbf{x}_i m_i \nabla (\overline{g}^u/k_B T)$ the proper temperature gradient terms

$$\mathbf{d}_i^{\text{cl}} = \mathbf{d}_i^{\text{th}} + \frac{\mathbf{x}_i m_i \widetilde{h}_i^u}{k_B T^2} \nabla T, \quad i \in \mathfrak{S}. \quad (4.46)$$

The resulting traditional diffusion driving forces \mathbf{d}_i^{cl} are then linear combinations of mole fractions and pressure gradients.

To relate the mass and heat transport coefficients L_{ij} , $i, j \in \mathfrak{S} \cup \{e\}$, to the traditional transport coefficients, we denote by L the matrix

$$L = \begin{pmatrix} L_{11} & \cdots & L_{1n_s} & L_{1e} \\ \vdots & \ddots & \vdots & \vdots \\ L_{n_s 1} & \cdots & L_{n_s n_s} & L_{n_s e} \\ L_{e1} & \cdots & L_{en_s} & L_{ee} \end{pmatrix}. \quad (4.47)$$

The matrix L is symmetric positive semidefinite and has a one-dimensional nullspace spanned by $(0, 1, \dots, 1)^t$. We introduce then the modified matrix $\widehat{L} = A^t L A$ with

$$\widehat{L} = \begin{pmatrix} \widehat{L}_{11} & \cdots & \widehat{L}_{1n_s} & \widehat{L}_{1e} \\ \vdots & \ddots & \vdots & \vdots \\ \widehat{L}_{n_s 1} & \cdots & \widehat{L}_{n_s n_s} & \widehat{L}_{n_s e} \\ \widehat{L}_{e1} & \cdots & \widehat{L}_{en_s} & \widehat{L}_{ee} \end{pmatrix}, \quad (4.48)$$

$$A = \begin{pmatrix} & & -\widetilde{h}_1^u \\ & \mathbb{I}_{n_s} & \vdots \\ 0 & \cdots & 0 & 1 \end{pmatrix},$$

where \mathbb{I}_{n_s} denotes the identity matrix in \mathbb{R}^{n_s} . The high pressure multicomponent diffusion coefficients D_{ij} , $i, j \in \mathfrak{S}$, thermal

diffusion coefficients D_i^{TD} , $i \in \mathfrak{S}$, and partial thermal conductivity $\widehat{\lambda}$ are next defined by [60,80]

$$D_{ij} = \frac{nk_b \widehat{L}_{ij}}{\rho_i \rho_j}, \quad i, j \in \mathfrak{S}, \quad D_i^{\text{TD}} = \frac{\widehat{L}_{ie}}{\rho_i T} = \frac{\widehat{L}_{ei}}{\rho_i T}, \quad i \in \mathfrak{S},$$

$$\widehat{\lambda} = \frac{\widehat{L}_{ee}}{T^2}. \quad (4.49)$$

Using the high pressure coefficients Eq. (4.49) and the traditional diffusion driving forces Eq. (4.46), the fluxes \mathcal{F}_i , $i \in \mathfrak{S}$, and \mathcal{Q} may be rewritten in the more familiar form

$$\overline{\mathcal{F}}_i = - \sum_{j \in \mathfrak{S}} \rho_j D_{ij} \mathbf{d}_j^{\text{cl}} - \rho_i D_i^{\text{TD}} \nabla \ln T, \quad i \in \mathfrak{S}, \quad (4.50)$$

$$\mathcal{Q} = -nk_b T \sum_{j \in \mathfrak{S}} D_j^{\text{TD}} \mathbf{d}_j^{\text{cl}} - \widehat{\lambda} \nabla T + \sum_{i \in \mathfrak{S}} \widetilde{h}_i^u \mathcal{F}_i, \quad (4.51)$$

where D_{ij} are the symmetric multicomponent diffusion coefficients, D_i^{TD} the thermal diffusion coefficients, and $\widehat{\lambda}$ the partial thermal conductivity. The symmetric multicomponent diffusion coefficients D_{ij} have notably been considered by Kurochkin *et al.* [80] and generalize the coefficients introduced for dilute gases by Waldmann [56,81,82].

F. Van der Waals equation of state

To recover the van der Waals equation of state, we may assume that the interaction potentials φ_{ij} are such that

$$\varphi_{ij}(r_{ij}) = \begin{cases} +\infty & \text{if } 0 \leq r_{ij} \leq \sigma_{ij}, \\ \varphi_{ij}(r_{ij}) < \infty & \text{if } \sigma_{ij} < r_{ij}, \end{cases} \quad (4.52)$$

for some positive collision diameters σ_{ij} depending on the species pairs (i, j) . One may also assume that φ_{ij} is attractive $\varphi_{ij} < 0$ for $2\sigma_{ij} < r_{ij}$, and increases towards zero as $r_{ij} \rightarrow \infty$. One may then recover the van der Waals equation of state by decomposing the integrals $2\pi \int \mathfrak{f}_{ij} d\mathbf{r}_{ij}$ in two zones and proceeding as for single-species fluids [83–85]. More specifically, one may write that

$$\int \mathfrak{f}_{ij} r_{ij}^2 d\mathbf{r}_{ij} = \int_0^{2\sigma_{ij}} \mathfrak{f}_{ij} r_{ij}^2 d\mathbf{r}_{ij} + \int_{2\sigma_{ij}}^{\infty} \mathfrak{f}_{ij} r_{ij}^2 d\mathbf{r}_{ij},$$

use $\mathfrak{f}_{ij} = -1$ over $(0, 2\sigma_{ij})$, linearize the Mayer functions $\mathfrak{f}_{ij} \approx -\varphi_{ij}/k_b T$ for $2\sigma_{ij} < r_{ij}$, to get that

$$2\pi k_b T \int \mathfrak{f}_{ij} d\mathbf{r}_{ij} \approx -4k_b T \frac{4\pi \sigma_{ij}^3}{3} - 2\pi \int_{2\sigma_{ij}}^{\infty} \varphi_{ij}(\mathbf{r}_{ij}) r_{ij}^2 d\mathbf{r}_{ij},$$

and the corresponding pressure law reads

$$p^u = \sum_{i \in \mathfrak{S}} n_i k_b T + \sum_{i, j \in \mathfrak{S}} n_i n_j k_b T \frac{16\pi \sigma_{ij}^3}{3}$$

$$+ \sum_{i, j \in \mathfrak{S}} n_i n_j 2\pi \int_{2\sigma_{ij}}^{\infty} \varphi_{ij}(\mathbf{r}_{ij}) r_{ij}^2 d\mathbf{r}_{ij}.$$

Assuming naturally that σ_{ij} is in the form $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)$, $i, j \in \mathfrak{S}$, where σ_i is a typical collision diameter of the i th species, the sum $\sum_{i, j \in \mathfrak{S}} n_i n_j \sigma_{ij}^3$ may be rewritten $\sum_{i, j \in \mathfrak{S}} \frac{1}{4} n_i n_j (\sigma_j^3 + 3\sigma_j^2 \sigma_i)$ and approximated as

$\sum_{i, j \in \mathfrak{S}} n_i n_j \sigma_j^3$. Assuming then that the volume occupied by the particles is small,

$$\sum_{j \in \mathfrak{S}} n_j \frac{4\pi \sigma_j^3}{3} \ll 1,$$

we obtain the state law

$$p^u = \sum_{i \in \mathfrak{S}} \frac{n_i k_b T}{1 - \sum_{j \in \mathfrak{S}} b_j n_j} - \sum_{i, j \in \mathfrak{S}} n_i n_j \mathbf{a}_{ij}, \quad (4.53)$$

where

$$b_j = 4 \frac{4\pi \sigma_j^3}{3}, \quad \mathbf{a}_{ij} = -2\pi \int_{2\sigma_{ij}}^{\infty} \varphi_{ij}(\mathbf{r}_{ij}) r_{ij}^2 d\mathbf{r}_{ij},$$

and the van der Waals equation of state for mixtures has been recovered from Eq. (4.10) in a similar way as in statistical physics [83–85]. Moreover, we have also obtained from Eq. (4.10) the traditional mixing rules for the covolume $\sum_{j \in \mathfrak{S}} b_j n_j$ as well as for the attractive term $\sum_{i, j \in \mathfrak{S}} n_i n_j \mathbf{a}_{ij}$ introduced by Berthelot [86].

G. Orders of magnitude

We estimate in this section the order of magnitude of nonideal terms in thermodynamic functions. To this aim, we introduce a characteristic temperature T^* , a characteristic interparticle distance r^* , and a characteristic particle mass m^* . The characteristic number density is then $n^* = 1/r^{*3}$ and the particle thermal velocity c^* such that $m^* c^{*2} = k_b T^*$. We also denote by τ_k^* a characteristic collision time, by $l_k^* = \tau_k^* c^*$ the mean free path, by τ_H^* a characteristic hydrodynamic time or fluid time and by $l_H^* = \tau_H^* c^*$ the corresponding fluid length. We further introduce a characteristic collision diameter σ^* , also typical of the range of the interaction potentials, and we generally have $\sigma^* \ll r^* \ll l_k^* \ll l_H^*$ as well as $\sigma^{*2} l_k^* = r^{*3}$ and the Knudsen number is given by l_k^*/l_H^* .

From Eq. (4.12) of the second virial coefficients β_{ij} , $i, j \in \mathfrak{S}$, we then obtain that $\beta^* = \beta_{ij}^* = \sigma^{*3}$. We may next estimate that the nonideal terms in the pressure Eq. (4.13) are typically of the order $k_b T^* \sigma^{*3}/r^{*6}$. The ratio of the nonideal terms $\sum_{i, j \in \mathfrak{S}} \frac{1}{2} n_i n_j \beta_{ij} k_b T$ to the ideal terms $\sum_{i \in \mathfrak{S}} n_i k_b T$ may then be estimated to be of the order $(\sigma^*/r^*)^3$ as discussed notably by Landau, Lifchitz and Pitaevskii [70,84]. The nonideal to ideal term ratio is thus usually modest but increase with the number density $n^* = 1/r^{*3}$ and is ultimately of order unity for liquid like states where the interparticle distance r^* is of the order of the collision diameter σ^* .

V. EULER AND VAN-DER-WAALS FLUID EQUATIONS

We derive in this section the Euler and van der Waals fluid equations at zeroth order of Enskog expansion. The method combines symmetrized zeroth-order pair distribution functions as well as higher-order Taylor expansions of pair distribution functions.

A. The symmetrized pair correlation functions

Previous work concerning single-species fluids has shown that higher-order expansions of pair distribution functions are

required to derive diffuse interface models [15]. It is thus important to select proper pair distribution functions before using Taylor expansions.

The zeroth-order pair distribution functions Eq. (4.5) of Sec. IV B have traditionally been used in the literature for investigating gas mixtures [49–51] as well as for investigating single-species fluids [52,54,56–58]. When substituted in the governing equations and when using *first-order* Taylor expansions, the nonideal fluid equations with normal diffusive processes [50], presented in Sec. IV, are obtained. However, these pair distribution functions $f_{ij}^{(0),cl}$ are not without criticism. A first point is that $f_{ij}^{(0),cl}$ is not symmetric in its arguments as it should be for a pair distribution function. Moreover, when r_{ij} is large, $g_{ij}(\mathbf{r}_i, r_{ij})$ become unity and $f_{ij}^{(0),cl}$ reduces to $f_i^{(0)}(\mathbf{r}_i, \mathbf{c}_i, t)f_j^{(0)}(\mathbf{r}_j, \mathbf{c}_j, t)$ that has no physical meaning.

In this section, instead of using the distributions $f_{ij}^{(0),cl}$, the following symmetrized pair distribution functions $f_{ij}^{(0),sy}$ are used [15]

$$f_{ij}^{(0),sy} = f_i^{(0)}(\mathbf{r}_i, \mathbf{c}_i, t)f_j^{(0)}(\mathbf{r}_j, \mathbf{c}_j, t)g_{ij}(\bar{\mathbf{r}}_{i,j}, r_{ij}), \quad i, j \in \mathfrak{S}, \quad (5.1)$$

where $\bar{\mathbf{r}}_{i,j}$ denotes a symmetric average of \mathbf{r}_i and \mathbf{r}_j like the center of mass $\bar{\mathbf{r}}_{i,j} = \mu_i \mathbf{r}_i + \mu_j \mathbf{r}_j$ or the midpoint $\frac{1}{2}(\mathbf{r}_i + \mathbf{r}_j)$. We first note that $f_{ij}^{(0),sy}$ and $f_{ij}^{(0),cl}$ coincide at zeroth order when $\mathbf{r}_i = \mathbf{r}_j = \bar{\mathbf{r}}_{i,j}$ so that $f_{ij}^{(0),sy}$ is also in the kernel of the operator $\mathcal{J}_i^{(0)}$ that only consider the values of f_{ij} on the linear subspace $\mathbf{r}_i = \mathbf{r}_j$. Moreover, $f_{ij}^{(0),sy}$ is symmetric in its argument and the limit for large r_{ij} is the natural uncorrelated pair distribution function $f_i^{(0)}(\mathbf{r}_i, \mathbf{c}_i, t)f_j^{(0)}(\mathbf{r}_j, \mathbf{c}_j, t)$. Previous work has also shown that diffuse interface fluid models may be recovered from such symmetrized distributions in the situation of single-species fluids [15]. To derive the macroscopic equations, the symmetrized zeroth-order pair distribution functions $f_{ij}^{(0),sy}$ are thus used with the general balance equations established in Sec. III B as well as with *higher-order* Taylor expansions of pair distribution functions.

Although a nonequilibrium correlation function g_{ij} could in principle also be used, we will nevertheless use a correlation function Eq. (4.6) in the simplified form $g_{ij}(\mathbf{r}_i, r_{ij})$ as if the temperature were locally uniform. There is indeed no clear expression for a nonequilibrium correlation function at interfaces and many solutions have been proposed like using various average temperatures, or the center of mass temperature, or else solving integral equations [3,87,88]. In addition, temperature variations during phase change are modest, keeping in mind that equilibrium fronts are isotherms, at variance with large density variations. Therefore, using either \mathbf{r}_i or a symmetric average $\bar{\mathbf{r}}_{i,j}$ would yield the same results and we will frequently denote by $g_{ij}(r_{ij})$ the corresponding function, the dependence on \mathbf{r}_i being left implicit. Using a locally uniform correlation function g_{ij} will imply that the capillary coefficients are naturally independent of temperature in agreement with the van der Waals and Rayleigh approximate expressions.

In summary, we have to revisit the Chapman-Enskog method for mixtures of dense gases using the Enskog scal-

ing Eq. (4.1), the zeroth pair distribution function Eq. (5.1), as well as higher-order Taylor expansions of pair distribution functions, following the derivation of single-species diffuse interface fluid equations [15]. Since new thermodynamic properties depending on derivatives will be obtained, we keep the superscript “u” to denote the nonideal bulk phase thermodynamic properties obtained in Sec. IV that do not involve gradients. As a general result, when pair distribution functions are expanded in the potential parts of the internal energy and the pressure tensor, nonideal terms are obtained at zeroth order, whereas diffuse interface terms involving density gradients are obtained at second order.

B. A generalized Korteweg tensor

We consider the tensor \mathcal{P}^p arising from interaction potentials Eq. (3.15) and look for *extra terms* with *two spatial derivatives* \mathcal{P}^{ex} arising from second-order expansions of the distribution functions $f_{ij}^{(0),sy}(\mathbf{r}_i, \mathbf{c}_i, \mathbf{r}_j, \mathbf{c}_j, t) = f_i^{(0)}(\mathbf{r}_i, \mathbf{c}_i, t)f_j^{(0)}(\mathbf{r}_j, \mathbf{c}_j, t)g_{ij}(r_{ij})$. We use Taylor expansions of $f_{ij}^{(0),sy}$ and only keep the extra terms involving two derivatives.

The relevant integrand factors in Eq. (3.15) may first be expanded in the form

$$\begin{aligned} n_{ij}(\mathbf{r}_i - (1 - \alpha)\mathbf{r}_{ij}, \mathbf{r}_i + \alpha\mathbf{r}_{ij}, t) \\ \approx [n_i(\mathbf{r}_i) - (1 - \alpha)\nabla n_i(\mathbf{r}_i) \cdot \mathbf{r}_{ij} \\ + \frac{1}{2}(1 - \alpha)^2 \nabla^2 n_i(\mathbf{r}_i) : (\mathbf{r}_{ij} \otimes \mathbf{r}_{ij})] \\ \times [n_j(\mathbf{r}_i) + \alpha \nabla n_j(\mathbf{r}_i) \cdot \mathbf{r}_{ij} \\ + \frac{1}{2}\alpha^2 \nabla^2 n_j(\mathbf{r}_i) : (\mathbf{r}_{ij} \otimes \mathbf{r}_{ij})] \times g_{ij}(r_{ij}), \end{aligned}$$

where the dependencies on time t have been left implicit. Extracting the terms with two derivatives, the relevant integrands involve the factors

$$-\alpha(1 - \alpha) \nabla n_i(\mathbf{r}_i) \cdot \mathbf{r}_{ij} \nabla n_j(\mathbf{r}_i) \cdot \mathbf{r}_{ij}$$

and

$$\begin{aligned} \frac{1}{2}(1 - \alpha)^2 n_j(\mathbf{r}_i) \nabla^2 n_i(\mathbf{r}_i) : (\mathbf{r}_{ij} \otimes \mathbf{r}_{ij}) \\ + \frac{1}{2}\alpha^2 n_i(\mathbf{r}_i) \nabla^2 n_j(\mathbf{r}_i) : (\mathbf{r}_{ij} \otimes \mathbf{r}_{ij}). \end{aligned}$$

Incidentally, the products $n_i(\mathbf{r}_i)n_j(\mathbf{r}_i)$ are already taken into account in the state law Eq. (4.13), whereas odd terms yield zero contributions. Odd terms only contribute in first-order linearized equations, that is, in the dissipative fluxes [50,54,57].

Focusing on the first integrands, we note that

$$\nabla n_i(\mathbf{r}_i) \cdot \mathbf{r}_{ij} \nabla n_j(\mathbf{r}_i) \cdot \mathbf{r}_{ij} = \nabla n_i(\mathbf{r}_i) \otimes \nabla n_j(\mathbf{r}_i) : (\mathbf{r}_{ij} \otimes \mathbf{r}_{ij}),$$

and using $\int_0^1 \alpha(1 - \alpha) d\alpha = \frac{1}{6}$ we obtain a first extra contribution \mathbf{p}_1 to the pressure tensor in the form

$$\begin{aligned} \mathbf{p}_1 = \sum_{i,j \in \mathfrak{S}} \frac{1}{12} \int \frac{\varphi'_{ij}(r_{ij})}{r_{ij}} g_{ij}(r_{ij}) \mathbf{r}_{ij} \otimes \mathbf{r}_{ij} \\ \times \nabla n_i \otimes \nabla n_j : (\mathbf{r}_{ij} \otimes \mathbf{r}_{ij}) d\mathbf{r}_{ij}. \end{aligned}$$

We may now use the identity Eq. (F3) from Appendix F to perform the integrations over $\mathbf{r}_{ij} \in \mathbb{R}^3$, and, using elementary

symmetries, we obtain that

$$\mathbf{p}_1 = \sum_{i,j \in \mathfrak{S}} \frac{\varkappa_{ij}}{6} (2\nabla n_i \otimes \nabla n_j + \nabla n_i \cdot \nabla n_j \mathbf{I}),$$

where the diffuse interface or capillarity coefficients \varkappa_{ij} are defined by

$$\begin{aligned} \varkappa_{ij} &= \frac{1}{30} \int \varphi'_{ij}(r_{ij}) g_{ij}(r_{ij}) r_{ij}^3 d\mathbf{r}_{ij} \\ &= \frac{2\pi}{15} \int \varphi'_{ij}(r_{ij}) g_{ij}(r_{ij}) r_{ij}^5 dr_{ij}. \end{aligned} \quad (5.2)$$

Focusing next on integrands from the Hessian matrices $\nabla^2 n_i$, using $\int_0^1 \alpha^2 d\alpha = \int_0^1 (1-\alpha)^2 d\alpha = \frac{1}{3}$, and using elementary symmetries, we obtain a second extra contribution \mathbf{p}_2 to the pressure tensor in the form

$$\mathbf{p}_2 = - \sum_{i,j \in \mathfrak{S}} \frac{n_i}{6} \int \frac{\varphi'_{ij}(r_{ij})}{r_{ij}} g_{ij}(r_{ij}) \mathbf{r}_{ij} \otimes \mathbf{r}_{ij} \nabla^2 n_j : (\mathbf{r}_{ij} \otimes \mathbf{r}_{ij}) d\mathbf{r}_{ij}.$$

Using again the identity Eq. (F3) to perform the integrations over $\mathbf{r}_{ij} \in \mathbb{R}^3$, and using elementary symmetries, we obtain that

$$\mathbf{p}_2 = - \sum_{i,j \in \mathfrak{S}} \frac{\varkappa_{ij}}{3} (2n_i \nabla^2 n_j + n_i \Delta n_j \mathbf{I}).$$

Collecting previous results, the extra pressure tensor \mathcal{P}^{ex} is found in the form

$$\begin{aligned} \mathcal{P}^{\text{ex}} &= \sum_{i,j \in \mathfrak{S}} \frac{\varkappa_{ij}}{6} (2\nabla n_i \otimes \nabla n_j + \nabla n_i \cdot \nabla n_j \mathbf{I} \\ &\quad - 4n_i \nabla^2 n_j - 2n_i \Delta n_j \mathbf{I}). \end{aligned}$$

We may then simplify \mathcal{P}^{ex} with an equivalent expression $\overline{\mathcal{P}}^{\text{ex}}$, that is, we seek $\overline{\mathcal{P}}^{\text{ex}}$ such that

$$\nabla \cdot \mathcal{P}^{\text{ex}} = \nabla \cdot \overline{\mathcal{P}}^{\text{ex}}.$$

Expressing the divergence of the Hessian matrices contributions $n_i \nabla^2 n_j$ with the help of differential identity Eq. (F7), we indeed obtain the simplified pressure tensor

$$\overline{\mathcal{P}}^{\text{ex}} = \sum_{i,j \in \mathfrak{S}} \varkappa_{ij} \left(\nabla n_i \otimes \nabla n_j - \frac{1}{2} \nabla n_i \cdot \nabla n_j \mathbf{I} - n_i \Delta n_j \mathbf{I} \right). \quad (5.3)$$

Introducing the mass-based diffuse interface coefficient $\overline{\varkappa}_{ij} = \varkappa_{ij}/m_i m_j$ and using $\rho_i = m_i n_i$ we may also rewrite the extra pressure tensor $\nabla \cdot \overline{\mathcal{P}}^{\text{ex}}$ as

$$\overline{\mathcal{P}}^{\text{ex}} = \sum_{i,j \in \mathfrak{S}} \overline{\varkappa}_{ij} \left(\nabla \rho_i \otimes \nabla \rho_j - \frac{1}{2} \nabla \rho_i \cdot \nabla \rho_j \mathbf{I} - \rho_i \Delta \rho_j \mathbf{I} \right), \quad (5.4)$$

which coincides with the generalized Korteweg tensor $\overline{\mathcal{P}}^{\text{ex}} = \mathcal{P}^{\text{KO}}$ given in Eq. (2.18) and derived from rational thermodynamics in the simplified situation of constant diffuse interface coefficients \varkappa_{ij} , $i, j \in \mathfrak{S}$. This tensor also coincide with the traditional Korteweg tensor derived for single-species fluids [15].

C. Diffuse interface coefficients

The diffuse interface or capillary coefficients \varkappa_{ij} have been found in the form (5.2) where $g_{ij}(r_{ij}) = \exp[-\varphi_{ij}(r_{ij})/k_b T(\mathbf{r}_i)]$. We may integrate by part the integral in Eq. (5.2) to get that

$$\varkappa_{ij} = \frac{1}{6} k_b T \int \mathfrak{f}_{ij} r_{ij}^2 d\mathbf{r}_{ij} = \frac{2\pi}{3} k_b T \int \mathfrak{f}_{ij} r_{ij}^4 dr_{ij}, \quad (5.5)$$

where \mathfrak{f}_{ij} is the Mayer function Eq. (4.11) of the (i, j) th species pair. The zeroth moments of the Mayer functions thus yield the second virial coefficients β_{ij} , whereas the second moments yield the diffuse interface coefficients \varkappa_{ij} , $i, j \in \mathfrak{S}$, up to the $\frac{1}{6} k_b T$ factor. A notable property of the diffuse interface coefficients \varkappa_{ij} given by Eq. (5.2) is that they are independent of the species number densities n_k , $k \in \mathfrak{S}$.

We may also simplify Eq. (5.5) to recover the van der Waals and Rayleigh capillarity coefficient. To this aim, we assume that the interaction potentials are like Eq. (4.52). We may simplify then the integral in Eq. (5.5) by neglecting the integrals over $(0, \sigma_{ij})$ and by linearizing \mathfrak{f}_{ij} in the form $\mathfrak{f}_{ij} \approx -\varphi_{ij}/k_b T$ for $r_{ij} > \sigma_{ij}$, and this yields

$$\varkappa_{ij} = -\frac{1}{6} \int_{r_{ij} > \sigma_{ij}} \varphi_{ij} r_{ij}^2 d\mathbf{r}_{ij}, \quad i, j \in \mathfrak{S}, \quad (5.6)$$

which coincides with the van der Waals and Rayleigh formula for single-species fluids [3].

The van der Waals and Rayleigh simplified capillarity coefficients Eq. (5.6) are then independent of species number densities and temperature. In a kinetic framework, the independence on temperature notably requires to neglect temperature derivative contributions of capillarity that would arise through the correlation function g_{ij} , and that are typically in the form $\int \varphi'_{ij}(r_{ij}) \varphi_{ij}^k(r_{ij}) \exp(-\frac{\varphi_{ij}}{k_b T}) r_{ij}^3 d\mathbf{r}_{ij}$ where $k \geq 1$ is an integer. We will assume in the kinetic derivation of Cahn-Hilliard equations that the diffuse interface coefficients are independent of temperature for the sake of simplicity.

We further deduce from Eq. (5.5) that the diffuse interface coefficients \varkappa_{ij} are of the order $\varkappa^* = \varkappa_{ij}^* = k_b T^* \sigma^{*5}$ and thus vary like the fifth power of the collision diameter σ^* whereas the second virial coefficients scale as $\beta^* = \sigma^{*3}$. We may thus estimate that the diffuse interface terms in the pressure Eq. (5.3) are typically of the order $\varkappa^* (\nabla n)^{*2} = k_b T^* n^* (\frac{\sigma^*}{r^*})^3 (\frac{\sigma^*}{l_{\nabla n}^*})^2$ where $l_{\nabla n}^*$ is a characteristic length typical of density gradients. The ratio of the diffuse interface terms $\sum_{i,j \in \mathfrak{S}} \varkappa_{ij} \nabla n_i \otimes \nabla n_j$ to the ideal terms $\sum_{i \in \mathfrak{S}} n_i k_b T$ may then be estimated to be

$$\left(\frac{\sigma^*}{r^*} \right)^3 \left(\frac{\sigma^*}{l_{\nabla n}^*} \right)^2. \quad (5.7)$$

The capillary terms are thus generally very small unless the interparticle distance r^* is becoming close to the collision diameter σ^* , i.e., within a liquid-like fluid, and, simultaneously, the density gradients length $l_{\nabla n}^*$ is also becoming close to σ^* , i.e., in a phase change interface like a vaporization front.

D. The energy density

We have to investigate the extra terms \mathcal{E}^{ex} arising from the energy density \mathcal{E}^{p} of potential origin Eq. (3.9)

using the pair distribution functions $f_{ij}^{(0),sy}$. Expanding the zeroth-order two-particle distribution functions $f_{ij}^{(0),sy} = f_i(\mathbf{x}_i, t)f_j(\mathbf{x}_j, t)g_{ij}(r_{ij})$ around $\mathbf{r}_j = \mathbf{r}_i + \mathbf{r}_{ij}$, the relevant extra terms involving two derivatives are in the form

$$\frac{1}{2} \int \varphi_{ij}(r_{ij})g_{ij}(r_{ij})n_i(\mathbf{r}_i)\frac{1}{2}\nabla^2 n_j(\mathbf{r}_i):(\mathbf{r}_{ij}\otimes\mathbf{r}_{ij})d\mathbf{r}_{ij}.$$

After some algebra, using the van der Waals and Rayleigh Eq. (5.6) for the capillarity coefficient, the resulting extra volumetric energy density \mathcal{E}^{ex} reads

$$\mathcal{E}^{\text{ex}} = - \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \varkappa_{ij} n_i \Delta n_j. \quad (5.8)$$

With the aim of simplifying Eq. (5.8), we may use the identity

$$\begin{aligned} - \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \varkappa_{ij} n_i \Delta n_j &= \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \varkappa_{ij} \nabla n_i \cdot \nabla n_j \\ &\quad - \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \nabla \cdot (\varkappa_{ij} n_i \nabla n_j), \end{aligned}$$

to recover the energy density in agreement with Eq. (2.7),

$$\bar{\mathcal{E}}^{\text{ex}} = \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \varkappa_{ij} \nabla n_i \cdot \nabla n_j, \quad (5.9)$$

provided we take into account the residual terms $-\sum_{i,j \in \mathfrak{S}} \frac{1}{2} \nabla \cdot (\varkappa_{ij} n_i \nabla n_j)$. By changing the energy density from \mathcal{E}^{ex} into $\bar{\mathcal{E}}^{\text{ex}}$ we indeed have to add an extra corrector term to the energy equation in the form

$$\Xi = - \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \{ \partial_t \nabla \cdot (\varkappa_{ij} n_i \nabla n_j) + \nabla \cdot [\nabla \cdot (\varkappa_{ij} n_i \nabla n_j) \mathbf{v}] \}. \quad (5.10)$$

We may rewrite this corrector as the divergence of a corrector flux \mathbf{q}_0 by using the zeroth-order species mass conservation equations $\partial_t n_i = -\nabla \cdot (n_i \mathbf{v})$, $i \in \mathfrak{S}$, keeping in mind that the capillarity coefficients \varkappa_{ij} are taken to be constant. After some algebra, the corrector term Ξ is obtained in the form $\Xi = \nabla \cdot \mathbf{q}_0$, where

$$\begin{aligned} \mathbf{q}_0 &= \sum_{i,j \in \mathfrak{S}} \varkappa_{ij} n_i \nabla \cdot \mathbf{v} \nabla n_j + \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \varkappa_{ij} n_i n_j \nabla (\nabla \cdot \mathbf{v}) \\ &\quad + \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \varkappa_{ij} n_i (\nabla \mathbf{v})^t \cdot \nabla n_j \\ &\quad + \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \varkappa_{ij} (\nabla n_i \otimes \nabla n_j + n_i \nabla^2 n_j \\ &\quad - \nabla n_i \cdot \nabla n_j \mathbf{I} - n_i \Delta n_j \mathbf{I}) \cdot \mathbf{v}. \end{aligned} \quad (5.11)$$

The change of energy density from $\mathcal{E}^{\text{ex}} = -\sum_{i,j \in \mathfrak{S}} \frac{1}{2} \varkappa_{ij} n_i \Delta n_j$ into the gradient expression $\bar{\mathcal{E}}^{\text{ex}} = \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \varkappa_{ij} \nabla n_i \cdot \nabla n_j$ has been addressed when investigating diffuse interface single-species fluids [15]. Aside from this derivation [15], it has been advocated in previous work that \mathcal{E}^{ex} may be transformed into $\bar{\mathcal{E}}^{\text{ex}}$ by integrating by parts over “a large volume” with boundary conditions insuring a null contribution of boundary terms.

This is unsatisfactory since an energy density must be a *local* quantity, not defined over “a large volume” or else under the nonlocal influence of a far boundary with unclear definition and unclear boundary conditions. Following the derivation of single-species diffuse interface fluid models [15], by *properly taking into account the correction heat flux* \mathbf{q}_0 , we clarify the *local* change of Cahn-Hilliard energy density from \mathcal{E}^{ex} to $\bar{\mathcal{E}}^{\text{ex}}$ for mixtures of fluids. Finally, since the capillarity coefficients are taken to be constant, we must have from thermodynamics that $\bar{p}^{\text{ex}} = -\bar{\mathcal{E}}^{\text{ex}}$ so that the pressure is in the form $p = p^{\text{u}} - \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \varkappa_{ij} \nabla n_i \cdot \nabla n_j$ and similarly we must have $\bar{g}_i = \bar{g}_i^{\text{u}}$.

E. A generalized Dunn and Serrin heat flux

To evaluate the extra heat flux \mathcal{Q}^{ex} arising from Taylor expansions of the zeroth pair distribution functions $f_{ij}^{(0),sy}$ in \mathcal{Q}_1^{p} and \mathcal{Q}_2^{p} and using Eq. (5.1), we need to evaluate the gradients of $f_i^{(0)}$. After some algebra we note that

$$\frac{\nabla f_i^{(0)}}{f_i^{(0)}} = \frac{m_i}{k_{\text{B}} T} (\mathbf{c}_i - \mathbf{v}) \cdot \nabla \mathbf{v} + \frac{\nabla n_i}{n_i} - \left(\frac{3}{2} - \frac{m_i |\mathbf{c}_i - \mathbf{v}|^2}{2k_{\text{B}} T} \right) \frac{\nabla T}{T}, \quad (5.12)$$

where all gradients are of course evaluated at \mathbf{r}_i and similarly that

$$\begin{aligned} \frac{\nabla^2 f_i^{(0)}}{f_i^{(0)}} &= \frac{\nabla f_i^{(0)} \otimes \nabla f_i^{(0)}}{(f_i^{(0)})^2} - \frac{m_i}{k_{\text{B}} T} \nabla \mathbf{v} \cdot \nabla \mathbf{v} + \frac{m_i}{k_{\text{B}} T} (\mathbf{c}_i - \mathbf{v}) \cdot \nabla^2 \mathbf{v} \\ &\quad - \frac{m_i}{k_{\text{B}} T^2} ((\mathbf{c}_i - \mathbf{v}) \cdot \nabla \mathbf{v}) \otimes \nabla T \\ &\quad - \frac{m_i}{k_{\text{B}} T^2} \nabla T \otimes ((\mathbf{c}_i - \mathbf{v}) \cdot \nabla \mathbf{v}) + \frac{\nabla^2 n_i}{n_i} \\ &\quad - \frac{\nabla n_i \otimes \nabla n_i}{n_i^2} - \left(\frac{3}{2} - \frac{m_i |\mathbf{c}_i - \mathbf{v}|^2}{2k_{\text{B}} T} \right) \frac{\nabla^2 T}{T} \\ &\quad + \left(\frac{3}{2} - \frac{m_i |\mathbf{c}_i - \mathbf{v}|^2}{k_{\text{B}} T} \right) \frac{\nabla T \otimes \nabla T}{T^2}. \end{aligned} \quad (5.13)$$

With \mathcal{Q}_1^{p} given by Eq. (3.19), we first need to select the integrands obtained from a Taylor expansion of $f_i^{(0)}(\mathbf{r}_i, \mathbf{c}_i, t) f_j^{(0)}(\mathbf{r}_j, \mathbf{c}_j, t)$ that involve the peculiar velocity of the first particle $\mathbf{c}_i - \mathbf{v}$ as well as two spatial derivatives and that are even in \mathbf{r}_{ij} . It appears, however, that there are not such terms in the Taylor expansion of $f_i^{(0)}(\mathbf{r}_i, \mathbf{c}_i, t) f_j^{(0)}(\mathbf{r}_j, \mathbf{c}_j, t)$ so that there is no extra capillary heat flux arising from \mathcal{Q}_1^{p} .

However, with \mathcal{Q}_2^{p} given by Eq. (3.20), from the isotropy of space and velocity space, we need to select the integrands in the Taylor expansion of

$$f_i^{(0)}(\mathbf{r}_i - (1 - \alpha)\mathbf{r}_{ij}, \mathbf{c}_i, t) f_j^{(0)}(\mathbf{r}_i + \alpha\mathbf{r}_{ij}, \mathbf{c}_j, t) g_{ij}(r_{ij}),$$

that involve two derivatives, are even with respect to \mathbf{r}_{ij} , and odd with respect to either $\mathbf{c}_i - \mathbf{v}$ or $\mathbf{c}_j - \mathbf{v}$. We first focus of integrands having such properties arising from the cross products of two first-order derivatives of $f_i^{(0)}$ and $f_j^{(0)}$

that are

$$-\alpha(1-\alpha)\frac{m_i}{k_b T}(\mathbf{c}_i - \mathbf{v}) \cdot \nabla \mathbf{v} \cdot \mathbf{r}_{ij} \frac{\nabla n_j \cdot \mathbf{r}_{ij}}{n_j} - \alpha(1-\alpha)\frac{m_j}{k_b T}(\mathbf{c}_j - \mathbf{v}) \cdot \nabla \mathbf{v} \cdot \mathbf{r}_{ij} \frac{\nabla n_i \cdot \mathbf{r}_{ij}}{n_i},$$

as well as

$$\alpha(1-\alpha)\frac{m_i}{k_b T}(\mathbf{c}_i - \mathbf{v}) \cdot \nabla \mathbf{v} \cdot \mathbf{r}_{ij} \left(\frac{3}{2} - \frac{m_j |\mathbf{c}_j - \mathbf{v}|^2}{2k_b T} \right) \frac{\nabla T \cdot \mathbf{r}_{ij}}{T} + \alpha(1-\alpha)\frac{m_j}{k_b T}(\mathbf{c}_j - \mathbf{v}) \cdot \nabla \mathbf{v} \cdot \mathbf{r}_{ij} \left(\frac{3}{2} - \frac{m_i |\mathbf{c}_i - \mathbf{v}|^2}{2k_b T} \right) \frac{\nabla T \cdot \mathbf{r}_{ij}}{T}.$$

The last integrands yield vanishing contributions for each species pair since

$$\int \left(\frac{3}{2} - \frac{m_i |\mathbf{c}_i - \mathbf{v}|^2}{2k_b T} \right) f_i^{(0)} d\mathbf{c}_i = 0, \quad i \in \mathfrak{S}.$$

Using then $\int_0^1 \alpha(1-\alpha) d\alpha = \frac{1}{6}$ as well as the isotropy of the velocity space and elementary symmetries, we next obtain from the first integrands a contribution \mathbf{q}_1 for the heat flux in the form

$$\mathbf{q}_1 = \sum_{i,j \in \mathfrak{S}} \frac{1}{12} \int \frac{\varphi'_{ij}(r_{ij})}{r_{ij}} \mathbf{r}_{ij} \mathbf{r}_{ij} \cdot (\mathbf{c}_i - \mathbf{v}) \frac{m_i}{k_b T} (\mathbf{c}_i - \mathbf{v}) \cdot \nabla \mathbf{v} \cdot \mathbf{r}_{ij} \frac{\nabla n_j \cdot \mathbf{r}_{ij}}{n_j} f_i^{(0)}(\mathbf{r}_i, \mathbf{c}_i) f_i^{(0)}(\mathbf{r}_i, \mathbf{c}_j) g_{ij}(r_{ij}) d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j.$$

The integration over \mathbf{c}_j is trivial and yields factors n_j , the integration over \mathbf{c}_i is performed using the reduced velocity $(\mathbf{c}_i - \mathbf{v})/(m_i/2k_b T)^{1/2}$ and Eq. (F1) from Appendix F, and this yields

$$\mathbf{q}_1 = \sum_{i,j \in \mathfrak{S}} \frac{1}{12} n_i \int \frac{\varphi'_{ij}(r_{ij})}{r_{ij}} \mathbf{r}_{ij} \otimes \mathbf{r}_{ij} \nabla \mathbf{v} : (\mathbf{r}_{ij} \otimes \mathbf{r}_{ij}) g_{ij}(r_{ij}) d\mathbf{r}_{ij} \cdot \nabla n_j.$$

Using the differential identity Eq. (F3) we then obtain that \mathbf{q}_1 is in the form

$$\mathbf{q}_1 = \sum_{i,j \in \mathfrak{S}} \frac{\varkappa_{ij}}{6} n_i (\nabla \mathbf{v} + (\nabla \mathbf{v})' + \nabla \cdot \mathbf{v} \mathbf{I}) \cdot \nabla n_j, \quad (5.14)$$

with the cohesion coefficients \varkappa_{ij} , $i, j \in \mathfrak{S}$, given by Eq. (5.2).

We now focus on contributions arising from the second-order derivatives $\nabla^2 f_i^{(0)}$ or $\nabla^2 f_j^{(0)}$ in the Taylor expansion of $f_i^{(0)}(\mathbf{r}_i - (1-\alpha)\mathbf{r}_{ij}, \mathbf{c}_i, t) f_j^{(0)}(\mathbf{r}_i + \alpha\mathbf{r}_{ij}, \mathbf{c}_j, t)$. The relevant integrands are those even with respect to \mathbf{r}_{ij} and odd with respect to either $\mathbf{c}_i - \mathbf{v}$ or $\mathbf{c}_j - \mathbf{v}$. These integrands are first

$$\begin{aligned} & \alpha^2 \frac{2m_i}{k_b T} (\mathbf{c}_i - \mathbf{v}) \cdot \nabla \mathbf{v} \cdot \mathbf{r}_{ij} \frac{\nabla n_j \cdot \mathbf{r}_{ij}}{n_j} + (1-\alpha)^2 \frac{2m_j}{k_b T} (\mathbf{c}_j - \mathbf{v}) \cdot \nabla \mathbf{v} \cdot \mathbf{r}_{ij} \frac{\nabla n_i \cdot \mathbf{r}_{ij}}{n_i}, \\ & + \alpha^2 \frac{m_i}{k_b T} (\mathbf{c}_i - \mathbf{v}) \cdot \nabla^2 \mathbf{v} : (\mathbf{r}_{ij} \otimes \mathbf{r}_{ij}) + (1-\alpha)^2 \frac{m_j}{k_b T} (\mathbf{c}_j - \mathbf{v}) \cdot \nabla^2 \mathbf{v} : (\mathbf{r}_{ij} \otimes \mathbf{r}_{ij}). \end{aligned}$$

The two first integrands yields a contribution \mathbf{q}_2 similar to \mathbf{q}_1 obtained in Eq. (5.14) but with the coefficient $-\frac{1}{3}$ instead on $\frac{1}{6}$.

$$\mathbf{q}_2 = - \sum_{i,j \in \mathfrak{S}} \frac{\varkappa_{ij}}{3} n_i (\nabla \mathbf{v} + (\nabla \mathbf{v})' + \nabla \cdot \mathbf{v} \mathbf{I}) \cdot \nabla n_j. \quad (5.15)$$

Using the isotropy of space and elementary symmetries, the integrands associated with $\nabla^2 \mathbf{v}$ further yield the contributions

$$\mathbf{q}_3 = - \sum_{i,j \in \mathfrak{S}} \frac{1}{12} \int \frac{\varphi'_{ij}(r_{ij})}{r_{ij}} \mathbf{r}_{ij} \mathbf{r}_{ij} \cdot (\mathbf{c}_i - \mathbf{v}) \frac{m_i}{k_b T} (\mathbf{c}_i - \mathbf{v}) \cdot \nabla^2 \mathbf{v} : (\mathbf{r}_{ij} \otimes \mathbf{r}_{ij}) f_i^{(0)}(\mathbf{r}_i, \mathbf{c}_i) f_i^{(0)}(\mathbf{r}_i, \mathbf{c}_j) g_{ij}(r_{ij}) d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j.$$

The integration over \mathbf{c}_j yield the factors n_j , the integration over \mathbf{c}_i is obtained with Eq. (F1) from Appendix F so that

$$\mathbf{q}_3 = - \sum_{i,j \in \mathfrak{S}} \frac{1}{12} n_i n_j \int \frac{\varphi'_{ij}(r_{ij})}{r_{ij}} \mathbf{r}_{ij} \mathbf{r}_{ij} \cdot \nabla^2 \mathbf{v} : (\mathbf{r}_{ij} \otimes \mathbf{r}_{ij}) g_{ij}(r_{ij}) d\mathbf{r}_{ij}.$$

We may then use the identity Eq. (F6) with $\nabla^2 \mathbf{v} : (\mathbf{r}_{ij} \otimes \mathbf{r}_{ij} \otimes \mathbf{r}_{ij}) = \mathbf{r}_{ij} \cdot \nabla^2 \mathbf{v} : (\mathbf{r}_{ij} \otimes \mathbf{r}_{ij})$ to deduce that

$$\mathbf{q}_3 = - \sum_{i,j \in \mathfrak{S}} \frac{1}{6} n_i n_j \varkappa_{ij} [\Delta \mathbf{v} + 2\nabla(\nabla \cdot \mathbf{v})]. \quad (5.16)$$

Finally, there are also integrands associated with temperature gradients in the form

$$-\frac{2m_i}{k_b T} (\mathbf{c}_i - \mathbf{v}) \cdot \nabla \mathbf{v} \cdot \mathbf{r}_{ij} \left(\frac{3}{2} - \frac{m_i |\mathbf{c}_i - \mathbf{v}|^2}{2k_b T} \right) \frac{\nabla T \cdot \mathbf{r}_{ij}}{T} - \frac{2m_j}{k_b T} (\mathbf{c}_j - \mathbf{v}) \cdot \nabla \mathbf{v} \cdot \mathbf{r}_{ij} \frac{\nabla T \cdot \mathbf{r}_{ij}}{T},$$

with a similar expression in terms of $(\mathbf{c}_j - \mathbf{v})$ but all these terms yield vanishing contributions since

$$\int |\mathbf{c}_i - \mathbf{v}|^2 \left(\frac{5}{2} - \frac{m_i |\mathbf{c}_i - \mathbf{v}|^2}{2k_b T} \right) f_i^{(0)} d\mathbf{c}_i = 0.$$

Collecting previous results, we have obtained an extra total energy flux $\mathcal{Q}^{\text{ex}} + \mathcal{P}^{\text{ex}} \cdot \mathbf{v}$ in the form

$$\mathcal{Q}^{\text{ex}} + \mathcal{P}^{\text{ex}} \cdot \mathbf{v} = \mathbf{q}_0 + \mathbf{q}_1 + \mathbf{q}_2 + \mathbf{q}_3 + \mathcal{P}^{\text{ex}} \cdot \mathbf{v},$$

where \mathbf{q}_0 arise from the change of energy density. The extra total energy flux $\mathcal{Q}^{\text{ex}} + \mathcal{P}^{\text{ex}} \cdot \mathbf{v}$ thus first reads

$$\begin{aligned} \mathcal{Q}^{\text{ex}} + \mathcal{P}^{\text{ex}} \cdot \mathbf{v} &= \sum_{i,j \in \mathfrak{S}} \varkappa_{ij} n_i \nabla \cdot \mathbf{v} \nabla n_j + \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \varkappa_{ij} n_i n_j \nabla (\nabla \cdot \mathbf{v}) + \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \varkappa_{ij} n_i (\nabla \mathbf{v})^t \cdot \nabla n_j \\ &+ \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \varkappa_{ij} (\nabla n_i \otimes \nabla n_j + n_i \nabla^2 n_j - \nabla n_i \cdot \nabla n_j \mathbf{I} - n_i \Delta n_j) \cdot \mathbf{v} \\ &- \sum_{i,j \in \mathfrak{S}} \frac{\varkappa_{ij}}{6} n_i (\nabla \mathbf{v} + (\nabla \mathbf{v})^t + \nabla \cdot \mathbf{v} \mathbf{I}) \cdot \nabla n_j - \sum_{i,j \in \mathfrak{S}} \frac{\varkappa_{ij}}{6} n_i n_j (\Delta \mathbf{v} + 2 \nabla (\nabla \cdot \mathbf{v})) \\ &+ \sum_{i,j \in \mathfrak{S}} \frac{\varkappa_{ij}}{6} (2 \nabla n_i \otimes \nabla n_j + \nabla n_i \cdot \nabla n_j \mathbf{I} - 4 n_i \nabla^2 n_j - 2 n_i \Delta n_j \mathbf{I}) \cdot \mathbf{v}. \end{aligned}$$

To simplify this expression we seek an *equivalent expression* $\overline{\mathcal{Q}}^{\text{ex}}$ of \mathcal{Q}^{ex} , that is, we seek a flux $\overline{\mathcal{Q}}^{\text{ex}}$ such that

$$\nabla \cdot (\mathcal{Q}^{\text{ex}} + \mathcal{P}^{\text{ex}} \cdot \mathbf{v}) = \nabla \cdot (\overline{\mathcal{Q}}^{\text{ex}} + \overline{\mathcal{P}}^{\text{ex}} \cdot \mathbf{v}),$$

allowing the simultaneous use of the simplified heat flux $\overline{\mathcal{Q}}^{\text{ex}}$ and the simplified pressure tensor $\overline{\mathcal{P}}^{\text{ex}}$. To simplify the divergence of $\mathcal{Q}^{\text{ex}} + \mathcal{P}^{\text{ex}} \cdot \mathbf{v}$, the first terms $\varkappa_{ij} n_i \nabla \cdot \mathbf{v} \nabla n_j$ are left unchanged since they corresponds to a generalized Dunn and Serrin heat flux, all terms proportional to \mathbf{v} are regrouped, and the differential identity Eq. (F8) is used to transform the divergence of all the terms $-\frac{1}{6} \varkappa_{ij} n_i \nabla \cdot \mathbf{v} \nabla n_j$ in the third line that originates from $\mathbf{q}_1 + \mathbf{q}_2$. After some lengthy algebra this yields the expression

$$\begin{aligned} \nabla \cdot (\mathcal{Q}^{\text{ex}} + \mathcal{P}^{\text{ex}} \cdot \mathbf{v}) &= \sum_{i,j \in \mathfrak{S}} \nabla \cdot \left[\varkappa_{ij} n_i \nabla \cdot \mathbf{v} \nabla n_j - \frac{1}{3} \varkappa_{ij} n_i \nabla \mathbf{v} \cdot \nabla n_j \right. \\ &+ \frac{1}{3} \varkappa_{ij} n_i (\nabla \mathbf{v})^t \cdot \nabla n_j - \frac{1}{6} \varkappa_{ij} n_i n_j \Delta \mathbf{v} + \frac{1}{6} \varkappa_{ij} n_i n_j \nabla (\nabla \cdot \mathbf{v}) \\ &\left. + \varkappa_{ij} \left(\nabla n_i \otimes \nabla n_j - \frac{1}{2} \nabla n_i \cdot \nabla n_j \mathbf{I} - n_i \Delta n_j \mathbf{I} \right) \cdot \mathbf{v} \right]. \end{aligned}$$

Using then the differential identity Eq. (F9), the divergence of the second to fifth terms (four terms) on the right-hand side vanishes for each species pair (i, j) , and we obtain

$$\begin{aligned} \nabla \cdot (\mathcal{Q}^{\text{ex}} + \mathcal{P}^{\text{ex}} \cdot \mathbf{v}) &= \sum_{i,j \in \mathfrak{S}} \nabla \cdot \left[\varkappa_{ij} n_i \nabla \cdot \mathbf{v} \nabla n_j + \varkappa_{ij} (\nabla n_i \otimes \nabla n_j \right. \\ &\left. - \frac{1}{2} \nabla n_i \cdot n_j \mathbf{I} - n_i \Delta n_j \mathbf{I}) \cdot \mathbf{v} \right], \end{aligned}$$

so that the equivalent heat flux $\overline{\mathcal{Q}}^{\text{ex}}$ is given by

$$\overline{\mathcal{Q}}^{\text{ex}} = \sum_{i,j \in \mathfrak{S}} \varkappa_{ij} n_i \nabla \cdot \mathbf{v} \nabla n_j. \quad (5.17)$$

Using the mass-based capillarity coefficients $\overline{\varkappa}_{ij} = \varkappa_{ij}/m_i m_j$, we obtain that the extra flux $\overline{\mathcal{Q}}^{\text{ex}}$ coincides with the generalized Dunn and Serrin heat flux $\overline{\mathcal{Q}}^{\text{ex}} = \mathcal{Q}^{\text{DS}}$ as derived from rational thermodynamics. A key point in the simplification of the zeroth-order capillary heat flux was notably the use of the modified density energy $\overline{\mathcal{E}}^{\text{ex}}$ to compensate complex corrections arising from \mathcal{Q}_2^{P} by similar terms arising from \mathbf{q}_0 .

In summary, the generalized Korteweg tensor Eq. (2.18) has been recovered as well as the generalized Dunn and Serrin heat flux Eq. (2.19) at zeroth order. We have also established that the energy density is in the form $\mathcal{E} = \mathcal{E}^u + \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \varkappa_{ij} \nabla n_i \cdot \nabla n_j$. The full capillary equations have thus been recovered at zeroth order and we now have to investigate the first-order regime, that is, we have to recover force terms \mathbf{X}_i that include the Cahn-Hilliard extra forces \mathbf{X}_i^{ch} , for $i \in \mathfrak{S}$, as well as the extra capillary-diffusive heat flux \mathcal{Q}^{CD} .

VI. CAHN-HILLIARD FLUID EQUATIONS

We derive in this section the Cahn-Hilliard fluid equations at first order of the Chapman-Enskog method. To this aim, we investigate higher-order derivative terms in the linearized equations and in the governing equations at first order of Enskog expansion. This is done by using the out-of-equilibrium symmetrized pair distribution functions f_{ij}^{sy} as well as higher-order Taylor expansions. The resulting equations then coincide with the model derived from rational thermodynamics. We also address the use of the pair distribution functions f_{ij}^{Bo} suggested by Bogoliubov theory

and establish that the deviations arising from the differences $f_{ij}^{\text{Bo}} - f_{ij}^{\text{sy}}$ may be seen as perturbations in some regime.

A. Cahn-Hilliard diffusion driving forces

The generalized Boltzmann Eqs. (4.1) and the use of higher-order Taylor expansions of pair distribution functions have led to the Euler and van der Waals equations at zeroth order. At first order of Enskog expansion Eq. (4.2), we next need to evaluate the linearized equations governing the perturbed distribution functions $\phi^{(1)} = (\phi_i^{(1)})_{i \in \mathfrak{S}}$. The linearized equations have been obtained in the form Eq. (4.18) with the linearized operator Eq. (4.19) and right-hand sides of Eqs. (4.20), (4.21). The right-hand sides Eq. (4.21) have only been evaluated using first-order Taylor expansions of pair distribution functions in Sec. IV or Appendix D. We must therefore reevaluate these right-hand sides using higher-order Taylor expansions of zeroth-order pair distribution functions. We denote with the superscript *u* the bulk phase thermodynamic properties obtained in Sec. IV that do not involve gradients. The higher-order derivative terms are again evaluated by using the symmetrized zeroth-order pair distribution functions $f_{ij}^{(0),\text{sy}}$, $i, j \in \mathfrak{S}$.

From the general expression of the right-hand sides of Eq. (4.20), we need to evaluate the extra terms arising from the material derivatives $\partial_t \log f_i^{(0)} + \mathbf{v} \cdot \nabla \log f_i^{(0)}$ as well as those arising from the potential parts $\mathcal{J}_i^{(1)}(f^{(0)})/f_i^{(0)}$. From Euler equations, derived by using the pair distribution functions $f_{ij}^{(0),\text{sy}}$, there are new terms arising in the material derivatives $\partial_t \log f^{(0)} + \mathbf{v} \cdot \nabla \log f^{(0)}$. More specifically, using Eqs. (5.4), (5.8), and (5.17), we obtain after some calculus the multi-component Euler equations with diffuse interface terms in the form

$$\partial_t n_i + \mathbf{v} \cdot \mathbf{n}_i = -n_i \nabla \cdot \mathbf{v}, \quad i \in \mathfrak{S}, \quad (6.1)$$

$$\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v} = -\frac{\nabla p^u}{\rho} + \sum_{i,j \in \mathfrak{S}} \frac{\varkappa_{ij} n_i}{\rho} \nabla \Delta n_j, \quad (6.2)$$

$$\partial_t T + \mathbf{v} \cdot \nabla T = \frac{1}{\partial_T \mathcal{E}^u} \left(\sum_{i \in \mathfrak{S}} n_i \partial_{n_i} \mathcal{E}^u - \mathcal{E}^u - p^u \right) \nabla \cdot \mathbf{v}, \quad (6.3)$$

instead of the standard Euler Eqs. (D2)–(D4). In particular, there is a cancellation of diffusive interface terms in the energy equation at zeroth order $\partial_t \mathcal{E}^u + \nabla \cdot (\mathbf{v} \mathcal{E}^u) + p^u \nabla \cdot \mathbf{v} = 0$ as well as in the corresponding temperature Eq. (6.3). There is, however, a diffuse interface term in the momentum conservation Eq. (6.2) involving the capillary forces.

To evaluate the material derivative of $\log f_i^{(0)}$, we may use the expression of Maxwellian distributions as well as Eqs. (6.1)–(6.3) and it is obtained that

$$-(\partial_t \log f_i^{(0)} + \mathbf{v} \cdot \nabla \log f_i^{(0)}) = \Psi_i^{\text{K},1} + \Psi_i^{\text{K},3}, \quad (6.4)$$

where $\Psi_i^{\text{K},1}$ has already been evaluated in Sec. IV and Appendix D and where $\Psi_i^{\text{K},3}$ is obtained from Eqs. (6.1)–(6.3) in the form

$$\Psi_i^{\text{K},3} = -\frac{m_i(\mathbf{c}_i - \mathbf{v})}{\rho k_B T} \cdot \sum_{k,l \in \mathfrak{S}} \varkappa_{kl} n_k \nabla \Delta n_l, \quad (6.5)$$

with the third-order derivative terms solely arising from the force term in Eq. (6.2).

We next need to investigate the higher-order terms arising from the potential parts $\mathcal{J}_i^{(1)}(f^{(0)})/f_i^{(0)}$ of the right-hand sides $\psi_i^{(1)}$, $i \in \mathfrak{S}$. Using the general definition of the perturbed operator Eq. (3.34), we may write

$$\frac{1}{f_i^{(0)}} \mathcal{J}_i^{(1)}(f^{(0)}) = \Psi_i^{\text{P},1} + \Psi_i^{\text{P},3}, \quad (6.6)$$

where the first-order terms $\Psi_i^{\text{P},1}$ have already been investigated in Sec. IV and Appendix D, whereas the contributions $\Psi_i^{\text{P},3}$ arise from third-order terms in Taylor expansion of pair distribution functions. All quadratic terms are indeed even in \mathbf{r}_{ij} or and \mathbf{r}'_{ij} and yield zero contributions in the expansion of $\mathcal{J}_i^{(1)}(f^{(0)})$.

To evaluate the third-order derivative contributions $\Psi_i^{\text{P},3}$ arising from the perturbed source term $\mathcal{J}_i^{(1)}(f^{(0)})$, for consistency with the Euler equations, and for the sake of simplicity, we again use the symmetrized pair distribution functions $f_{ij}^{(0),\text{sy}}$. In other words, keeping in mind the zeroth-order identity Eq. (4.5), the corrector terms $f_{ij}^{(0),\text{Bo}} - f_{ij}^{(0),\text{cl}}$ in the decompositions Eq. (3.31) used in $\mathcal{J}_i^{(1)}(f^{(0)})$ are replaced by $f_{ij}^{(0),\text{sy}} - f_{ij}^{(0),\text{cl}}$, where $f_{ij}^{(0),\text{Bo}} = f_i^{(0)}(\mathbf{x}'_i, t) f_j^{(0)}(\mathbf{x}'_j, t)$ and $f_{ij}^{(0),\text{sy}} = g_{ij}(r_{ij}) f_i^{(0)}(\mathbf{x}_i, t) f_j^{(0)}(\mathbf{x}_j, t)$. The deviations arising from the differences between the Bogoliubov zeroth-order distribution functions $f_{ij}^{(0),\text{Bo}}$ and the symmetrized zeroth-order distribution functions $f_{ij}^{(0),\text{sy}}$ will be shown to be negligible in some regime in Sec. VIC. Using the symmetrized pair distribution functions $f_{ij}^{(0),\text{sy}}$, the third-order corrections in $\mathcal{J}_i^{(1)}(f^{(0)})$ are then obtained in the form

$$\Psi_i^{\text{P},3} = \sum_{j \in \mathfrak{S}} \frac{1}{6 f_i^{(0)}} \int \theta_{ij} \partial_{(\mathbf{r}_i, \mathbf{r}_j)}^3 f_{ij}^{(0),\text{sy}} : (0, \mathbf{r}_{ij})^{\otimes 3} d\mathbf{x}_j, \quad (6.7)$$

so that

$$\Psi_i^{\text{P},3} = \sum_{j \in \mathfrak{S}} \frac{1}{6} \int \frac{\varphi'_{ij}(r_{ij})}{r_{ij}} \mathbf{r}_{ij} \cdot \frac{(\mathbf{c}_i - \mathbf{v})}{k_B T} g_{ij} \partial_{\mathbf{r}_j}^3 n_j^{(0)} : \mathbf{r}_{ij}^{\otimes 3} d\mathbf{r}_{ij}.$$

After some algebra, using the identity Eq. (F5) of Appendix F, as well as the definition Eq. (5.2), it is obtained that

$$\Psi_i^{\text{P},3} = \sum_{j \in \mathfrak{S}} \frac{\varkappa_{ij}}{k_B T} (\mathbf{c}_i - \mathbf{v}) \cdot \nabla \Delta n_j. \quad (6.8)$$

Combining the results without capillarity derived in Appendix D as well as the extra contributions in $\Psi_i^{\text{K},3}$ and that of $\Psi_i^{\text{P},3}$, we finally obtain new right-hand sides $\psi_i^{(1)}$ with the same structure as Eq. (4.21) with *unchanged* functions ψ_i^η , ψ_i^κ , $\psi_i^{D_j}$, $j \in \mathfrak{S}$, and ψ_i^λ , but with the force terms

$$\mathbf{X}_i = n_i k_B T \left[\nabla \left(\frac{g_i^u}{k_B T} \right) - \sum_{j \in \mathfrak{S}} \frac{\varkappa_{ij}}{k_B T} \nabla \Delta n_j \right]. \quad (6.9)$$

These force terms include both the thermodynamics \mathbf{X}_i^{th} and Cahn-Hilliard \mathbf{X}_i^{ch} contributions, generalizing Eq. (4.22). These force terms \mathbf{X}_i also coincide with those obtained from rational thermodynamics in Eqs. (2.16) and (2.17). The corresponding perturbed distribution functions $\phi^{(1)} = (\phi_i^{(1)})_{i \in \mathfrak{S}}$

also satisfy Enskog-type constraints that are found to be similar to that of normal diffusion processes as detailed in Appendix E. Therefore, we still have the expansion Eqs. (4.21) and (4.32) with the new forces Eq. (6.9) but with *unchanged* functions $\phi_i^\eta, \phi_i^\kappa, \phi^{D_j}, j \in \mathfrak{S}$, and ϕ_i^λ . We have thus recovered the Cahn-Hilliard force terms \mathbf{X}_i^{ch} in diffusive fluxes and we must now investigate diffuse interface terms in first-order conservation equations.

B. Conservation equations at first order

The conservation equations at first order are obtained by adding all first-order contributions to the already derived conservation equations at the Euler level.

To investigate the extra capillary terms arising at first order of the Enskog expansion we use the symmetrized pair nonequilibrium distribution functions in the form

$$f_{ij}^{\text{sy}} = f_i(\mathbf{r}_i, \mathbf{c}_i, t) f_j(\mathbf{r}_j, \mathbf{c}_j, t) g_{ij}(\bar{\mathbf{r}}_{i,j}, r_{ij}), \quad i, j \in \mathfrak{S}, \quad (6.10)$$

where g_{ij} is the correlation function Eq. (4.6) evaluated at a symmetric average $\bar{\mathbf{r}}_{i,j}$ of \mathbf{r}_i and \mathbf{r}_j . This distribution first coincide with the zeroth-order distribution $f_{ij}^{(0),\text{sy}}$ when evaluated for Maxwellian distribution, it is also symmetric in its arguments and the limit for large r_{ij} is the natural uncorrelated nonequilibrium pair distribution function $f_i(\mathbf{r}_i, \mathbf{c}_i, t) f_j(\mathbf{r}_j, \mathbf{c}_j, t)$. The Euler equations for capillary fluids have also been evaluated by using $f_{ij}^{(0),\text{sy}}$. The correlation functions $g_{ij}(\bar{\mathbf{r}}_{i,j}, r_{ij})$ are also simplified in the form $g_{ij}(\mathbf{r}_i, r_{ij})$ as in the zeroth-order derivation, and will be denoted by $g_{ij}(r_{ij})$. To derive the macroscopic equations at first order, the symmetrized pair distribution functions f_{ij}^{sy} are then used with $f_i = f_i^{(0)} + f_i^{(1)} \phi_i^{(1)}$, $i \in \mathfrak{S}$, with the general balance equations established in Sec. III B, using again higher-order Taylor expansions. Denoting Bogoliubov pair distribution functions Eq. (3.30) by $f_{ij}^{\text{Bo}} = f_i(\mathbf{r}_i', \mathbf{c}_i') f_j(\mathbf{r}_j', \mathbf{c}_j')$, the deviations arising from the difference $f_{ij}^{\text{Bo}} - f_{ij}^{\text{sy}}$ are addressed in the next section. In addition, we only need to consider the higher-order terms in the Taylor expansions to evaluate the capillary contributions to the transport fluxes since the lower order terms have already been taken into account.

We first consider the tensor \mathcal{P}^{P} and look for *new extra terms* with *two spatial derivatives* arising from the first-order Enskog contributions. The new terms—at first order of Enskog expansion—are in the form

$$-\sum_{i,j \in \mathfrak{S}} \frac{1}{2} \int \frac{\varphi'_{ij}(r_{ij})}{r_{ij}} g_{ij}(r_{ij}) \mathbf{r}_{ij} \otimes \mathbf{r}_{ij} f_i^{(0)}(\mathbf{r}_i^\alpha) f_j^{(0)}(\mathbf{r}_j^\alpha) (\phi_i^{(1)}(\mathbf{r}_i^\alpha) + \phi_j^{(1)}(\mathbf{r}_j^\alpha)) d\alpha d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j,$$

where we have denoted $\mathbf{r}_i^\alpha = \mathbf{r}_i - (1 - \alpha)\mathbf{r}_{ij}$ and $\mathbf{r}_j^\alpha = \mathbf{r}_i + \alpha\mathbf{r}_{ij}$ and have left implicit the dependence on the velocities \mathbf{c}_i and \mathbf{c}_j as well as on time. These extra terms vanish since the average value with respect to \mathbf{c}_i of $\phi_i^{(1)}$ at \mathbf{r}_i^α vanishes as well as the average value with respect to \mathbf{c}_j of $\phi_j^{(1)}$ at \mathbf{r}_j^α . As a consequence, there are no new contributions to the pressure tensor at first order, and in particular no extra capillary terms.

We now investigate the new contributions to the heat fluxes \mathcal{Q}_1^{P} and \mathcal{Q}_2^{P} at first order of Enskog expansion as well as those arising from the internal energy \mathcal{E} . Indeed, even though there is no first-order corrector to the internal energy \mathcal{E} , by definition of the Enskog's constraints, there is nevertheless a first-order corrector when transforming $\mathcal{E}^{\text{ex}} = -\sum_{i,j \in \mathfrak{S}} \frac{1}{2} \varkappa_{ij} n_i \Delta n_j$ into $\bar{\mathcal{E}}^{\text{ex}} = \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \varkappa_{ij} \nabla n_i \cdot \nabla n_j$. At first order of Enskog expansion, we indeed have to use the first-order governing equation $\partial_t n_i = -\nabla \cdot (n_i \mathbf{v}) - \nabla \cdot \mathcal{F}_i$, $i \in \mathfrak{S}$, instead of $\partial_t n_i = -\nabla \cdot (n_i \mathbf{v})$, $i \in \mathfrak{S}$, where $\mathcal{F}_i = \int (\mathbf{c}_i - \mathbf{v}) f_i^{(0)} \phi_i^{(1)} d\mathbf{c}_i$ is the diffusive flux of particles with $\mathcal{F}_i = m_i \mathcal{F}_i$. The corrector Ξ , given in the general form by Eq. (5.10), yields new terms solely arising from the time derivatives. Since the time derivatives in Ξ arise through the divergence of $-\frac{1}{2} \varkappa_{ij} (\partial_t n_i + \mathbf{v} \cdot \nabla n_i) \nabla n_j$ and $-\frac{1}{2} \varkappa_{ij} n_i \nabla (\partial_t n_j + \mathbf{v} \cdot \nabla n_j)$, and keeping in mind that the capillarity coefficients \varkappa_{ij} are taken to be constant, we obtain after some algebra that the corrector Ξ is in the form $\Xi = \nabla \cdot (\mathbf{q}_0 + \mathbf{q}'_0)$ with a new first-order corrective flux \mathbf{q}'_0 given by

$$\mathbf{q}'_0 = \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \varkappa_{ij} \nabla \cdot \mathcal{F}_i \nabla n_j + \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \varkappa_{ij} n_j \nabla (\nabla \cdot \mathcal{F}_i). \quad (6.11)$$

Concentrating then on the flux \mathcal{Q}_1^{P} , we have to investigate extra terms with second-order derivatives arising from

$$\sum_{i,j \in \mathfrak{S}} \frac{1}{2} \int \varphi_{ij}(\mathbf{c}_i - \mathbf{v}) g_{ij} f_i^{(0)}(\mathbf{r}_i) f_j^{(0)}(\mathbf{r}_j) [\phi_i^{(1)}(\mathbf{r}_i) + \phi_j^{(1)}(\mathbf{r}_j)] \times d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j. \quad (6.12)$$

Using the zero average constraint for $\phi_j^{(1)}$ at \mathbf{r}_j , using the definition of \mathcal{F}_i as well as that of \varkappa_{ij} , this contribution may be rewritten in the form $\sum_{i,j \in \mathfrak{S}} \frac{1}{2} \int \varphi_{ij} g_{ij} n_j(\mathbf{r}_j) \mathcal{F}_i(\mathbf{r}_i) d\mathbf{r}_{ij}$. Using a Taylor expansion of $n_j(\mathbf{r}_j)$, the diffuse interface extra second-order derivatives terms are finally obtained in the form

$$\mathbf{q}'_1 = -\sum_{i,j \in \mathfrak{S}} \frac{1}{2} \varkappa_{ij} \Delta n_j \mathcal{F}_i, \quad (6.13)$$

whereas the zeroth-order terms in Eq. (6.12) are taken into account in the standard dissipative heat flux.

Concentrating then on the flux \mathcal{Q}_2^{P} , we must extract second derivative terms from the contributions

$$-\sum_{i,j \in \mathfrak{S}} \frac{1}{4} \int \frac{\varphi'_{ij}(r_{ij})}{r_{ij}} g_{ij}(r_{ij}) \mathbf{r}_{ij} \mathbf{r}_{ij} \cdot (\mathbf{c}_i - \mathbf{v} + \mathbf{c}_j - \mathbf{v}) \times f_i^{(0)}(\mathbf{r}_i^\alpha) f_j^{(0)}(\mathbf{r}_j^\alpha) [\phi_i^{(1)}(\mathbf{r}_i^\alpha) + \phi_j^{(1)}(\mathbf{r}_j^\alpha)] d\alpha d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j.$$

Using the definition of diffusive fluxes, these terms may be rewritten

$$-\sum_{i,j \in \mathfrak{S}} \frac{1}{4} \int \frac{\varphi'_{ij}(r_{ij})}{r_{ij}} g_{ij}(r_{ij}) \mathbf{r}_{ij} \mathbf{r}_{ij} \cdot [n_j(\mathbf{r}_j^\alpha) \mathcal{F}_i(\mathbf{r}_i^\alpha) + n_i(\mathbf{r}_i^\alpha) \mathcal{F}_j(\mathbf{r}_j^\alpha)] d\alpha d\mathbf{r}_{ij}. \quad (6.14)$$

We next use Taylor expansions for both number densities and diffusion fluxes and extract all the diffuse interface terms with two spatial derivatives. Considering first the integrands associated with the second-order derivatives of number densities

in Eq. (6.14), we obtain a corrector term in the form

$$\mathbf{q}'_2 = - \sum_{i,j \in \mathfrak{S}} \frac{1}{4} \int \frac{\phi'_{ij}(r_{ij})}{r_{ij}} g_{ij}(r_{ij}) \mathbf{r}_{ij} \mathbf{r}_{ij} \cdot \frac{1}{2} \\ \times [\nabla^2 n_j : (\delta \mathbf{r}_j^\alpha)^{\otimes 2} \mathcal{F}_i + \nabla^2 n_i : (\delta \mathbf{r}_i^\alpha)^{\otimes 2} \mathcal{F}_j] d\alpha d\mathbf{r}_{ij},$$

where for any vector \mathbf{z} the tensor $\mathbf{z} \otimes \mathbf{z}$ is also denoted for short by $\mathbf{z}^{\otimes 2}$. We may then integrate with respect to α by using $\int (\delta \mathbf{r}_j^\alpha)^{\otimes 2} d\alpha = \frac{1}{3} \mathbf{r}_{ij} \otimes \mathbf{r}_{ij}$ as well as $\int (\delta \mathbf{r}_i^\alpha)^{\otimes 2} d\alpha = \frac{1}{3} \mathbf{r}_{ij} \otimes \mathbf{r}_{ij}$ and this yields

$$\mathbf{q}'_2 = - \sum_{i,j \in \mathfrak{S}} \frac{1}{12} \int \frac{\phi'_{ij}(r_{ij})}{r_{ij}} g_{ij}(r_{ij}) \mathbf{r}_{ij} \mathbf{r}_{ij} \cdot \frac{1}{2} \\ \times [\nabla^2 n_j : (\mathbf{r}_{ij})^{\otimes 2} \mathcal{F}_i + \nabla^2 n_i : (\mathbf{r}_{ij})^{\otimes 2} \mathcal{F}_j] d\mathbf{r}_{ij}.$$

Symmetrizing the sum and using the differential identity Eq. (F3) we then obtain that \mathbf{q}'_2 is in the form

$$\mathbf{q}'_2 = - \sum_{i,j \in \mathfrak{S}} \frac{\varkappa_{ij}}{6} (2\nabla^2 n_j + \Delta n_j \mathbf{I}) \cdot \mathcal{F}_i, \quad (6.15)$$

with the cohesion coefficients \varkappa_{ij} , $i, j \in \mathfrak{S}$, given by Eq. (5.2). Considering then the integrands arising from products of first-order derivatives of number densities and diffusive fluxes in Eq. (6.14) we obtain an extra corrector term in the form

$$\mathbf{q}'_3 = - \sum_{i,j \in \mathfrak{S}} \frac{1}{4} \int \frac{\phi'_{ij}(r_{ij})}{r_{ij}} g_{ij}(r_{ij}) \mathbf{r}_{ij} \mathbf{r}_{ij} \cdot (\nabla n_j \cdot \delta \mathbf{r}_j^\alpha \nabla \mathcal{F}_i \cdot \delta \mathbf{r}_i^\alpha + \nabla n_i \cdot \delta \mathbf{r}_i^\alpha \nabla \mathcal{F}_j \cdot \delta \mathbf{r}_j^\alpha) d\alpha d\mathbf{r}_{ij}.$$

We may integrate with respect to α by using $\int (\delta \mathbf{r}_i^\alpha) \otimes (\delta \mathbf{r}_j^\alpha) d\alpha = -\frac{1}{6} \mathbf{r}_{ij} \otimes \mathbf{r}_{ij}$ as well as $\int (\delta \mathbf{r}_j^\alpha) \otimes (\delta \mathbf{r}_i^\alpha) d\alpha = -\frac{1}{6} \mathbf{r}_{ij} \otimes \mathbf{r}_{ij}$ and this yields

$$\mathbf{q}'_3 = \sum_{i,j \in \mathfrak{S}} \frac{1}{12} \int \frac{\phi'_{ij}(r_{ij})}{r_{ij}} g_{ij}(r_{ij}) \mathbf{r}_{ij} \mathbf{r}_{ij} \cdot \nabla \mathcal{F}_i \cdot \mathbf{r}_{ij} \nabla n_j \cdot \mathbf{r}_{ij} d\mathbf{r}_{ij}.$$

We may next use again the differential identity Eq. (F3) and after some algebra, it is obtained that

$$\mathbf{q}'_3 = \sum_{i,j \in \mathfrak{S}} \frac{1}{6} \varkappa_{ij} (\nabla \mathcal{F}_i + (\nabla \mathcal{F}_i)^t + \nabla \cdot \mathcal{F}_i \mathbf{I}) \cdot \nabla n_j. \quad (6.16)$$

Considering finally the integrands involving second derivatives of diffusive fluxes in Eq. (6.14) we obtain an extra corrector term in the form

$$\mathbf{q}'_4 = - \sum_{i,j \in \mathfrak{S}} \frac{1}{4} \int \frac{\phi'_{ij}(r_{ij})}{r_{ij}} g_{ij}(r_{ij}) \mathbf{r}_{ij} \mathbf{r}_{ij} \cdot \frac{1}{2} [n_j \nabla^2 \mathcal{F}_i : (\delta \mathbf{r}_i^\alpha)^{\otimes 2} + n_i \nabla^2 \mathcal{F}_j : (\delta \mathbf{r}_j^\alpha)^{\otimes 2}] d\alpha d\mathbf{r}_{ij}.$$

We may then integrate with respect to α by using $\int (\delta \mathbf{r}_j^\alpha)^{\otimes 2} d\alpha = \frac{1}{3} \mathbf{r}_{ij} \otimes \mathbf{r}_{ij}$ as well as $\int (\delta \mathbf{r}_i^\alpha)^{\otimes 2} d\alpha = \frac{1}{3} \mathbf{r}_{ij} \otimes \mathbf{r}_{ij}$ and this yields

$$\mathbf{q}'_4 = - \sum_{i,j \in \mathfrak{S}} \frac{1}{12} \int \frac{\phi'_{ij}(r_{ij})}{r_{ij}} g_{ij}(r_{ij}) \mathbf{r}_{ij} \mathbf{r}_{ij} \cdot \frac{1}{2} [n_j \nabla^2 \mathcal{F}_i : (\mathbf{r}_{ij})^{\otimes 2} + n_i \nabla^2 \mathcal{F}_j : (\mathbf{r}_{ij})^{\otimes 2}] d\mathbf{r}_{ij}.$$

Using then the identity Eq. (F6) it is obtained after some algebra that

$$\mathbf{q}'_4 = - \sum_{i,j \in \mathfrak{S}} \frac{1}{6} \varkappa_{ij} [\Delta \mathcal{F}_i + 2\nabla(\nabla \cdot \mathcal{F}_i)] n_j. \quad (6.17)$$

The new capillary heat flux at first order \mathcal{Q}^{ex} may now be evaluated from

$$\mathcal{Q}^{\text{ex}} = \mathbf{q}'_0 + \mathbf{q}'_1 + \mathbf{q}'_2 + \mathbf{q}'_3 + \mathbf{q}'_4,$$

with the terms evaluated from Eqs. (6.11), (6.13), (6.15), (6.16), and (6.17). The extra heat flux \mathcal{Q}^{ex} is thus given by

$$\mathcal{Q}^{\text{ex}} = \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \varkappa_{ij} \nabla \cdot \mathcal{F}_i \nabla n_j + \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \varkappa_{ij} n_j \nabla(\nabla \cdot \mathcal{F}_i) - \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \varkappa_{ij} \Delta n_j \mathcal{F}_i \\ - \sum_{i,j \in \mathfrak{S}} \frac{1}{6} \varkappa_{ij} (2\nabla^2 n_j + \Delta n_j \mathbf{I}) \cdot \mathcal{F}_i + \sum_{i,j \in \mathfrak{S}} \frac{1}{6} \varkappa_{ij} (\nabla \mathcal{F}_i + (\nabla \mathcal{F}_i)^t + \nabla \cdot \mathcal{F}_i \mathbf{I}) \cdot \nabla n_j \\ - \sum_{i,j \in \mathfrak{S}} \frac{1}{6} \varkappa_{ij} (\Delta \mathcal{F}_i + 2\nabla(\nabla \cdot \mathcal{F}_i)) n_j.$$

To simplify this expression we seek an *equivalent expression* $\overline{\mathcal{Q}}^{\text{ex}}$ of \mathcal{Q}^{ex} , that is, we seek a flux $\overline{\mathcal{Q}}^{\text{ex}}$ such that

$$\nabla \cdot \mathcal{Q}^{\text{ex}} = \nabla \cdot \overline{\mathcal{Q}}^{\text{ex}}.$$

To this aim, we use the identity Eq. (F10) to eliminate the contributions involving $\nabla^2 n_j \cdot \mathcal{F}_i$ and regroup similar terms and this yields

$$\begin{aligned} \nabla \cdot \mathcal{Q}^{\text{ex}} = \nabla \cdot \left[- \sum_{i,j \in \mathfrak{S}} \varkappa_{ij} \Delta n_j \mathcal{F}_i + \sum_{i,j \in \mathfrak{S}} \varkappa_{ij} \nabla \cdot \mathcal{F}_i \nabla n_j - \sum_{i,j \in \mathfrak{S}} \frac{1}{6} \varkappa_{ij} \nabla \mathcal{F}_i \cdot \nabla n_j \right. \\ \left. + \sum_{i,j \in \mathfrak{S}} \frac{1}{6} \varkappa_{ij} (\nabla \mathcal{F}_i)^t \cdot \nabla n_j + \sum_{i,j \in \mathfrak{S}} \frac{1}{6} \varkappa_{ij} n_j \nabla (\nabla \cdot \mathcal{F}_i) - \sum_{i,j \in \mathfrak{S}} \frac{1}{6} \varkappa_{ij} n_j \Delta \mathcal{F}_i \right]. \end{aligned}$$

Using then the differential identity Eq. (F11), for each species pair (i, j) , the divergence of the third to sixth terms (four terms) in the right-hand side vanishes, and we obtain that

$$\nabla \cdot \mathcal{Q}^{\text{ex}} = \nabla \cdot \left(- \sum_{i,j \in \mathfrak{S}} \varkappa_{ij} \Delta n_j \mathcal{F}_i + \sum_{i,j \in \mathfrak{S}} \varkappa_{ij} \nabla \cdot \mathcal{F}_i \nabla n_j \right),$$

and finally that

$$\overline{\mathcal{Q}}^{\text{ex}} = - \sum_{i,j \in \mathfrak{S}} \varkappa_{ij} \Delta n_j \mathcal{F}_i + \sum_{i,j \in \mathfrak{S}} \varkappa_{ij} \nabla \cdot \mathcal{F}_i \nabla n_j. \quad (6.18)$$

Using then the mass-based diffuse interface coefficient $\overline{\varkappa}_{ij} = \varkappa_{ij}/m_i m_j$ with the relations $\rho_i = m_i n_i$ and $\overline{\mathcal{F}}_i = m_i \mathcal{F}_i$, we may rewrite the extra first-order heat flux $\overline{\mathcal{Q}}^{\text{ex}}$ in the form $-\sum_{i \in \mathfrak{S}} \nabla \cdot \overline{\gamma}_i \overline{\mathcal{F}}_i + \sum_{i \in \mathfrak{S}} \overline{\gamma}_i \nabla \cdot \overline{\mathcal{F}}_i$ so that $\overline{\mathcal{Q}}^{\text{ex}}$ coincides with \mathcal{Q}^{CD} . A key point in the simplification of the capillary-diffusive flux was the use of the modified energy density Eq. (5.9) instead of Eq. (5.8), as already observed at zeroth order.

In summary, the generalized Korteweg tensor Eq. (2.18), the generalized Dunn and Serrin heat flux Eq. (2.19), the cohesive-dissipative heat flux Eq. (2.20), the energy density Eq. (2.7), the Cahn-Hilliard diffusive fluxes, as well as non-ideal fluid thermodynamics have been recovered from the kinetic theory.

C. Agreement with Bogoliubov distributions

The higher-order diffuse interface contributions in the conservation equations and the linearized equations have been derived by using the natural symmetrized pair distribution functions f_{ij}^{sy} , $i, j \in \mathfrak{S}$. More specifically, the Euler and van der Waals equations including the generalized Korteweg tensor Eq. (2.18), the generalized Dunn and Serrin heat flux Eq. (2.19), and the energy density Eq. (2.7) have been derived by using the zeroth order $f_{ij}^{(0),\text{sy}}$ pair distribution functions. Similarly, the Cahn-Hilliard diffusive fluxes and the capillary-diffusive heat flux Eq. (2.20) have been obtained by using the symmetrized pair distribution functions f_{ij}^{sy} . The symmetrized distributions are natural and Bogoliubov pair distribution functions are unfortunately not practical as typically shown by the explicit use of streaming operators in the dense gas mixture collision integrals $\tilde{\alpha}_{ij}^\eta$, $\tilde{\alpha}_{ij}^\kappa$, $\tilde{\alpha}_{ij}^{\hat{\kappa}}$ of the linearized right-hand sides Eqs. (4.23)–(4.27). Nevertheless, the Bogoliubov pair distribution functions have been used to evaluated the normal

diffusive fluxes following Cohen *et al.* [50]. As a consequence, to establish that the model derived with the symmetrized distributions is in agreement with Bogoliubov distributions, we have to establish that the deviations in diffuse interface terms arising from the difference of pair distribution functions may be neglected in some regime. Since Bogoliubov pair distribution functions are unfortunately not practical, their moments cannot be evaluated, and it is inevitable to introduce some approximations.

We investigate the deviations in diffuse interfaces terms arising from the differences $f_{ij}^{\text{Bo}} - f_{ij}^{\text{sy}}$ in a regime where the dominant terms arise from the density derivatives and we make use of hard potential approximations. That is, we establish that the deviations arising from $f_{ij}^{\text{Bo}} - f_{ij}^{\text{sy}}$ may be neglected in a regime where *temperature gradients and relative Mach numbers inside interphase fronts are small*. To this aim, we introduce a characteristic length of temperature gradients $l_{\nabla T}^*$, a characteristic length of velocity gradients $l_{\nabla v}^*$, a typical macroscopic velocity variation inside interphase fronts δv^* , and the corresponding relative Mach number $\text{Ma}^* = \delta v^* / \sqrt{k_B T^* / m^*}$. The Bogoliubov corrections are then estimated in a regime where density gradients dominate the dynamics of interphase fronts, that is, in the regime where

$$\left(\frac{\sigma^*}{r^*} \right)^3 \left(\frac{\sigma^*}{l_{\nabla n}^*} \right) \left(\frac{\sigma^*}{l_{\nabla T}^*} \right) \ll 1, \quad (6.19)$$

and

$$\left(\frac{\sigma^*}{r^*} \right)^3 \left(\frac{\sigma^*}{l_{\nabla n}^*} \right) \left(\frac{\sigma^*}{l_{\nabla v}^*} \right) \left(\frac{\delta v^*}{\sqrt{k_B T^* / m^*}} \right) \ll 1. \quad (6.20)$$

The first condition Eq. (6.19) ensure that all terms in the form $\varkappa_{ij} n_i \nabla n_j \cdot \nabla T$ are negligible with respect to the density gradient terms $\varkappa_{ij} \nabla n_i \cdot \nabla n_j$ within interphase fronts, and a similar condition holds for the gradient of these quantities. Similarly,

the second condition Eq. (6.20) ensure that all terms in the form $\varkappa_{ij} n_i \nabla n_j \cdot \nabla \mathbf{v} / \sqrt{k_B T / m}$ are negligible with respect to the density gradient terms $\varkappa_{ij} \nabla n_i \cdot \nabla n_j$ within interphase fronts, and the same rule applies to gradients of these quantities.

We may next introduce the decomposition

$$f_i^{(0)} = n_i \tilde{f}_i^{(0)}, \quad \tilde{f}_i^{(0)} = \left(\frac{m_i}{2\pi k_B T} \right)^{\frac{3}{2}} \exp \left(- \frac{m_i |\mathbf{c}_i - \mathbf{v}|^2}{2k_B T} \right), \quad (6.21)$$

such that

$$\begin{aligned} \nabla f_i^{(0)} &= \nabla n_i \tilde{f}_i^{(0)} + n_i \nabla \tilde{f}_i^{(0)}, \\ \nabla^2 f_i^{(0)} &= \nabla^2 n_i \tilde{f}_i^{(0)} + \nabla n_i \otimes \nabla \tilde{f}_i^{(0)} + \nabla \tilde{f}_i^{(0)} \otimes \nabla n_i + n_i \nabla^2 \tilde{f}_i^{(0)}. \end{aligned}$$

the form

$$\delta^{\text{Bo}} \mathcal{E} = \sum_{i,j \in \mathfrak{S}} \int \frac{1}{2} \varphi_{ij} (f_{ij}^{(0),\text{Bo}} - f_{ij}^{(0),\text{sy}}) d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j, \quad (6.22)$$

where we have denoted by $f_{ij}^{(0),\text{Bo}} = f_i^{(0)}(\mathbf{r}'_i, \mathbf{c}'_i) f_j^{(0)}(\mathbf{r}'_j, \mathbf{c}'_j)$ the zeroth-order Bogoliubov distribution functions. With second-order expansions of the pair distribution functions, the difference in internal energy reads

$$\delta^{\text{Bo}} \mathcal{E} = \sum_{i,j \in \mathfrak{S}} \frac{1}{4} \int \varphi_{ij} [\partial_{(\mathbf{r}_i, \mathbf{r}_j)}^2 f_{ij}^{(0),\text{Bo}} : (\delta \mathbf{r}_i, \delta \mathbf{r}_j)^{\otimes 2} - \partial_{\mathbf{r}_j}^2 f_{ij}^{(0),\text{sy}} : \mathbf{r}_{ij}^{\otimes 2}] d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j,$$

where for any vector $\mathbf{z} \in \mathbb{R}^3$ we denote for short by $\mathbf{z}^{\otimes 2}$ the tensor product $\mathbf{z} \otimes \mathbf{z}$ and where $\delta \mathbf{r}_i = \mathbf{r}'_i - \mathbf{r}_i$ and $\delta \mathbf{r}_j = \mathbf{r}'_j - \mathbf{r}_j$ have been defined in Sec. III D. The leading terms in $\delta^{\text{Bo}} \mathcal{E}$ are thus

$$\sum_{i,j \in \mathfrak{S}} \frac{1}{4} \int \varphi_{ij} g_{ij} \tilde{f}_i^{(0)} \tilde{f}_j^{(0)} [n_j \partial_{\mathbf{r}_i}^2 n_i : (\delta \mathbf{r}_i)^{\otimes 2} + 2 \partial_{\mathbf{r}_i} n_i \cdot \delta \mathbf{r}_i \partial_{\mathbf{r}_j} n_j \cdot \delta \mathbf{r}_j + n_i \partial_{\mathbf{r}_j}^2 n_j : (\delta \mathbf{r}_j)^{\otimes 2} - n_i \partial_{\mathbf{r}_j}^2 n_j : \mathbf{r}_{ij}^{\otimes 2}] d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j, \quad (6.23)$$

and all these terms vanish from the integral relations Eq. (D12) for hard potentials that are simply obtained by letting $\delta \mathbf{r}_i = 0$ and $\delta \mathbf{r}_j = \mathbf{r}_{ij}$ inside the integrals. The remaining correction terms are then given by

$$\begin{aligned} & \sum_{i,j \in \mathfrak{S}} \frac{1}{4} \int \varphi_{ij} g_{ij} n_i n_j [\partial_{(\mathbf{r}_i, \mathbf{r}_j)}^2 \tilde{f}_{ij}^{(0),\text{Bo}} : (\delta \mathbf{r}_i, \delta \mathbf{r}_j)^{\otimes 2} - \partial_{\mathbf{r}_j}^2 \tilde{f}_{ij}^{(0),\text{sy}} : \mathbf{r}_{ij}^{\otimes 2}] d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j \\ & + \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \int \varphi_{ij} g_{ij} [(n_j \partial_{\mathbf{r}_i} n_i \cdot \delta \mathbf{r}_i + n_i \partial_{\mathbf{r}_j} n_j \cdot \delta \mathbf{r}_j) \partial_{(\mathbf{r}_i, \mathbf{r}_j)} \tilde{f}_{ij}^{(0),\text{Bo}} : (\delta \mathbf{r}_i, \delta \mathbf{r}_j) - \partial_{\mathbf{r}_j} n_j \cdot \mathbf{r}_{ij} \partial_{\mathbf{r}_j} \tilde{f}_{ij}^{(0),\text{sy}} : \mathbf{r}_{ij}] d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j, \end{aligned}$$

where $\tilde{f}_{ij}^{(0),\text{Bo}} = \tilde{f}_i^{(0)}(\mathbf{r}'_i, \mathbf{c}'_i) \tilde{f}_j^{(0)}(\mathbf{r}'_j, \mathbf{c}'_j)$ and $\tilde{f}_{ij}^{(0),\text{sy}} = g_{ij} \tilde{f}_i^{(0)}(\mathbf{r}_i, \mathbf{c}_i) \tilde{f}_j^{(0)}(\mathbf{r}_j, \mathbf{c}_j)$. These corrections are thus negligible since $\varkappa^* = k_B T^* \sigma^{*5}$ as established in Sec. V C, and the ratio $\delta^{\text{Bo}} \mathcal{E} / \mathcal{E}$ is majorized by $(\frac{\sigma^*}{r^*})^3 \frac{\sigma^*}{l_{\nabla n}^*} \frac{\sigma^*}{l_{\nabla T}^*} \ll 1$ or $(\frac{\sigma^*}{r^*})^3 \frac{\sigma^*}{l_{\nabla n}^*} \frac{\sigma^*}{l_{\nabla v}^*} \frac{\delta v^*}{\sqrt{k_B T^* / m^*}} \ll 1$ in such a way that from Eqs. (6.19) and (6.20) the correction term $\delta^{\text{Bo}} \mathcal{E}$ may be neglected.

The lengthy estimates for the deviations of the pressure tensor $\delta^{\text{Bo}} \mathcal{P} = \delta^{\text{Bo}} \mathcal{P}^p$ and of the heat fluxes $\delta^{\text{Bo}} \mathcal{Q}_1^p$ and $\delta^{\text{Bo}} \mathcal{Q}_2^p$, arising from $f_{ij}^{(0),\text{Bo}} - f_{ij}^{(0),\text{sy}}$, are discussed in Appendix G. These estimates are obtained in a similar way as for the energy with dominant terms vanishing under the hard potential approximation Eqs. (D11) and (D12) and remaining terms involving gradients of $\tilde{f}_i^{(0)}$ and $\tilde{f}_j^{(0)}$ that are negligible under the regime Eqs. (6.19) and (6.20). The result is that the corrections arising from $f_{ij}^{(0),\text{Bo}} - f_{ij}^{(0),\text{sy}}$ may be neglected and the first-order corrections in the conservation equations, that are of multiplied by the knudsen number, are also negligible. The Bogoliubov corrections in the conservation equations are thus negligible in the regime under consideration and it is legitimate to use $f_{ij}^{(0),\text{sy}}$ instead of $f_{ij}^{(0),\text{Bo}}$ in the derivation of the conservation equations. To complete the analysis, we now have to investigate the deviations arising from $f_{ij}^{(0),\text{Bo}} - f_{ij}^{(0),\text{sy}}$ in the linearized equations.

The differences in the right-hand sides of the linearized equations $\delta^{\text{Bo}} \psi_i$, arise from the material derivatives $\partial_t f_i^{(0)} + \mathbf{v} \cdot \partial_{\mathbf{r}_i} f_i^{(0)}$ and the perturbed source terms $\mathcal{J}_i^{(1)}$. From the estimates of the pressure tensor, the energy and the heat fluxes, the differences in $\partial_t f_i^{(0)} + \mathbf{v} \cdot \partial_{\mathbf{r}_i} f_i^{(0)}$ due to $f_{ij}^{(0),\text{Bo}} - f_{ij}^{(0),\text{sy}}$ in ψ_i are negligible and we must solely examine the differences arising from the perturbed operators $\mathcal{J}_i^{(1)}$. We have introduced in Eq. (6.6) the decomposition $\frac{1}{f_i^{(0)}} \mathcal{J}_i^{(1)}(f^{(0)}) = \Psi_i^{p,1} + \Psi_i^{p,3}$ and the first-order terms $\Psi_i^{p,1} = \sum_{j \in \mathfrak{S}} \frac{1}{f_j^{(0)}} \int \theta_{ij} \partial_{(\mathbf{r}_i, \mathbf{r}_j)} f_{ij}^{(0),\text{Bo}} : (\delta \mathbf{r}_i, \delta \mathbf{r}_j) d\mathbf{x}_j$ have already been taken into account in the linearized equations. We

From the expression

$$\nabla \log \tilde{f}_i^{(0)} = \frac{m_i}{k_B T} (\mathbf{c}_i - \mathbf{v}) \cdot \nabla \mathbf{v} - \left(\frac{3}{2} - \frac{m_i |\mathbf{c}_i - \mathbf{v}|^2}{2k_B T} \right) \frac{\nabla T}{T},$$

we then note that the ratio of the terms in $\nabla \log \tilde{f}_i^{(0)}$ with respect to $\nabla \log n_i$ is of the order of $\frac{l_{\nabla n}^*}{l_{\nabla v}^*} \text{Ma}^*$ or $\frac{l_{\nabla n}^*}{l_{\nabla T}^*}$ in such a way that $\nabla \log n_i$ is the main contribution in $\nabla \log f_i^{(0)}$ inside interphase fronts where $\sigma^* \approx l_{\nabla n}^*$, $\sigma^* \ll l_{\nabla T}^*$ and $\sigma^* \times \delta v^* \ll l_{\nabla v}^* \times (k_B T^* / m^*)^{1/2}$. The conditions Eqs. (6.19) and (6.20) thus ensure that the main contributions in the gradients $\nabla f_i^{(0)}$ in interphase fronts are those associated with ∇n_i .

The number densities n_i , $i \in \mathfrak{S}$, and the fluid velocity \mathbf{v} are unchanged by correction terms concerning pair distribution functions but there is first a difference of internal energies in

only have to investigate the differences in the third-order terms

$$\delta^{\text{Bo}}\Psi_i^{P,3} = \sum_{j \in \mathfrak{S}} \frac{1}{6f_i^{(0)}} \int \theta_{ij} [\partial_{(\mathbf{r}_i, \mathbf{r}_j)}^3 f_{ij}^{(0), \text{Bo}} : (\delta \mathbf{r}_i, \delta \mathbf{r}_j)^{\otimes 3} - \partial_{(\mathbf{r}_i, \mathbf{r}_j)}^3 f_{ij}^{(0), \text{sy}} : (0, \mathbf{r}_{ij})^{\otimes 3}] d\mathbf{x}_j, \quad (6.24)$$

where $\partial_{(\mathbf{r}_i, \mathbf{r}_j)}$ denotes the differential operator with respect to the pair coordinates $(\mathbf{r}_i, \mathbf{r}_j)$, where $\delta \mathbf{r}_i = \mathbf{r}'_i - \mathbf{r}_i = \mu_j \mathbf{r}_{ij} - \mu_i \mathbf{r}'_{ij}$ and $\delta \mathbf{r}_j = \mathbf{r}'_j - \mathbf{r}_j = \mu_j \mathbf{r}_{ij} + \mu_i \mathbf{r}'_{ij}$, and with the differentials $\partial_{(\mathbf{r}_i, \mathbf{r}_j)}^3 f_{ij}^{(0)}$ evaluated at $(\mathbf{r}_i, \mathbf{r}_i)$. All terms that are quadratic in the increments $\delta \mathbf{r}_i$ and $\delta \mathbf{r}_j$ indeed yield zero contributions in the expansion of $\mathcal{J}_i^{(1)}(f^{(0)})$, being even with respect to \mathbf{r}_{ij} and \mathbf{r}'_{ij} , keeping in mind that θ_{ij} is even with respect to \mathbf{r}_{ij} . The higher-order density derivatives contributions then vanish with the hard potentials approximation Eqs. (D11) and (D12) as in the analysis of the energy. The remaining terms then involve derivatives of the rescaled Maxwellians $\tilde{f}_i^{(0)}$ or $\tilde{f}_j^{(0)}$ that are negligible in the regime under consideration Eqs. (6.19), (6.20).

We conclude this section by presenting a more *qualitative argument* that directly relate the zeroth-order pair distribution functions. The distribution $f_{ij}^{(0), \text{Bo}} = f_i^{(0)}(\mathbf{r}'_i, \mathbf{c}'_i) f_j^{(0)}(\mathbf{r}'_j, \mathbf{c}'_j)$ is first decomposed as

$$f_{ij}^{(0), \text{Bo}} = n_i(\mathbf{r}'_i) n_j(\mathbf{r}'_j) \tilde{f}_i^{(0)}(\mathbf{r}'_i, \mathbf{c}'_i) \tilde{f}_j^{(0)}(\mathbf{r}'_j, \mathbf{c}'_j),$$

and in the regime under consideration we may write $T(\mathbf{r}_i) = T(\mathbf{r}'_i) = T(\mathbf{r}_j) = T(\mathbf{r}'_j) = \bar{T}$ as well as $\mathbf{v}(\mathbf{r}_i) = \bar{\mathbf{v}} + \delta \mathbf{v}_i$, $\mathbf{v}(\mathbf{r}'_i) = \bar{\mathbf{v}} + \delta \mathbf{v}'_i$, $\mathbf{v}(\mathbf{r}_j) = \bar{\mathbf{v}} + \delta \mathbf{v}_j$, $\mathbf{v}(\mathbf{r}'_j) = \bar{\mathbf{v}} + \delta \mathbf{v}'_j$ where all relative Mach numbers $\delta \mathbf{v}_i \sqrt{m_i/2k_B T(\mathbf{r})}$, $\delta \mathbf{v}'_i \sqrt{m_i/2k_B T(\mathbf{r})}$, $\delta \mathbf{v}_j \sqrt{m_j/2k_B T(\mathbf{r})}$, and $\delta \mathbf{v}'_j \sqrt{m_j/2k_B T(\mathbf{r})}$ are negligible. The rescaled Maxwellian distributions may thus be written

$$\tilde{f}_i^{(0)}(\mathbf{r}, \mathbf{c}) = \left(\frac{m_i}{2\pi k_B \bar{T}} \right)^{\frac{3}{2}} \exp \left(- \frac{m_i |\mathbf{c} - \bar{\mathbf{v}}|^2}{2k_B \bar{T}} \right), \quad i \in \mathfrak{S},$$

for any velocity \mathbf{c} , so that

$$\tilde{f}_i^{(0)}(\mathbf{r}'_i, \mathbf{c}'_i) \tilde{f}_i^{(0)}(\mathbf{r}'_j, \mathbf{c}'_j) = \left(\frac{\sqrt{m_i m_j}}{2\pi k_B \bar{T}} \right)^3 \exp \left(- \frac{m_i |\mathbf{c}'_i - \bar{\mathbf{v}}|^2 + m_j |\mathbf{c}'_j - \bar{\mathbf{v}}|^2}{2k_B \bar{T}} \right).$$

Using the conservation of energy Eq. (3.29) and of momentum Eq. (3.28) we next obtain that

$$\tilde{f}_i^{(0)}(\mathbf{r}'_i, \mathbf{c}'_i) \tilde{f}_i^{(0)}(\mathbf{r}'_j, \mathbf{c}'_j) = g_{ij} \left(\frac{\sqrt{m_i m_j}}{2\pi k_B \bar{T}} \right)^3 \exp \left(- \frac{m_i |\mathbf{c}_i - \bar{\mathbf{v}}|^2 + m_j |\mathbf{c}_j - \bar{\mathbf{v}}|^2}{2k_B \bar{T}} \right).$$

Using the same arguments for $\tilde{f}_i^{(0)}(\mathbf{r}_i, \mathbf{c}_i) \tilde{f}_i^{(0)}(\mathbf{r}_j, \mathbf{c}_j)$ then yields $\tilde{f}_i^{(0)}(\mathbf{r}'_i, \mathbf{c}'_i) \tilde{f}_i^{(0)}(\mathbf{r}'_j, \mathbf{c}'_j) = g_{ij} \tilde{f}_i^{(0)}(\mathbf{r}_i, \mathbf{c}_i) \tilde{f}_i^{(0)}(\mathbf{r}_j, \mathbf{c}_j)$. We may then use the hard potential approximation for the number densities $n_i(\mathbf{r}'_i) n_j(\mathbf{r}'_j) = n_i(\mathbf{r}_i) n_j(\mathbf{r}_j)$ and this finally yields that, in the regime under consideration,

$$f_{ij}^{(0), \text{Bo}} = g_{ij} f_i^{(0)}(\mathbf{r}_i, \mathbf{c}_i) f_j^{(0)}(\mathbf{r}_j, \mathbf{c}_j) = f_{ij}^{(0), \text{sy}}.$$

In summary, the equations derived with the symmetrized pair distribution functions also agree with Bogoliubov distribution functions in a regime where density gradients dominate the dynamics of interphase fronts and when interaction potentials are hard.

VII. COMPARISON AND DISCUSSION

We discuss in this section the model derived from the kinetic theory, the other models derived from thermodynamics in the literature as well as the domain of validity of the resulting equations.

A. Derivation from thermodynamics

A Cahn-Hilliard fluid model has been derived from the kinetic theory of dense gas mixtures. The model, derived at the molecular level, is in full agreement with the model derived from rational thermodynamic in Sec. II. In comparison with the equations governing nonideal fluids derived in Sec. IV,

the Cahn-Hilliard fluid model involve various extra gradient terms. Such extra terms arise as *gradient approximations of nonlocalities due to the perturbed kinetic operators* $\mathcal{J}_i^{(1)}$, $i \in \mathfrak{S}$. At zeroth order of Enskog expansion, nonlocalities of Maxwellian distributions yield the Korteweg-type tensor, the van der Waals and Cahn-Hilliard gradient energy terms as well as the Dunn and Serrin-type heat flux. At first order of Enskog expansion, nonlocalities in Maxwellian distributions yield the Cahn-Hilliard diffusion driving forces in the linearized equations whereas nonlocalities in the perturbed distribution functions yield the capillary-diffusive contributions in the heat flux.

An important task is now to compare the resulting model with those derived in previous work [2, 19–23]. All terms are found to agree with the exception of the capillary-diffusive heat flux \mathcal{Q}^{CD} and the force terms \mathbf{X}_i , $i \in \mathfrak{S}$. More specifically, the kinetic theory yields an heat flux in the form

$$\mathcal{Q} = \sum_{i \in \mathfrak{S}} \bar{\gamma}_i \rho_i \nabla \cdot \mathbf{v} + \sum_{i \in \mathfrak{S}} \bar{\gamma}_i \nabla \cdot \bar{\mathcal{F}}_i - \sum_{i \in \mathfrak{S}} \nabla \cdot \bar{\gamma}_i \bar{\mathcal{F}}_i + \mathcal{Q}^{\text{d}}, \quad (7.1)$$

and forces terms as

$$\mathbf{X}_i = n_i k_B T \left[\nabla \frac{g_i}{k_B T} - \sum_{j \in \mathfrak{S}} \frac{\nabla \nabla \cdot (\chi_{ij} \nabla n_j)}{k_B T} \right]. \quad (7.2)$$

However, by using Eq. (A6) for the entropy production rate, the following heat flux and force terms are obtained

$$\mathcal{Q}' = \sum_{i \in \mathfrak{S}} \bar{\gamma}_i \rho_i \nabla \cdot \mathbf{v} + \sum_{i \in \mathfrak{S}} \bar{\gamma}_i \nabla \cdot \bar{\mathcal{F}}_i + \mathcal{Q}^d, \quad (7.3)$$

$$\mathbf{X}'_i = n_i k_B T \nabla \left[\frac{g_i}{k_B T} - \sum_{j \in \mathfrak{S}} \frac{\nabla \cdot (\chi_{ij} \nabla n_j)}{k_B T} \right], \quad (7.4)$$

so that $\mathbf{X}'_i - \mathbf{X}_i = n_i \nabla \cdot \boldsymbol{\gamma}_i \nabla T / T$. These expressions have notably been derived by Anderson *et al.* [2], Verschuere *et al.* [20], and Liu *et al.* [23]. Similarly, by using the Eq. (A8) for the entropy production rate, the following heat flux and force terms are obtained:

$$\mathcal{Q}'' = \sum_{i \in \mathfrak{S}} \bar{\gamma}_i \rho_i \nabla \cdot \mathbf{v} + \mathcal{Q}^d, \quad (7.5)$$

$$\mathbf{X}''_i = n_i k_B T \nabla \left[\frac{g_i}{k_B T} - \sum_{j \in \mathfrak{S}} \nabla \cdot \left(\frac{\chi_{ij} \nabla n_j}{k_B T} \right) \right], \quad (7.6)$$

and then $\mathbf{X}''_i - \mathbf{X}_i = n_i T \nabla (\bar{\boldsymbol{\gamma}}_i \cdot \nabla T / T^2) + n_i \nabla \cdot \boldsymbol{\gamma}_i \nabla T / T$. These expressions have notably been obtained by Falk [19], and by Alt and Pawlow [24] without convection phenomena.

We then first note that the model Eqs. (7.3)–(7.4) and Eqs. (7.5)–(7.6) first exactly agree with Eqs. (7.1)–(7.2) when all capillary coefficients are equal $\bar{\alpha}_{ij} = \bar{\alpha}$ since then all difference terms automatically vanish from mass conservation constraints. Indeed, in this situation, the vectors $\bar{\boldsymbol{\gamma}}_i$ are given by $\bar{\boldsymbol{\gamma}}_i = \bar{\alpha} \nabla \rho$, $i \in \mathfrak{S}$, and are all equal so that $\sum_{i \in \mathfrak{S}} \bar{\boldsymbol{\gamma}}_i \nabla \cdot \bar{\mathcal{F}}_i = \bar{\alpha} \nabla \rho \nabla \cdot (\sum_{i \in \mathfrak{S}} \bar{\mathcal{F}}_i) = 0$ from the mass conservation constraint, $\sum_{i \in \mathfrak{S}} \bar{\mathcal{F}}_i = 0$ and similarly $\sum_{i \in \mathfrak{S}} \nabla \cdot \bar{\boldsymbol{\gamma}}_i \bar{\mathcal{F}}_i = \nabla \bar{\alpha} \nabla \rho \sum_{i \in \mathfrak{S}} \bar{\mathcal{F}}_i = 0$. This was the model used in particular by Gaillard *et al.* [9] to simulate hydrogen-air transcritical flames. In this situation the capillary terms in the Cahn-Hilliard diffusive fluxes also vanish [9]. The resulting model may be seen as a generalization to mixtures of the van der Waals model with a simplified $\bar{\alpha} |\nabla \rho|^2$ gradient energy in the free energy [9].

More generally, we note that the model Eqs. (7.3)–(7.4) and Eqs. (7.5)–(7.6) essentially agree with Eqs. (7.1)–(7.2) in the regimes under consideration. Indeed, the differences between the forces terms involve temperature gradients and the relative errors scale as $(\frac{\sigma^*}{r^*})^3 \frac{\sigma^*}{l_{v_n}^*} \frac{\sigma^*}{l_{v_T}^*} \ll 1$ where σ^* denotes a typical collision diameter, r^* the average interparticle distance, $l_{v_n}^*$ a characteristic length of density gradients, and $l_{v_T}^*$ a characteristic length of velocity or temperature gradients, and may thus be neglected since temperature gradients remain modest in interphase fronts. For similar reasons, the first-order contributions in the heat fluxes may be estimated to be negligible in the regime under consideration, keeping in mind that the force terms vanish at equilibrium interfaces. With these approximations, the three models Eqs. (7.3)–(7.4), Eqs. (7.5)–(7.6), and Eqs. (7.1)–(7.2) are essentially similar.

However, various authors have further extracted the natural $1/T$ factor in the thermodynamic fluxes. The resulting expression of the entropy production rate Eq. (A9) then leads to the heat flux

$$\mathcal{Q} = \sum_{i \in \mathfrak{S}} \bar{\gamma}_i \rho_i \nabla \cdot \mathbf{v} + \sum_{i \in \mathfrak{S}} \bar{\boldsymbol{\gamma}}_i \nabla \cdot \bar{\mathcal{F}}_i - \sum_{i \in \mathfrak{S}} (\bar{g}_i - \nabla \cdot \bar{\boldsymbol{\gamma}}_i) \bar{\mathcal{F}}_i + \mathcal{Q}^d, \quad (7.7)$$

with an unphysical component $\sum_{i \in \mathfrak{S}} \bar{g}_i \bar{\mathcal{F}}_i$, and such fluxes have been considered in particular by Heida *et al.* [21] and Guo *et al.* [22]. Letting the capillary coefficient to zero, the resulting heat flux is in the form $\mathcal{Q} = -\sum_{i \in \mathfrak{S}} \bar{g}_i \bar{\mathcal{F}}_i + \mathcal{Q}^d$ in contradiction with classical results on gas mixtures [56,57,62–64].

A mathematical analysis of the structure of these systems of partial differential equations should next be conducted. Such mathematical studies have already concerned the isothermal as well as nonisothermal single-species diffuse interface fluids [89–91]. The situation of nonisothermal Cahn-Hilliard fluids, however, has not yet been considered, and will be considered in future studies.

B. Entropic considerations

The macroscopic entropy $S^{K,(0)}$ obtained from the kinetic model when using higher-order Taylor expansion of pair distribution functions may be shown to be in the form

$$S^{K,(0)} = S^u + \sum_{i,j \in \mathfrak{S}} \frac{\chi_{ij}}{2T} \rho_i \Delta \rho_j, \quad (7.8)$$

where $S^u = S^{(0)}$ is the nonideal entropy obtained in from the kinetic theory Eq. (4.16) in the absence of diffuse interface effects. In the situation of constant capillary coefficients, this entropy $S^u = S^{(0)}$ has also been shown to be the Gibbsian entropy of the diffuse interface model. We may also transform this entropy Eq. (7.8) into

$$\tilde{S}^{K,(0)} = S^u - \sum_{i,j \in \mathfrak{S}} \frac{\chi_{ij}}{2T} \nabla \rho_i \cdot \nabla \rho_j, \quad (7.9)$$

by modifying the entropy flux.

We thus conclude that the macroscopic entropies $S^{K,(0)}$ or $\tilde{S}^{K,(0)}$ obtained from the kinetic theory by using higher-order Taylor expansion of pair distribution functions differ from the Gibbsian entropy S^u naturally arising from the structure of the governing equations. This Gibbsian entropy S^u may be seen as a *thermodynamic mathematical construction* derived from the structure of the system of partial differential equations. This difference between $\tilde{S}^{K,(0)}$ and $S^u = S^{(0)}$ may also be interpreted as an indication that there is no H theorem in general for the generalized Boltzmann equations derived from the BBGKY hierarchy.

A similar situation is that of second-order entropies in Enskog expansions, i.e., entropies obtained in Burnett regimes, discussed notably by de Groot and Mazur [59] and Giovangigli [92–94]. These entropies also differ from the Gibbsian entropies associated with the fluid equations [59].

C. Nonideal fluid thermodynamics and transport

The derivation of the van der Waals equation of state from the kinetic theory of gas mixtures has used the assumption that the volume ratio is small $\sum_{j \in \mathfrak{S}} n_j b_j \ll 1$. This property then implies that $(1 - \sum_{j \in \mathfrak{S}} n_j b_j)^{-1} \approx 1 + \sum_{j \in \mathfrak{S}} n_j b_j$ as in the traditional derivation from equilibrium statistical mechanics for a single gas [83–85]. The domain of validity of van der Waals equation of state, however, is *much larger* than that of the hypotheses made in the derivation and notably

includes liquids where the volume ratio $\sum_{j \in \mathfrak{S}} n_j \mathbf{b}_j$ is of order unity. Another derivation of the van der Waals equation of state is also possible by directly including factors in the form $(1 - \sum_{j \in \mathfrak{S}} n_j \mathbf{b}_j)^{-1}$ in the correlation function g_{ij} as first suggested by Sobrino for single-species fluids [34] and used in various work [40,42]. This would have the advantage of directly giving factors $(1 - \sum_{j \in \mathfrak{S}} n_j \mathbf{b}_j)^{-1}$ in the repulsive part but would also yield such factors in the attractive part of the equation of state and in all capillary terms without further simplifications. This is why we have used the equilibrium correlation functions given by statistical mechanics Eq. (4.6) and followed the traditional derivation of van der Waals equation of state from statistical mechanics [83–85].

Including triple collisions in the model, taking into account the triplet distributions f_{ijk} , would lead to cubic terms in the equation of state. Equations of states like the Redlich-Kwong equation of state [77,95] could eventually be derived from a kinetic theory including triple collisions. Such equations of state, that are variants of that of van der Waals', and their corresponding thermodynamics [77], yield accurate results over the range of pressure, temperature and mixture states of interest of many phenomena like supercritical combustion [9,96]. An alternative method could be to modify the collision operators as in Sobrino [34].

The traditional multicomponent diffusion driving forces \mathbf{d}_i^{cl} are defined by subtracting temperature gradients from thermodynamic diffusion driving forces \mathbf{d}_i^{th} naturally related to chemical potential gradients Eq. (4.46). The traditional multicomponent diffusion coefficients are then obtained as detailed in Sec. IV E 2 and involve pressure-based thermodynamic properties. These traditional expressions may thus only be used when mechanical stability holds and solely the thermodynamic formulation is generally valid. The pressure-based species enthalpies and specific volume even explode at mechanical instability limits as detailed in Gaillard *et al.* [9]. The impact of nonideal thermodynamic forces in multicomponent diffusion has also been investigated in Refs. [96,97].

D. Cahn-Hilliard fluids

We have presented in previous sections the first molecular derivation of Cahn-Hilliard fluids models in the framework of the kinetic theory of dense gas mixtures. This resulting model notably includes generalized van der Waals and Cahn-Hilliard gradient energy, Korteweg tensor, Dunn and Serrin-type heat flux, as well as Cahn-Hilliard multicomponent diffusive-type fluxes and first-order capillary contribution in the heat flux. The capillarity coefficients have also been related to intermolecular forces and the van der Waals equation of state has also been derived. We now address the validity domain of the derivation from the kinetic theory.

The capillary fluid equations have been derived within the kinetic theory of moderately dense gas mixtures essentially assuming that $\sigma^* \ll r^* \ll l_k^* \ll l_h^*$, where σ^* is a typical collision diameter or equivalently a typical range of the interaction potentials φ_{ij} , r^* a characteristic interparticle distance, l_k^* the mean free path, and l_h^* a hydrodynamic length. We have also assumed that the interaction potentials are hard to simplify some of the collision integrals associated with dense gases. We have also assumed that the temperature gradients remain

of macroscopic scale as well as and that the velocity gradients multiplied by the relative Mach number are small in interphase fronts when estimating the deviations arising from Bogoliubov distributions. However, these capillary equation also apply to liquids where $\sigma^* = r^* = l_k^*$ and are exactly the equations derived from thermodynamics. Therefore, as for the van der Waals equation of state, the domain of validity of the resulting equations is *much larger* than that of the kinetic theory of moderately dense gases since it also applies to liquids.

We have also used a new Enskog-type scaling of the generalized Boltzmann equations. This scaling clarifies the derivation of the macroscopic equations and directly yields the equilibrium Maxwellian distributions. This scaling also yields the Euler capillary fluid equations at zeroth order, whereas in previous work for single-species fluids the diffuse interface terms were only obtained at first order [15]. In other words, the diffuse interface terms in Euler equations, as well as the nonideal thermodynamic functions, are direct consequences of the perturbed source terms $\mathcal{J}_i^{(1)}$, $i \in \mathfrak{S}$. The importance of diffuse interface Euler fluid equations in conjunction with Hilbert's sixth problem has notably been emphasized by Gorban and Karlin [98,99] and Slemrod [100].

The derivation from the kinetic theory has been performed by simplifying the capillarity coefficients \varkappa_{ij} so that it is independent of T and from the number densities n_i , $i \in \mathfrak{S}$. The temperature dependence of the capillarity coefficients could next be investigated by using nonequilibrium correlation functions g_{ij} that may also lead to temperature gradients in the capillary terms. However, there is no clear expression for a nonequilibrium correlation function at interfaces so that it should be chosen carefully [3,87,88].

Finally, a key argument in the derivation is the use of a generalized Boltzmann equation with distribution functions are evaluated *at different spatial positions*.

VIII. CONCLUSION

We have derived the full Cahn-Hilliard fluid equations from the kinetic theory of dense gas mixtures. Only monatomic mixtures of gases have been taken into account and investigating polyatomic gas mixtures in a semiquantum framework would be of high scientific interest. In the same vein, it would be interesting to investigate reactive source terms treated typically as perturbations. Taking into account triple collisions in the kinetic model would also lead to richer thermodynamic models and state law with third powers of concentrations like an approximate Redlich-Kwong state law. The situation of temperature dependent diffuse interface coefficients would also be of high scientific interest and may further lead to extra temperature gradients in the capillary terms. Boundary conditions at solid walls and three-phase lines could also be investigated with kinetic methods by taking into account interaction potentials with crystal atoms as well as collisions with phonons. Numerical simulations would also be an outstanding tool for comparing kinetic models and their corresponding macroscopic diffuse interface equations. Last but not least, the mathematical structure of the resulting systems of partial differential equations should be investigated in depth.

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APPENDIX A: ENTROPY PRODUCTION IN FLUID MODELS

We derive in this section the rate of entropy production Eq. (2.12) from Gibbs relation Eq. (2.8) and the fluid governing Eqs. (2.9)–(2.11). The species conservation equations are first written in the form

$$\partial_t \rho_i + \mathbf{v} \cdot \nabla \rho_i = -\rho_i \nabla \cdot \mathbf{v} - \nabla \cdot \bar{\mathcal{F}}_i, \quad i \in \mathfrak{S}, \quad (\text{A1})$$

and we also have the differential identity

$$(\partial_t + \mathbf{v} \cdot \nabla) \nabla \rho_i = \nabla (\partial_t \rho_i + \mathbf{v} \cdot \nabla \rho_i) - (\nabla \mathbf{v})^t \cdot \nabla \rho_i, \quad i \in \mathfrak{S}. \quad (\text{A2})$$

Multiplying the momentum conservation Eq. (2.10) by the velocity vector \mathbf{v} and subtracting the result from the total energy conservation Eq. (2.11) also yields the balance equation for internal energy \mathcal{E} in the form

$$\partial_t \mathcal{E} + \mathbf{v} \cdot \nabla \mathcal{E} = -\mathcal{E} \nabla \cdot \mathbf{v} - \nabla \cdot \mathcal{Q} - \mathcal{P} : \nabla \mathbf{v}. \quad (\text{A3})$$

Using Gibbs relation Eq. (2.8), we further obtain that

$$T(\partial_t \mathcal{S} + \mathbf{v} \cdot \nabla \mathcal{S}) = \partial_t \mathcal{E} + \mathbf{v} \cdot \nabla \mathcal{E} - \sum_{i \in \mathfrak{S}} \bar{g}_i (\partial_t \rho_i + \mathbf{v} \cdot \nabla \rho_i) - \sum_{i \in \mathfrak{S}} \bar{\mathcal{Y}}_i \cdot (\partial_t + \mathbf{v} \cdot \nabla) \nabla \rho_i,$$

and combining this with relations Eqs. (A1)–(A3) yields

$$\begin{aligned} \partial_t \mathcal{S} + \mathbf{v} \cdot \nabla \mathcal{S} = & -\frac{1}{T} (\mathcal{E} \nabla \cdot \mathbf{v} + \nabla \cdot \mathcal{Q} + \mathcal{P} : \nabla \mathbf{v}) \\ & + \sum_{i \in \mathfrak{S}} \frac{\bar{g}_i}{T} (\rho_i \nabla \cdot \mathbf{v} + \nabla \cdot \bar{\mathcal{F}}_i) + \sum_{i \in \mathfrak{S}} \frac{\bar{\mathcal{Y}}_i}{T} \cdot [\nabla (\rho_i \nabla \cdot \mathbf{v} + \nabla \cdot \bar{\mathcal{F}}_i) + (\nabla \mathbf{v})^t \cdot \nabla \rho_i]. \end{aligned} \quad (\text{A4})$$

The aim is now to decompose the right-hand side of Eq. (A4) into an entropy flux and a nonnegative production term. A key argument is that derivatives may take arbitrary values so that *only products of derivatives of the same order may have a sign*. We may also regroup all terms proportional to $\nabla \cdot \mathbf{v}$ by using $(\mathcal{G} - \mathcal{E})/T = p/T - \mathcal{S}$.

Since the divergence of the total heat flux $\nabla \cdot \mathcal{Q}$ involves second-order derivatives of temperature, it must be integrated by part. Similarly, the terms $\nabla (\nabla \cdot \bar{\mathcal{F}}_i)$ involves fifth order derivatives with Cahn-Hilliard-type fluxes—third-order with standard diffusion—and must also be integrated by parts. The terms $\bar{\mathcal{Y}}_i \cdot (\nabla \mathbf{v})^t \cdot \nabla \rho_i$ may further be regrouped with the velocity gradient terms and these operations yield

$$\begin{aligned} \partial_t \mathcal{S} + \nabla \cdot (\mathbf{v} \mathcal{S}) + \nabla \cdot \left[\frac{\mathcal{Q}}{T} - \sum_{i \in \mathfrak{S}} \frac{\bar{\mathcal{Y}}_i}{T} (\rho_i \nabla \cdot \mathbf{v} + \nabla \cdot \bar{\mathcal{F}}_i) \right] = & -\frac{1}{T} \left(\mathcal{P} - p\mathbf{I} - \sum_{i \in \mathfrak{S}} \nabla \rho_i \otimes \bar{\mathcal{Y}}_i \right) : \nabla \mathbf{v} - \mathcal{Q} \cdot \frac{\nabla T}{T^2} \\ & + \sum_{i \in \mathfrak{S}} \left(\frac{\bar{g}_i}{T} - \nabla \cdot \frac{\bar{\mathcal{Y}}_i}{T} \right) \nabla \cdot \bar{\mathcal{F}}_i - \sum_{i \in \mathfrak{S}} \nabla \cdot \frac{\bar{\mathcal{Y}}_i}{T} \rho_i \nabla \cdot \mathbf{v}. \end{aligned} \quad (\text{A5})$$

The derivatives $\nabla \cdot (\bar{\mathcal{Y}}_i/T)$ appearing in the two last sums on the right-hand side are then developed and the resulting terms split between temperature and velocity gradients, as for a single-species fluid [15]. The diffusive fluxes are also integrated by parts and these operations yield

$$\begin{aligned} \partial_t \mathcal{S} + \nabla \cdot (\mathbf{v} \mathcal{S}) + \nabla \cdot \left[\frac{\mathcal{Q}}{T} - \sum_{i \in \mathfrak{S}} \frac{\bar{\mathcal{Y}}_i}{T} (\rho_i \nabla \cdot \mathbf{v} + \nabla \cdot \bar{\mathcal{F}}_i) - \sum_{i \in \mathfrak{S}} \left(\frac{\bar{g}_i}{T} - \frac{\nabla \cdot \bar{\mathcal{Y}}_i}{T} \right) \bar{\mathcal{F}}_i \right] \\ = & -\frac{1}{T} \left[\mathcal{P} - p\mathbf{I} - \sum_{i \in \mathfrak{S}} (\nabla \rho_i \otimes \bar{\mathcal{Y}}_i - \rho_i \nabla \cdot \bar{\mathcal{Y}}_i \mathbf{I}) \right] : \nabla \mathbf{v} \\ & - \left[\mathcal{Q} - \sum_{i \in \mathfrak{S}} \bar{\mathcal{Y}}_i (\rho_i \nabla \cdot \mathbf{v} + \nabla \cdot \bar{\mathcal{F}}_i) \right] \cdot \nabla \left(\frac{-1}{T} \right) \\ & - \sum_{i \in \mathfrak{S}} \nabla \cdot \left(\frac{\bar{g}_i}{T} - \frac{\nabla \cdot \bar{\mathcal{Y}}_i}{T} \right) \cdot \bar{\mathcal{F}}_i. \end{aligned} \quad (\text{A6})$$

We may finally develop the terms $\nabla \frac{\bar{y}_i}{T}$ in the diffusion driving forces to finally obtain that

$$\begin{aligned}
\partial_t \mathcal{S} + \nabla \cdot (\mathbf{v} \mathcal{S}) + \nabla \cdot \left[\frac{\mathcal{Q}}{T} - \sum_{i \in \mathfrak{S}} \frac{\bar{y}_i}{T} (\rho_i \nabla \cdot \mathbf{v} + \nabla \cdot \bar{\mathcal{F}}_i) - \sum_{i \in \mathfrak{S}} \left(\frac{\bar{g}_i}{T} - \frac{\nabla \cdot \bar{y}_i}{T} \right) \bar{\mathcal{F}}_i \right] \\
= -\frac{1}{T} \left[\mathcal{P} - p \mathbf{I} - \sum_{i \in \mathfrak{S}} (\nabla \rho_i \otimes \bar{y}_i - \rho_i \nabla \cdot \bar{y}_i \mathbf{I}) \right] : \nabla \mathbf{v} \\
- \left[\mathcal{Q} - \sum_{i \in \mathfrak{S}} \bar{y}_i (\rho_i \nabla \cdot \mathbf{v} + \nabla \cdot \bar{\mathcal{F}}_i) + \sum_{i \in \mathfrak{S}} \nabla \cdot \bar{y}_i \bar{\mathcal{F}}_i \right] \cdot \nabla \left(\frac{-1}{T} \right) \\
- \sum_{i \in \mathfrak{S}} \left[\nabla \frac{\bar{g}_i}{T} - \frac{\nabla (\nabla \cdot \bar{y}_i)}{T} \right] \cdot \bar{\mathcal{F}}_i. \tag{A7}
\end{aligned}$$

This is the balance of entropy used in Sec. II B involving notably the force terms $\nabla (\bar{g}_i/T) - \nabla \nabla \cdot \bar{y}_i/T$, a Korteweg-type tensor and a Dunn and Serrin-type heat flux.

Another variant is then to integrate by part the diffusion terms in Eq. (A5) to get that

$$\begin{aligned}
\partial_t \mathcal{S} + \nabla \cdot (\mathbf{v} \mathcal{S}) + \nabla \cdot \left[\frac{\mathcal{Q}}{T} - \sum_{i \in \mathfrak{S}} \frac{\bar{y}_i}{T} (\rho_i \nabla \cdot \mathbf{v} + \nabla \cdot \bar{\mathcal{F}}_i) - \sum_{i \in \mathfrak{S}} \left(\frac{\bar{g}_i}{T} - \nabla \cdot \frac{\bar{y}_i}{T} \right) \bar{\mathcal{F}}_i \right] \\
= -\frac{1}{T} \left[\mathcal{P} - p \mathbf{I} - \sum_{i \in \mathfrak{S}} (\nabla \rho_i \otimes \bar{y}_i - \rho_i \nabla \cdot \bar{y}_i \mathbf{I}) \right] : \nabla \mathbf{v} \\
- \left(\mathcal{Q} - \sum_{i \in \mathfrak{S}} \rho_i \bar{y}_i \nabla \cdot \mathbf{v} \right) \cdot \nabla \left(\frac{-1}{T} \right) - \sum_{i \in \mathfrak{S}} \nabla \left(\frac{\bar{g}_i}{T} - \nabla \cdot \frac{\bar{y}_i}{T} \right) \cdot \bar{\mathcal{F}}_i. \tag{A8}
\end{aligned}$$

Finally, a fourth variant is obtained by developing the derivatives $\nabla (\bar{g}_i/T)$ in the diffusion driving forces of Eq. (A7) and the result reads

$$\begin{aligned}
\partial_t \mathcal{S} + \nabla \cdot (\mathbf{v} \mathcal{S}) + \nabla \cdot \left[\frac{\mathcal{Q}}{T} - \sum_{i \in \mathfrak{S}} \frac{\bar{y}_i}{T} (\rho_i \nabla \cdot \mathbf{v} + \nabla \cdot \bar{\mathcal{F}}_i) - \sum_{i \in \mathfrak{S}} \left(\frac{\bar{g}_i}{T} - \frac{\nabla \cdot \bar{y}_i}{T} \right) \bar{\mathcal{F}}_i \right] \\
= -\frac{1}{T} \left[\mathcal{P} - p \mathbf{I} - \sum_{i \in \mathfrak{S}} (\nabla \rho_i \otimes \bar{y}_i - \rho_i \nabla \cdot \bar{y}_i \mathbf{I}) \right] : \nabla \mathbf{v} \\
- \left[\mathcal{Q} - \sum_{i \in \mathfrak{S}} \bar{y}_i (\rho_i \nabla \cdot \mathbf{v} + \nabla \cdot \bar{\mathcal{F}}_i) - \sum_{i \in \mathfrak{S}} (\bar{g}_i - \nabla \cdot \bar{y}_i) \bar{\mathcal{F}}_i \right] \cdot \nabla \left(\frac{-1}{T} \right) - \sum_{i \in \mathfrak{S}} \frac{1}{T} [\nabla \bar{g}_i - \nabla (\nabla \cdot \bar{y}_i)] \cdot \bar{\mathcal{F}}_i. \tag{A9}
\end{aligned}$$

The four Eqs. (A6)–(A9) are discussed in Sec. VII A and also reveals the ambiguity of rational thermodynamics.

APPENDIX B: CAHN-HILLIARD MODELS WITH MASS FRACTION GRADIENTS

The general form for free energies \mathcal{A} in Cahn-Hilliard models has been written in Sec. II A by using partial density gradients Eq. (2.1). Such energies have notably been used by Cahn [16], Rowlinson and Widom [3], Verschueren [20], Liu *et al.* [23], and Heida *et al.* [21] and reduce to the traditional van der Waals energy for a single-species fluid.

However, historically, gradient energies in terms of mole fraction gradients have first been considered by Cahn and Hilliard. We thus briefly address such a situation in this section, easily derived from the general case of density gradients. More specifically, we consider energies written in terms of mass fraction gradients as Anderson *et al.* [2], that are more convenient than mole fractions for multicomponent mixtures and mass-based diffusion fluxes. Note still that mole and mass also coincide for isomass mixtures. We have to establish in particular that there are not anymore second derivatives in the generalized Korteweg Pressure tensor as traditionally established with such energies [2].

We consider thus an energy written in the form

$$\mathcal{A} = \mathcal{A}^u + \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \bar{\chi}_{ij} \nabla y_i \cdot \nabla y_j, \tag{B1}$$

where $y_i = \rho_i/\rho$ denotes the mass fraction of the i th species and $\rho = \sum_{i \in \mathfrak{S}} \rho_i$ the mixture mass density. Noting then that

$$\nabla y_i = \frac{1}{\rho} (\nabla \rho_i - y_i \nabla \rho) = \frac{1}{\rho} \sum_{k \in \mathfrak{S}} (\delta_{ik} - y_i) \nabla \rho_k,$$

we may rewrite the energy Eq. (B1) in the general form Eq. (2.1), provided the mass-based capillary coefficients $\bar{\alpha}_{kl}$ are in the special form

$$\bar{\alpha}_{kl} = \sum_{i,j \in \mathfrak{S}} \bar{\chi}_{ij} \frac{1}{\rho^2} (\delta_{ik} - y_i)(\delta_{jl} - y_j), \quad k, l \in \mathfrak{S}. \quad (\text{B2})$$

We may now evaluate the Korteweg tensor \mathcal{P}^{KO} by first noting that

$$\begin{aligned} - \sum_{k,l \in \mathfrak{S}} \rho_k \nabla \cdot (\bar{\alpha}_{kl} \nabla \rho_l) &= - \sum_{i,j,k,l \in \mathfrak{S}} \rho_k \nabla \cdot \left[\bar{\chi}_{ij} \frac{1}{\rho^2} (\delta_{ik} - y_i)(\delta_{jl} - y_j) \nabla \rho_l \right] \\ &= - \sum_{i,j,k \in \mathfrak{S}} \rho_k \nabla \cdot \left[\bar{\chi}_{ij} \frac{1}{\rho} (\delta_{ik} - y_i) \nabla y_j \right] \\ &= \sum_{i,j \in \mathfrak{S}} \bar{\chi}_{ij} \nabla y_i \cdot \nabla y_j, \end{aligned}$$

where use has been made of $\sum_{k \in \mathfrak{S}} \rho_k (\delta_{ik} - y_i) = 0$ after expanding the divergence term. However, a direct calculations yields

$$\frac{1}{2} \sum_{k,l \in \mathfrak{S}} \left(\sum_{m \in \mathfrak{S}} \rho_m \partial_{\rho_m} \bar{\alpha}_{kl} - \bar{\alpha}_{kl} \right) \nabla \rho_k \cdot \nabla \rho_l = \frac{1}{2} \sum_{i,j \in \mathfrak{S}} \left(\sum_{m \in \mathfrak{S}} \rho_m \partial_{\rho_m} \bar{\chi}_{ij} - 3\bar{\chi}_{ij} \right) \nabla y_i \cdot \nabla y_j,$$

in such a way that

$$\mathcal{P}^{\text{KO}} = \frac{1}{2} \sum_{i,j \in \mathfrak{S}} \left(\sum_{k \in \mathfrak{S}} \rho_k \partial_{\rho_k} \bar{\chi}_{ij} - \bar{\chi}_{ij} \right) \nabla y_i \cdot \nabla y_j \mathbf{I} + \sum_{i,j \in \mathfrak{S}} \bar{\chi}_{ij} \nabla y_i \otimes \nabla y_j. \quad (\text{B3})$$

In particular, there are not anymore second derivatives in the pressure tensor \mathcal{P}^{KO} as traditionally obtained [2] when using mass or mole fractions gradients in the free energy as in Eq. (B1).

Finally, a direct calculation yields that the generalized Dunn and Serrin heat flux vanishes $\mathcal{Q}^{\text{DS}} = 0$ and that we also have

$$\mathcal{Q}^{\text{CD}} = - \sum_{i,j \in \mathfrak{S}} \nabla \cdot \left(\frac{1}{\rho} \bar{\chi}_{ij} \nabla y_j \right) \mathcal{F}_i + \sum_{i,j \in \mathfrak{S}} \frac{1}{\rho} \bar{\chi}_{ij} \nabla y_j \cdot \nabla \cdot \mathcal{F}_i. \quad (\text{B4})$$

APPENDIX C: MACROSCOPIC EQUATIONS FROM THE KINETIC THEORY

1. Derivation from the hierarchy

Multiplying by m_i the Boltzmann equation of the i th species Eq. (3.1), integrating with respect to \mathbf{c}_i , and decomposing $\mathbf{c}_i = \mathbf{v} + \mathbf{c}_i - \mathbf{v}$, it is obtained that

$$\partial_t \rho_i + \nabla \cdot (\rho_i \mathbf{v}) + \nabla \cdot \bar{\mathcal{F}}_i = 0, \quad (\text{C1})$$

where the diffusive mass flux of the i th species $\bar{\mathcal{F}}_i$ is defined by

$$\bar{\mathcal{F}}_i(\mathbf{r}, t) = \int m_i (\mathbf{c}_i - \mathbf{v}) f_i(\mathbf{r}, \mathbf{c}_i, t) d\mathbf{c}_i. \quad (\text{C2})$$

Multiplying by $m_i \mathbf{c}_i$ the Boltzmann Eq. (3.1), integrating with respect to \mathbf{c}_i , summing over the species $i \in \mathfrak{S}$, and using the definition of \mathbf{v} then yields

$$\partial_t (\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) + \nabla \cdot \mathcal{P}^{\text{K}} + \mathcal{R}^{\mathbf{v}} = 0,$$

where \mathcal{P}^{K} is the traditional kinetic part of the pressure tensor

$$\mathcal{P}^{\text{K}}(\mathbf{r}, t) = \sum_{i \in \mathfrak{S}} \int m_i (\mathbf{c}_i - \mathbf{v}) \otimes (\mathbf{c}_i - \mathbf{v}) f_i(\mathbf{r}, \mathbf{c}_i, t) d\mathbf{c}_i, \quad (\text{C3})$$

and the term $\mathcal{R}^{\mathbf{v}}$ reads

$$\mathcal{R}^{\mathbf{v}}(\mathbf{r}, t) = - \sum_{i,j \in \mathfrak{S}} \int m_i \mathbf{c}_i \theta_{ij} f_{ij}(\mathbf{r}, \mathbf{c}_i, \mathbf{r} + \mathbf{r}_{ij}, \mathbf{c}_j, t) d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j,$$

with $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$. Using the expression of θ_{ij} , integrating by parts with respect to \mathbf{c}_i and \mathbf{c}_j , using the definition of n_{ij} and $\partial_{\mathbf{r}_i}\varphi_{ij} = -\varphi'_{ij}(r_{ij})\mathbf{r}_{ij}/r_{ij}$, it is obtained that

$$\mathcal{R}^v(\mathbf{r}, t) = - \sum_{i,j \in \mathfrak{S}} \int \frac{\varphi'_{ij}(r_{ij})}{r_{ij}} \mathbf{r}_{ij} n_{ij}(\mathbf{r}, \mathbf{r} + \mathbf{r}_{ij}, t) d\mathbf{r}_{ij}.$$

We may now use that $n_{ij}(\mathbf{r}, \mathbf{r} + \mathbf{r}_{ij}, t) = n_{ji}(\mathbf{r} + \mathbf{r}_{ij}, \mathbf{r}, t)$, letting $\mathbf{r}_{ji} = -\mathbf{r}_{ij}$, and exchanging i and j in the resulting sum, we get

$$\mathcal{R}^v(\mathbf{r}, t) = \sum_{i,j \in \mathfrak{S}} \int \frac{\varphi'_{ij}(r_{ij})}{r_{ij}} \mathbf{r}_{ij} n_{ij}(\mathbf{r} - \mathbf{r}_{ij}, \mathbf{r}, t) d\mathbf{r}_{ij},$$

and thus

$$\mathcal{R}^v(\mathbf{r}, t) = - \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \int \frac{\varphi'_{ij}(r_{ij})}{r_{ij}} \mathbf{r}_{ij} [n_{ij}(\mathbf{r}, \mathbf{r} + \mathbf{r}_{ij}, t) - n_{ij}(\mathbf{r} - \mathbf{r}_{ij}, \mathbf{r}, t)] d\mathbf{r}_{ij},$$

Letting then $\bar{n}_{ij}(\mathbf{r}, \mathbf{r}_{ij}, \alpha) = n_{ij}[\mathbf{r} - (1 - \alpha)\mathbf{r}_{ij}, \mathbf{r} + \alpha\mathbf{r}_{ij}, t]$ we have

$$\bar{n}_{ij}(1) - \bar{n}_{ij}(0) = n_{ij}(\mathbf{r}, \mathbf{r} + \mathbf{r}_{ij}, t) - n_{ij}(\mathbf{r} - \mathbf{r}_{ij}, \mathbf{r}, t) = \int_0^1 \partial_\alpha \bar{n}_{ij}(\alpha) d\alpha.$$

Since $\partial_\alpha \bar{n}_{ij}(\alpha) = \partial_{\mathbf{r}} \bar{n}_{ij} \cdot \mathbf{r}_{ij}$ we finally obtain that $\mathcal{R}^v(\mathbf{r}, t) = \nabla \cdot \mathcal{P}^p(\mathbf{r}, t)$, where

$$\mathcal{P}^p(\mathbf{r}, t) = - \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \int \frac{\varphi'_{ij}(r_{ij})}{r_{ij}} \mathbf{r}_{ij} \otimes \mathbf{r}_{ij} n_{ij}[\mathbf{r} - (1 - \alpha)\mathbf{r}_{ij}, \mathbf{r} + \alpha\mathbf{r}_{ij}, t] d\alpha d\mathbf{r}_{ij}, \quad (\text{C4})$$

and the scalar α must be integrated over $(0,1)$. The tensor \mathcal{P}^k corresponds to the transfer of momentum due to the flow of particles and \mathcal{P}^p to the transfer of momentum between the species particles due to intermolecular forces [56,57].

The kinetic part of the internal energy conservation equation is first obtained by multiplying Boltzmann Eq. (3.1) by $\frac{1}{2}m_i|\mathbf{c}_i - \mathbf{v}|^2$, integrating with respect to \mathbf{c}_i , and summing over the species $i \in \mathfrak{S}$. Using the definitions of \mathcal{E}^k and \mathcal{P}^k yields after some algebra

$$\partial_t \mathcal{E}^k + \nabla \cdot (\mathbf{v} \mathcal{E}^k) + \nabla \cdot \mathcal{Q}^k + \mathcal{R}_1^\mathcal{E} = -\mathcal{P}^k : \nabla \mathbf{v}, \quad (\text{C5})$$

where

$$\mathcal{Q}^k(\mathbf{r}, t) = \sum_{i \in \mathfrak{S}} \int \frac{1}{2} m_i |\mathbf{c}_i - \mathbf{v}|^2 (\mathbf{c}_i - \mathbf{v}) f_i(\mathbf{r}, \mathbf{c}_i, t) d\mathbf{c}_i, \quad (\text{C6})$$

$$\mathcal{R}_1^\mathcal{E} = - \sum_{i,j \in \mathfrak{S}} \int \frac{1}{2} m_i |\mathbf{c}_i - \mathbf{v}|^2 \theta_{ij} f_{ij}(\mathbf{r}, \mathbf{c}_i, \mathbf{r} + \mathbf{r}_{ij}, \mathbf{c}_j, t) d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j.$$

Using the definition of θ_{ij} , $\partial_{\mathbf{r}_i}\varphi_{ij} = -\varphi'_{ij}(r_{ij})\mathbf{r}_{ij}/r_{ij}$, integrating by parts with respect to \mathbf{c}_i and \mathbf{c}_j , we next obtain that

$$\mathcal{R}_1^\mathcal{E} = - \sum_{i,j \in \mathfrak{S}} \int (\mathbf{c}_i - \mathbf{v}) \cdot \mathbf{r}_{ij} \frac{\varphi'_{ij}(r_{ij})}{r_{ij}} f_{ij}(\mathbf{r}, \mathbf{c}_i, \mathbf{r} + \mathbf{r}_{ij}, \mathbf{c}_j, t) d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j.$$

The governing equation for the potential part \mathcal{E}^p of the internal energy may then conveniently be obtained from the second equation of the BBGKY hierarchy. Multiplying the two-particle distribution function Eqs. (3.2) by the potential energy $\frac{1}{2}\varphi_{ij}(r_{ij})$ integrating with respect to \mathbf{c}_i , \mathbf{c}_j , and \mathbf{r}_{ij} , and summing with respect to $i, j \in \mathfrak{S}$, the resulting equation is in the form

$$\partial_t \mathcal{E}^p + \nabla \cdot (\mathbf{v} \mathcal{E}^p) + \nabla \cdot \mathcal{Q}_1^p + \mathcal{R}_2^\mathcal{E} = 0, \quad (\text{C7})$$

where

$$\mathcal{Q}_1^p(\mathbf{r}, t) = \sum_{i,j \in \mathfrak{S}} \int \frac{1}{2} \varphi_{ij}(r_{ij}) (\mathbf{c}_i - \mathbf{v}) f_{ij}(\mathbf{r}, \mathbf{c}_i, \mathbf{r}_j, \mathbf{c}_j, t) d\mathbf{c}_i d\mathbf{r}_j d\mathbf{c}_j,$$

$$\mathcal{R}_2^\mathcal{E} = - \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \int (\mathbf{c}_j - \mathbf{c}_i) \cdot \mathbf{r}_{ij} \frac{\varphi'_{ij}(r_{ij})}{r_{ij}} f_{ij}(\mathbf{r}, \mathbf{c}_i, \mathbf{r} + \mathbf{r}_{ij}, \mathbf{c}_j, t) d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j.$$

Adding both Eqs. (C5) and (C7) for the conservation of \mathcal{E}^k and \mathcal{E}^p then yields

$$\partial_t \mathcal{E} + \nabla \cdot (\mathcal{E} \mathbf{v}) + \nabla \cdot (\mathcal{Q}^k + \mathcal{Q}_1^p) + \mathcal{R}_3^\mathcal{E} = -\mathcal{P}^k : \nabla \mathbf{v},$$

where $\mathcal{R}_3^\mathcal{E} = \mathcal{R}_1^\mathcal{E} + \mathcal{R}_2^\mathcal{E}$ reads

$$\mathcal{R}_3^\mathcal{E} = - \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \int (\mathbf{c}_i - \mathbf{v} + \mathbf{c}_j - \mathbf{v}) \cdot \mathbf{r}_{ij} \frac{\phi'_{ij}(r_{ij})}{r_{ij}} f_{ij}(\mathbf{r}, \mathbf{c}_i, \mathbf{r} + \mathbf{r}_{ij}, \mathbf{c}_j, t) d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j.$$

To transform $\mathcal{R}_3^\mathcal{E}$ we may proceed as for the momentum equation. More specifically, using

$$f_{ij}(\mathbf{r}, \mathbf{c}_i, \mathbf{r} + \mathbf{r}_{ij}, \mathbf{c}_j, t) = f_{ji}(\mathbf{r} + \mathbf{r}_{ij}, \mathbf{c}_j, \mathbf{r}, \mathbf{c}_i, t),$$

letting $\mathbf{r}_{ji} = -\mathbf{r}_{ij}$, and exchanging i and j in the sum, we obtain that

$$\mathcal{R}_3^\mathcal{E} = \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \int (\mathbf{c}_i - \mathbf{v} + \mathbf{c}_j - \mathbf{v}) \cdot \mathbf{r}_{ij} \frac{\phi'_{ij}(r_{ij})}{r_{ij}} f_{ij}(\mathbf{r} - \mathbf{r}_{ij}, \mathbf{c}_i, \mathbf{r}, \mathbf{c}_j, t) d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j,$$

so that

$$\mathcal{R}_3^\mathcal{E} = - \sum_{i,j \in \mathfrak{S}} \frac{1}{4} \int (\mathbf{c}_i - \mathbf{v} + \mathbf{c}_j - \mathbf{v}) \cdot \mathbf{r}_{ij} \frac{\phi'_{ij}(r_{ij})}{r_{ij}} [f_{ij}] d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j,$$

with

$$[f_{ij}] = f_{ij}(\mathbf{r}, \mathbf{c}_i, \mathbf{r} + \mathbf{r}_{ij}, \mathbf{c}_j, t) - f_{ij}(\mathbf{r} - \mathbf{r}_{ij}, \mathbf{c}_i, \mathbf{r}, \mathbf{c}_j, t).$$

Letting then $\bar{f}_{ij}(\alpha) = f_{ij}[\mathbf{r} - (1 - \alpha)\mathbf{r}_{ij}, \mathbf{c}_i, \mathbf{r} + \alpha\mathbf{r}_{ij}, \mathbf{c}_j, t]$ we have

$$[f_{ij}] = \bar{f}_{ij}(1) - \bar{f}_{ij}(0) = \int_0^1 \partial_\alpha \bar{f}_{ij}(\alpha) d\alpha,$$

and since $\partial_\alpha [f_{ij}](\alpha) = \partial_{\mathbf{r}} f_{ij}[\mathbf{r} - (1 - \alpha)\mathbf{r}_{ij}, \mathbf{c}_i, \mathbf{r} + \alpha\mathbf{r}_{ij}, \mathbf{c}_j, t] \cdot \mathbf{r}_{ij}$ we obtain

$$\begin{aligned} \mathcal{R}_3^\mathcal{E} &= - \sum_{i,j \in \mathfrak{S}} \frac{1}{4} \int (\mathbf{c}_i - \mathbf{v} + \mathbf{c}_j - \mathbf{v}) \cdot \mathbf{r}_{ij} \frac{\phi'_{ij}(r_{ij})}{r_{ij}} \\ &\quad \times \partial_{\mathbf{r}} f_{ij}[\mathbf{r} - (1 - \alpha)\mathbf{r}_{ij}, \mathbf{c}_i, \mathbf{r} + \alpha\mathbf{r}_{ij}, \mathbf{c}_j, t] \cdot \mathbf{r}_{ij} d\alpha d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j, \end{aligned}$$

and the scalar α must be integrated over $(0,1)$. Finally, letting $\partial_{\mathbf{r}}$ in front of the integrals and using $\partial_{\mathbf{r}}(\mathbf{c}_i - \mathbf{v} + \mathbf{c}_j - \mathbf{v}) = -2\nabla\mathbf{v}$ we obtain that $\mathcal{R}_3^\mathcal{E} = \mathcal{P}^p : \nabla\mathbf{v} + \nabla \cdot \mathcal{Q}_2^p$ where

$$\begin{aligned} \mathcal{Q}_2^p(\mathbf{r}, t) &= - \sum_{i,j \in \mathfrak{S}} \frac{1}{4} \int \frac{\phi'_{ij}(r_{ij})}{r_{ij}} \mathbf{r}_{ij} \mathbf{r}_{ij} \cdot (\mathbf{c}_i - \mathbf{v} + \mathbf{c}_j - \mathbf{v}) \\ &\quad \times f_{ij}[\mathbf{r} - (1 - \alpha)\mathbf{r}_{ij}, \mathbf{c}_i, \mathbf{r} + \alpha\mathbf{r}_{ij}, \mathbf{c}_j, t] d\alpha d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j, \end{aligned}$$

and the energy equation is established.

2. Derivation from generalized Boltzmann equations

The above derivation of the macroscopic equations has used the two first equations of the hierarchy. An equivalent derivation may be obtained by directly using the generalized Boltzmann Eqs. (3.24). We denote by $\widehat{\psi}^l$, $1 \leq l \leq n_s + 3$ the $n_s + 3$ first collision invariants given by $\widehat{\psi}^l = (\delta_{il})_{i \in \mathfrak{S}}$, $\widehat{\psi}^{n_s + \nu} = [m_i(c_{i\nu} - v_\nu)]_{i \in \mathfrak{S}}$ for $1 \leq \nu \leq 3$, and by \mathcal{E}' the differential of the energy \mathcal{E} with respect to $f = (f_i)_{i \in \mathfrak{S}}$, that is, \mathcal{E}' is such that for any increment distribution $\delta f = (\delta f_i)_{i \in \mathfrak{S}}$ we have

$$\delta \mathcal{E} = \langle \langle \mathcal{E}', \delta f \rangle \rangle = \sum_{i \in \mathfrak{S}} \int \frac{1}{2} m_i |\mathbf{c}_i - \mathbf{v}|^2 \delta f_i d\mathbf{c}_i + \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \int \varphi_{ij} \tau_{ij} (f_i \delta f_j + f_j \delta f_i) d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j,$$

where $\langle \langle \rangle \rangle$ is the scalar product Eq. (4.41). The governing equations are then obtained by taking the scalar product of the generalized equations $(\partial_t f_i + \mathbf{c}_i \cdot \partial_{\mathbf{r}_i} f_i - \mathcal{J}_i^{(1)})_{i \in \mathfrak{S}}$ by the invariants $\widehat{\psi}^l$, $1 \leq l \leq n_s + 3$ and \mathcal{E}' . The derivation of the mass and momentum conservation from Eq. (3.24) is then unchanged but the derivation of the energy conservation equation is slightly modified.

The energy conservation equation first reads

$$\begin{aligned} &\sum_{i \in \mathfrak{S}} \int \frac{1}{2} m_i |\mathbf{c}_i - \mathbf{v}|^2 (\partial_t f_i + \mathbf{c}_i \cdot \partial_{\mathbf{r}_i} f_i - \mathcal{J}_i^{(1)}) d\mathbf{c}_i + \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \int \varphi_{ij} \tau_{ij} [f_i (\partial_t f_j + \mathbf{c}_j \cdot \partial_{\mathbf{r}_j} f_j - \mathcal{J}_j^{(1)}) \\ &\quad + f_j (\partial_t f_i + \mathbf{c}_i \cdot \partial_{\mathbf{r}_i} f_i - \mathcal{J}_i^{(1)})] d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j \\ &= 0. \end{aligned} \tag{C8}$$

The kinetic terms in this relation are easily transformed into

$$\partial \mathcal{E}^K + \nabla \cdot (\mathbf{v} \mathcal{E}^K + \mathcal{Q}^K) + \mathcal{P}^K : \nabla \mathbf{v} + \mathcal{R}_1^\mathcal{E}, \quad (\text{C9})$$

using standard kinetic theory manipulations. Considering next the potential part of the relation Eq. (C8), we first note that

$$\Xi_{ij} = \int \varphi_{ij} \tau_{ij} (f_i \mathcal{J}_j^{(1)} + f_j \mathcal{J}_i^{(1)}) d\mathbf{c}_i d\mathbf{r}_i d\mathbf{c}_j = 0.$$

Indeed, we may write

$$\begin{aligned} \Xi_{ij} &= - \int \varphi_{ij} \tau_{ij} [f_i (\partial_t f_j + \mathbf{c}_j \cdot \partial_{\mathbf{r}_j} f_j) + f_j (\partial_t f_i + \mathbf{c}_i \cdot \partial_{\mathbf{r}_i} f_i)] d\mathbf{c}_i d\mathbf{r}_i d\mathbf{c}_j \\ &= - \int \varphi_{ij} \tau_{ij} [\partial_t (f_i f_j) + \mathbf{c}_i \cdot \partial_{\mathbf{r}_i} (f_i f_j) + \mathbf{c}_j \cdot \partial_{\mathbf{r}_j} (f_i f_j)] d\mathbf{c}_i d\mathbf{r}_i d\mathbf{c}_j. \end{aligned}$$

We may then use the identity

$$\tau_{ij} \partial_t = \partial_t \tau_{ij}, \quad (\text{C10})$$

since τ_{ij} is independent of time from Eq. (3.22) as well as the commutation relation

$$\tau_{ij} (\mathbf{c}_i \cdot \partial_{\mathbf{r}_i} + \mathbf{c}_j \cdot \partial_{\mathbf{r}_j}) = (\mathbf{c}_i \cdot \partial_{\mathbf{r}_i} + \mathbf{c}_j \cdot \partial_{\mathbf{r}_j} - \theta_{ij}) \tau_{ij}, \quad (\text{C11})$$

established by Green [101] using the definition Eq. (3.22). These relations now yields

$$\Xi_{ij} = - \int \varphi_{ij} (\partial_t + \mathbf{c}_i \cdot \partial_{\mathbf{r}_i} + \mathbf{c}_j \cdot \partial_{\mathbf{r}_j} - \theta_{ij}) \tau_{ij} f_i f_j d\mathbf{c}_i d\mathbf{r}_i d\mathbf{c}_j = 0,$$

since by definition of $\tau_{ij} f_i f_j = \exp(-t \mathfrak{H}_{ij}) f_i(0) f_j(0)$ we have $(\partial_t + \mathbf{c}_i \cdot \partial_{\mathbf{r}_i} + \mathbf{c}_j \cdot \partial_{\mathbf{r}_j} - \theta_{ij}) f_i f_j = 0$. The potential remainder of the energy Eq. (C8) then reads after some algebra

$$\begin{aligned} &\sum_{i,j \in \mathfrak{S}} \frac{1}{2} \int \varphi_{ij} \tau_{ij} [f_i (\partial_t f_j + \mathbf{c}_j \cdot \partial_{\mathbf{r}_j} f_j) + f_j (\partial_t f_i + \mathbf{c}_i \cdot \partial_{\mathbf{r}_i} f_i)] d\mathbf{c}_i d\mathbf{r}_i d\mathbf{c}_j \\ &= \sum_{i,j \in \mathfrak{S}} \frac{1}{2} \int \varphi_{ij} (\partial_t + \mathbf{c}_i \cdot \partial_{\mathbf{r}_i} + \mathbf{c}_j \cdot \partial_{\mathbf{r}_j} - \theta_{ij}) \tau_{ij} f_i f_j d\mathbf{c}_i d\mathbf{r}_i d\mathbf{c}_j \\ &= \partial_t \mathcal{E}^P + \nabla \cdot (\mathbf{v} \mathcal{E}^P + \mathcal{Q}_2^P) + \mathcal{P}^P : \nabla \mathbf{v} - \mathcal{R}_1^\mathcal{E}, \end{aligned} \quad (\text{C12})$$

and the equation for the conservation of energy is then a consequence of Eq. (C8) with Eqs. (C9) and (C12).

APPENDIX D: NORMAL LINEARIZED KINETIC EQUATIONS

We evaluate in this section the linearized equations for nonideal fluid with normal diffusive processes, that is, we evaluate the right-hand sides by solely using first-order Taylor expansions of pair distribution functions. The thermodynamic properties are those from Sec. IV without diffuse interface terms and are denoted with the superscript ‘‘u.’’

The right-hand sides of Eq. (4.20) are in the form

$$\psi_i = -(\partial_t \log f_i^{(0)} + \mathbf{c}_i \cdot \nabla_{\mathbf{r}_i} \log f_i^{(0)}) + \frac{1}{f_i^{(0)}} \mathcal{J}_i^{(1)}(f^{(0)}), \quad i \in \mathfrak{S}, \quad (\text{D1})$$

and the differential expression $\partial_t \log f_i^{(0)} + \mathbf{c}_i \cdot \nabla_{\mathbf{r}_i} \log f_i^{(0)}$ may be split as $\partial_t \log f_i^{(0)} + \mathbf{v} \cdot \nabla_{\mathbf{r}_i} \log f_i^{(0)} + (\mathbf{c}_i - \mathbf{v}) \cdot \nabla_{\mathbf{r}_i} \log f_i^{(0)}$. The material derivatives $\partial_t \log f_i^{(0)} + \mathbf{v} \cdot \nabla_{\mathbf{r}_i} \log f_i^{(0)}$ are evaluated by using the expression of Maxwellian distributions and the multicomponent Euler equations that are obtained in the form

$$\partial_t n_i + \mathbf{v} \cdot \nabla n_i = -n_i \nabla \cdot \mathbf{v}, \quad (\text{D2})$$

$$\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v} = -\nabla p^u / \rho, \quad (\text{D3})$$

$$\partial_t T + \mathbf{v} \cdot \nabla T = \frac{1}{\partial_T \mathcal{E}^u} \left(\sum_{l \in \mathfrak{S}} n_l \partial_{n_l} \mathcal{E}^u - \mathcal{E}^u - p^u \right) \nabla \cdot \mathbf{v}. \quad (\text{D4})$$

The resulting differential expressions are in the form

$$-(\partial_t \log f_i^{(0)} + \mathbf{v} \cdot \nabla_{\mathbf{r}_i} \log f_i^{(0)}) = \nabla \cdot \mathbf{v} + \frac{m_i}{\rho k_B T} (\mathbf{c}_i - \mathbf{v}) \cdot \nabla p^u + \left(\frac{3}{2} - \frac{m_i |\mathbf{c}_i - \mathbf{v}|^2}{2k_B T} \right) \frac{1}{T \partial_T \mathcal{E}^u} \left(\sum_{l \in \mathfrak{S}} n_l \partial_{n_l} \mathcal{E}^u - \mathcal{E}^u - p^u \right) \nabla \cdot \mathbf{v}, \quad (\text{D5})$$

and

$$-(\mathbf{c}_i - \mathbf{v}) \cdot \nabla_{\mathbf{r}_i} \log f_i^{(0)} = -(\mathbf{c}_i - \mathbf{v}) \cdot \frac{\nabla n_i}{n_i} - \frac{m_i}{k_B T} (\mathbf{c}_i - \mathbf{v}) \otimes (\mathbf{c}_i - \mathbf{v}) : \nabla \mathbf{v} + \left(\frac{3}{2} - \frac{m_i |\mathbf{c}_i - \mathbf{v}|^2}{2k_B T} \right) (\mathbf{c}_i - \mathbf{v}) \cdot \frac{\nabla T}{T}. \quad (\text{D6})$$

The terms arising from the collision operators $\mathcal{J}_i^{(1)}(f^{(0)})$ are next evaluated from the differential Eqs. (3.45) and (3.46) of Sec. III D. Indeed, we deduce from Sec. III D that *at first order in the gradients*, we have

$$\nabla f_{ij}^{(0), \text{cl}}(\alpha \mathbf{r}_i + (1 - \alpha) \mathbf{r}_j^m, \mathbf{c}_i, \mathbf{c}_j, t) = \nabla f_{ij}^{(0), \text{cl}}(\mathbf{r}_i, \mathbf{c}_i, \mathbf{c}_j, t).$$

Therefore, $\mathcal{J}_i^{(1), s}(f^{(0)})$ reads

$$\mathcal{J}_i^{(1), s}(f^{(0)}) = \sum_{j \in \mathfrak{S}} \nabla \cdot \int \mu_j \theta_{ij} f_i^{(0)}(\mathbf{r}_i, \mathbf{c}_i, t) f_j^{(0)}(\mathbf{r}_i, \mathbf{c}_j, t) g_{ij}(\mathbf{r}_i, r_{ij}) \mathbf{r}_{ij} d\mathbf{x}_j,$$

and after some calculus

$$\mathcal{J}_i^{(1), s}(f^{(0)}) = \nabla \cdot \left[\sum_{j \in \mathfrak{S}} \frac{m_j n_j}{m_i + m_j} \beta_{ij} f_i^{(0)}(\mathbf{c}_i - \mathbf{v}) \right]. \quad (\text{D7})$$

Similarly, we have from Sec. III D that *at first order in the gradients*, we have

$$\mathcal{J}_i^{(1), a}(f^{(0)}) = - \sum_{j \in \mathfrak{S}} \mu_{ij} \int \theta_{ij} \left[\frac{1}{m_i} \partial_{\mathbf{r}} f_i^{(0)}(\mathbf{r}_i, \mathbf{c}'_i, t) f_j^{(0)}(\mathbf{r}_i, \mathbf{c}'_j, t) - f_i^{(0)}(\mathbf{r}_i, \mathbf{c}'_i, t) \frac{1}{m_j} \partial_{\mathbf{r}} f_j^{(0)}(\mathbf{r}_i, \mathbf{c}'_j, t) \right] \cdot \mathbf{r}'_{ij} d\mathbf{x}_j. \quad (\text{D8})$$

After some calculus we may write

$$\frac{1}{f_i^{(0)}} \mathcal{J}_i^{(1), a}(f^{(0)}) = - \sum_{j \in \mathfrak{S}} \mu_{ij} n_j \left[\tilde{\mathbf{a}}_{ij}^\eta : \nabla \mathbf{v} + \tilde{\mathbf{a}}_{ij}^k \cdot \nabla \cdot \mathbf{v} + \tilde{\mathbf{a}}_{ij}^\lambda \cdot \nabla \left(\frac{-1}{k_B T} \right) + \tilde{\mathbf{a}}_{ij}^D \cdot \left(\frac{\nabla n_i}{m_i n_i} - \frac{\nabla n_j}{m_j n_j} \right) \right], \quad (\text{D9})$$

where the collision integrals for dense gases $\tilde{\mathbf{a}}_{ij}^\eta$, $\tilde{\mathbf{a}}_{ij}^k$, $\tilde{\mathbf{a}}_{ij}^\lambda$, and $\tilde{\mathbf{a}}_{ij}^D$ are defined by

$$\begin{aligned} \tilde{f}_i^{(0)} \tilde{\mathbf{a}}_{ij}^\eta &= \frac{1}{2k_B T} \int \theta_{ij} \tau_{ij} \tilde{f}_i^{(0)} \tilde{f}_j^{(0)} \left[\mathbf{r}_{ij} \otimes (\mathbf{c}_i - \mathbf{c}_j) + (\mathbf{c}_i - \mathbf{c}_j) \otimes \mathbf{r}_{ij} - \frac{2}{3} (\mathbf{c}_i - \mathbf{c}_j) \cdot \mathbf{r}_{ij} \mathbf{I} \right] d\mathbf{x}_j, \\ \tilde{f}_i^{(0)} \tilde{\mathbf{a}}_{ij}^k &= \frac{1}{3k_B T} \int \theta_{ij} \tau_{ij} \tilde{f}_i^{(0)} \tilde{f}_j^{(0)} \mathbf{r}_{ij} \cdot (\mathbf{c}_i - \mathbf{c}_j) d\mathbf{x}_j, \\ \tilde{f}_i^{(0)} \tilde{\mathbf{a}}_{ij}^D &= \int \theta_{ij} \tau_{ij} \tilde{f}_i^{(0)} \tilde{f}_j^{(0)} \mathbf{r}_{ij} d\mathbf{x}_j, \\ \tilde{f}_i^{(0)} \tilde{\mathbf{a}}_{ij}^\lambda &= \int \theta_{ij} \tau_{ij} \tilde{f}_i^{(0)} \tilde{f}_j^{(0)} \mathbf{r}_{ij} \left(\frac{3k_B T}{2m_j} - \frac{1}{2} |\mathbf{c}_j - \mathbf{v}|^2 - \frac{3k_B T}{2m_i} + \frac{1}{2} |\mathbf{c}_i - \mathbf{v}|^2 \right) d\mathbf{x}_j. \end{aligned}$$

Equations (D5) and (D6) as well as Eq. (D9) are essentially similar to those presented by Cohen *et al.* [50].

We now further assume that the repulsive potentials between particles are hard and use the corresponding value for the integrals $\tilde{\mathbf{a}}_{ij}^D$. The integrals $\tilde{\mathbf{a}}_{ij}^D$ may indeed be written

$$\tilde{\mathbf{a}}_{ij}^D = \frac{1}{\tilde{f}_i^{(0)}} \int \theta_{ij} g_{ij} \tilde{f}_i^{(0)} \tilde{f}_j^{(0)} \mathbf{r}'_{ij} d\mathbf{x}_j, \quad (\text{D10})$$

and assuming that the interaction potentials φ_{ij} are hard, we may use the rigid sphere relation $\mathbf{r}'_{ij} = \mathbf{r}_{ij}$ in Eq. (D10), discussed in particular by Hoffman and Curtiss [102]. A straightforward calculation then yields

$$\tilde{\mathbf{a}}_{ij}^D = \beta_{ij} (\mathbf{c}_i - \mathbf{v}). \quad (\text{D11})$$

More generally, for functions $A(\mathbf{r}_{ij}, \mathbf{r}'_{ij})$, depending on \mathbf{r}_{ij} and \mathbf{r}'_{ij} , we may occasionally use the hard potential relation

$$\int \theta_{ij} g_{ij} \tilde{f}_i^{(0)} \tilde{f}_j^{(0)} A(\mathbf{r}_{ij}, \mathbf{r}'_{ij}) d\mathbf{r}_{ij} = \int \theta_{ij} g_{ij} \tilde{f}_i^{(0)} \tilde{f}_j^{(0)} A(\mathbf{r}_{ij}, \mathbf{r}_{ij}) d\mathbf{r}_{ij}. \quad (\text{D12})$$

With the hard potential relation Eq. (D11), there is a simplification for density gradient and pressure terms in $\psi_i^{(1)}$ that are then in the form

$$-(\mathbf{c}_i - \mathbf{v}) \cdot \left(\frac{\nabla n_i}{n_i} - \sum_{j \in \mathfrak{S}} \beta_{ij} \nabla n_j - \frac{m_i}{\rho k_B T} \nabla p \right).$$

We may also use that

$$\nabla \left(\frac{g_i^u}{k_B T} \right) = \frac{\nabla n_i}{n_i} - \sum_{j \in \mathfrak{S}} \beta_{ij} \nabla n_j - \left(\frac{3}{2} + \sum_{j \in \mathfrak{S}} n_j \beta'_{ij} k_B T \right) \nabla T, \quad (\text{D13})$$

and

$$\sum_{k \in \mathfrak{S}} n_k k_B T \nabla \left(\frac{g_k^u}{k_B T} \right) = \nabla p - (\mathcal{E}^u + p^u) \frac{\nabla T}{T}, \quad (\text{D14})$$

to rewrite $\psi_i^{(1)}$ as well as the natural thermodynamic force terms for dissipative fluids without capillary effects

$$\mathbf{X}_i^{\text{th}} = n_i k_B T \nabla \left(\frac{g_i^u}{k_B T} \right) = \rho_i T \nabla \left(\frac{\bar{g}_i^u}{T} \right). \quad (\text{D15})$$

By combining the relations Eqs. (D5), (D6), (D9), (D11), (D13), and (D14) is obtained after lengthy algebra that

$$\psi_i^{(1)} = -\psi_i^\eta \cdot \nabla \mathbf{v} - \psi_i^\kappa \nabla \cdot \mathbf{v} - \sum_{j \in \mathfrak{S}} \psi_i^{D_j} \cdot \mathbf{X}_j^{\text{th}} - \psi_i^{\hat{\lambda}} \cdot \nabla \left(\frac{-1}{k_B T} \right),$$

which is relation Eq. (4.21), together with the expressions of ψ_i^η , ψ_i^κ , ψ^{D_j} , $j \in \mathfrak{S}$, and $\psi_i^{\hat{\lambda}}$, given in Sec. IV D.

We denote by $\hat{\psi}^l$, $1 \leq l \leq n_s + 4$ the $n_s + 4$ collisional invariants given by $\hat{\psi}^l = (\delta_{il})_{i \in \mathfrak{S}}$, $\hat{\psi}^{n_s + \nu} = [m_i (c_{i\nu} - v_\nu)]_{i \in \mathfrak{S}}$ for $1 \leq \nu \leq 3$, and $\hat{\psi}^{n_s + 4} = (\frac{1}{2} m_i |\mathbf{c}_i - \mathbf{v}|^2)_{i \in \mathfrak{S}}$, and by $\langle\langle \rangle\rangle$ the scalar product Eq. (4.41). The tensorial right-hand sides ψ_i^η , ψ_i^κ , ψ^{D_j} , $j \in \mathfrak{S}$, and $\psi_i^{\hat{\lambda}}$, given in Sec. IV D, then satisfy the orthogonality relations

$$\langle\langle \psi^\mu, \hat{\psi}^l \rangle\rangle = 0, \quad (\text{D16})$$

for $\mu \in \eta, \kappa, D_j, j \in \mathfrak{S}, \hat{\lambda}$, and $1 \leq l \leq n_s + 4$. These relations are easily established excepted for the energy for which it is necessary to use the approximation [50]

$$n k_B T + \frac{\frac{3}{2} n k_B}{\partial_T \mathcal{E}^u} \left(\sum_{l \in \mathfrak{S}} n_l \partial_{n_l} \mathcal{E}^u - \mathcal{E}^u - p^u \right) = \sum_{i, j \in \mathfrak{S}} n_i n_j \left[\frac{1}{2} \beta_{ij} k_B T + \frac{7}{6} \beta'_{ij} (k_B T)^2 + \frac{1}{3} \beta''_{ij} (k_B T)^3 \right],$$

as well as the identity [50]

$$\sum_{i, j \in \mathfrak{S}} \mu_{ij} n_i n_j \int \frac{1}{2} m_i |\mathbf{c}_i - \mathbf{v}|^2 \tilde{f}_i^{(0)} \tilde{a}_{ij}^k d\mathbf{c}_i = - \sum_{i, j \in \mathfrak{S}} n_i n_j \left[\frac{7}{6} \beta'_{ij} (k_B T)^2 + \frac{1}{3} \beta''_{ij} (k_B T)^3 \right],$$

established notably in Chaos and Colin [103].

APPENDIX E: CONSTRAINTS FOR PERTURBED DISTRIBUTION FUNCTIONS

The perturbed distribution functions $\phi_i^{(1)}$, $i \in \mathfrak{S}$, are uniquely determined by imposing Enskog-type constraints. These constraints ensure that the true value of the local macroscopic variables n_i , \mathbf{v} and T , or equivalently \mathcal{E} , are determined by $f_i^{(0)}$ alone [50,54,57].

The constraints associated with mass and momentum are identical to that for dilute gases $\int f_i^{(0)} \phi_i^{(1)} d\mathbf{c}_i = 0$ for $i \in \mathfrak{S}$, and $\sum_{i \in \mathfrak{S}} \int m_i (\mathbf{c}_i - \mathbf{v}) f_i^{(0)} \phi_i^{(1)} d\mathbf{c}_i = 0$ and corresponds to Eqs. (4.29) and (4.30).

The constraint associated with internal energy is more complex since it involves pair distribution functions. The Enskog constraint for energy is generally in the form

$$\sum_{i \in \mathfrak{S}} \int \frac{1}{2} m_i |\mathbf{c}_i - \mathbf{v}|^2 f_i^{(0)} \phi_i^{(1)} d\mathbf{c}_i + \sum_{i, j \in \mathfrak{S}} \int \frac{1}{2} \varphi_{ij} (f_{ij} - f_{ij}^{(0)}) d\mathbf{r}_{ij} d\mathbf{c}_i d\mathbf{c}_j = 0, \quad (\text{E1})$$

where the f_{ij} denote the nonequilibrium pair distribution functions, $f_{ij}^{(0)}$ the zeroth-order pair distribution functions, and where the f_{ij} are evaluated with $f_i = f_i^{(0)} + f_i^{(0)}\phi_i^{(1)}$. The kinetic part of the constraint (E1) is thus traditional whereas the potential part depends on the nonequilibrium pair distribution functions f_{ij} , the zeroth-order pair distribution functions $f_{ij}^{(0)}$, as well as on the order of Taylor expansions.

Considering first the kinetic theory of nonideal fluids with normal diffusive processes presented in Sec. IV, the potential part of the constraint is first in the form

$$\sum_{i,j \in \mathfrak{S}} \int \frac{1}{2} \varphi_{ij} (f_{ij}^{\text{Bo}} - f_{ij}^{(0),\text{cl}}) d\mathbf{r}_{ij} d\mathbf{c}_i d\mathbf{c}_j,$$

with $f_{ij} = f_{ij}^{\text{Bo}} = \tau_{ij} f_i(\mathbf{r}_i) f_j(\mathbf{r}_j)$, $f_{ij}^{(0)} = f_{ij}^{(0),\text{cl}} = g_{ij} f_i^{(0)}(\mathbf{r}_i) f_j^{(0)}(\mathbf{r}_j)$ and $f_i = f_i^{(0)} + f_i^{(0)}\phi_i^{(1)}$, $i, j \in \mathfrak{S}$. For such a kinetic theory of nonideal fluids, we may use first-order Taylor expansions and neglect any gradient of first-order terms [50,54,57]. This yields

$$f_{ij}^{\text{Bo}} - f_{ij}^{(0),\text{cl}} = g_{ij} f_i^{(0)} f_j^{(0)} (\phi_i^{(1)} + \phi_j^{(1)}) + g_{ij} f_i^{(0)} f_j^{(0)} (\nabla \log f_i^{(0)} \cdot \delta \mathbf{r}_i + \nabla \log f_j^{(0)} \cdot \delta \mathbf{r}_j),$$

where $\delta \mathbf{r}_i = \mathbf{r}'_i - \mathbf{r}_i$ and $\delta \mathbf{r}_j = \mathbf{r}'_j - \mathbf{r}_j$. The Maxwellian gradient contributions then vanish in Eq. (E1) since they are odd with respect to \mathbf{r}_{ij} or \mathbf{r}'_{ij} and the remaining terms are localized at \mathbf{r}_i so that the constraint reads

$$\sum_{i \in \mathfrak{S}} \int \frac{1}{2} m_i |\mathbf{c}_i - \mathbf{v}|^2 f_i^{(0)} \phi_i^{(1)} d\mathbf{c}_i + \sum_{i,j \in \mathfrak{S}} \int \frac{1}{2} \varphi_{ij} \tau_{ij} f_i^{(0)} f_j^{(0)} (\phi_i^{(1)} + \phi_j^{(1)}) d\mathbf{r}_{ij} d\mathbf{c}_i d\mathbf{c}_j = 0.$$

This constraint is further simplified by using the structure of the perturbed distribution functions for fluid mixtures [50,51] as for single-species fluids [54,57]. The only difficult terms are those associated with the potential part of the volume viscosity terms for which expansions with respect to density are generally used and the resulting constraint is obtained in the form Eq. (4.31) and is of the classical form [50,51,54,57].

Considering next the kinetic theory using second-order expansions of pair distribution functions that leads to capillary effects, the potential part of the energy constraint is in the form

$$\sum_{i,j \in \mathfrak{S}} \int \frac{1}{2} \varphi_{ij} (f_{ij}^{\text{Bo}} - f_{ij}^{(0),\text{sy}}) d\mathbf{r}_{ij} d\mathbf{c}_i d\mathbf{c}_j,$$

with $f_{ij} = f_{ij}^{\text{Bo}} = \tau_{ij} f_i(\mathbf{r}_i) f_j(\mathbf{r}_j)$, $f_{ij}^{(0)} = f_{ij}^{(0),\text{sy}} = g_{ij} f_i(\mathbf{r}_i) f_j(\mathbf{r}_j)$ and $f_i = f_i^{(0)} + f_i^{(0)}\phi_i^{(1)}$, $i, j \in \mathfrak{S}$. For the kinetic theory of nonideal fluids including diffuse interface effects, we have to use second-order Taylor expansions and write

$$f_{ij}^{\text{Bo}} - f_{ij}^{(0),\text{cl}} = f_i^{(0)}(\mathbf{r}'_i) f_j^{(0)}(\mathbf{r}'_j) [1 + \phi_i^{(1)}(\mathbf{r}'_i)] [1 + \phi_j^{(1)}(\mathbf{r}'_j)] - g_{ij} f_i^{(0)}(\mathbf{r}_i) f_j^{(0)}(\mathbf{r}_j),$$

where the dependence on particle velocities has been left implicit. Considering first the terms arising solely from the Maxwellian distributions $f_i^{(0)}(\mathbf{r}'_i) f_j^{(0)}(\mathbf{r}'_j) - g_{ij} f_i^{(0)}(\mathbf{r}_i) f_j^{(0)}(\mathbf{r}_j)$, and using a second-order Taylor expansion, the zeroth-order terms are zero, the first-order terms yield zero contributions to the energy constraint since they are odd with respect to \mathbf{r}_{ij} or \mathbf{r}'_{ij} and we are left with the second-order terms in the form

$$\partial_{(\mathbf{r}_i, \mathbf{r}_j)}^2 f_{ij}^{(0),\text{Bo}} : (\delta \mathbf{r}_i, \delta \mathbf{r}_j)^{\otimes 2} - \partial_{\mathbf{r}_j}^2 f_{ij}^{(0),\text{sy}} : \mathbf{r}_{ij}^{\otimes 2}.$$

The leading terms that only involve density gradients then vanish using the hard potential relations. The remaining part are then negligible in the regime under consideration when $(\frac{\sigma^*}{r^*})^3 (\frac{\sigma^*}{l_{\text{vn}}^*}) (\frac{\sigma^*}{l_{\text{vT}}^*}) \ll 1$ and $(\frac{\sigma^*}{r^*})^3 (\frac{\sigma^*}{l_{\text{vn}}^*}) (\frac{\sigma^*}{l_{\text{vT}}^*}) (\frac{\delta v^*}{\sqrt{k_{\text{B}} T^* / m^*}}) \ll 1$, using notably the decompositions Eq. (6.21) as well as the approximate collision integrals for dense gases Eq. (D11).

Considering then the terms involving the first-order perturbations $\phi_i^{(1)}$, $i \in \mathfrak{S}$, using second-order Taylor expansions, and discarding quadratic terms in first-order perturbations. The zeroth-order terms are then zero from the zero average constraints of the $\phi_i^{(1)}$, the first-order terms yields zero contributions since they are odd with respect to \mathbf{r}_{ij} or \mathbf{r}'_{ij} and we are left with second-order terms in the form

$$g_{ij} f_i^{(0)} f_j^{(0)} \partial_{\mathbf{r}_i} \phi_i^{(1)} \cdot \delta \mathbf{r}_i \partial_{\mathbf{r}_j} \log f_j^{(0)} \cdot \delta \mathbf{r}_j$$

and

$$g_{ij} f_i^{(0)} f_j^{(0)} \partial_{\mathbf{r}_i}^2 \phi_i^{(1)} : \delta \mathbf{r}_i^{\otimes 2},$$

and similar terms obtained by permuting i and j . For the first-type terms, we may replace $\partial_{\mathbf{r}_i} \log f_j^{(0)} \cdot \delta \mathbf{r}_j$ by $\nabla \log n_j$ and use the zero average constraint of $\phi_i^{(1)}$ and the same zero average argument also applies for the second-type terms so that finally the energy constraint is again reduced to the classical constraint Eq. (4.31) as for fluid with standard diffusive processes.

APPENDIX F: TENSORIAL INTEGRAL AND DIFFERENTIAL IDENTITIES

We summarize in this Appendix various tensorial integral relations used in the derivation of the capillary fluid equations. We denote by $\mathbf{z} \in \mathbb{R}^3$ an integration variable that may either represents the rescaled particle velocity $(\mathbf{c}_i - \mathbf{v})(m_i/2k_B T)^{1/2}$ of the i th species or else the relative position $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$.

Letting $z = |\mathbf{z}|$ for $\mathbf{z} \in \mathbb{R}^3$ then for any isotropic function $\gamma(z)$ of \mathbf{z} , we have

$$\int z_i^2 \gamma(z) d\mathbf{z} = \frac{1}{3} \int z^2 \gamma(z) d\mathbf{z}, \quad 1 \leq i \leq 3,$$

and this implies

$$\int \mathbf{z}(\mathbf{z} \cdot \mathbf{a}) \gamma(z) d\mathbf{z} = \frac{1}{3} \int z^2 \gamma(z) d\mathbf{z} \mathbf{a}, \quad (\text{F1})$$

for any vector \mathbf{a} independent of \mathbf{z} . Similarly, we have [57]

$$\int \mathbf{z} \otimes \mathbf{z} \gamma(z) d\mathbf{z} = \frac{1}{3} \int z^2 \gamma(z) d\mathbf{z} \mathbf{I}, \quad (\text{F2})$$

where \mathbf{I} is the identity tensor in \mathbb{R}^3 and $\mathbf{z} \otimes \mathbf{z}$ the tensor product of \mathbf{z} with itself having components $z_i z_j$ for $1 \leq i, j \leq 3$.

In the same vein, for any isotropic function $\gamma(z)$ of \mathbf{z} we have [57]

$$\int z_i^4 \gamma(z) d\mathbf{z} = \frac{1}{5} \int z^4 \gamma(z) d\mathbf{z}, \quad 1 \leq i \leq 3,$$

as well as

$$\int z_i^2 z_j^2 \gamma(z) d\mathbf{z} = \frac{1}{15} \int z^4 \gamma(z) d\mathbf{z}, \quad 1 \leq i, j \leq 3, \quad i \neq j.$$

As a consequence, for any second rank tensor \mathbf{w} independent of \mathbf{z} we have

$$\int \gamma(z) \mathbf{z} \otimes \mathbf{z} (\mathbf{z} \otimes \mathbf{z} : \mathbf{w}) d\mathbf{z} = \frac{1}{15} \int z^4 \gamma(z) d\mathbf{z} (\mathbf{w} + \mathbf{w}^t + \mathbf{w} : \mathbf{I} \mathbf{I}), \quad (\text{F3})$$

where $\mathbf{w} : \mathbf{v}$ is the full contraction between the two tensors \mathbf{w} and \mathbf{v} , so that $\mathbf{w} : \mathbf{I}$ is the trace of the tensor \mathbf{w} , and \mathbf{w}^t denotes the transpose of \mathbf{w} . The tensor $\mathbf{z} \otimes \mathbf{z}$ is also denoted for short by $\mathbf{z}^{\otimes 2}$ and the tensor $\mathbf{z} \otimes \mathbf{z} \otimes \mathbf{z}$ by $\mathbf{z}^{\otimes 3}$.

More generally, for any pair of second rank tensors \mathbf{w} and \mathbf{v} independent of \mathbf{z} , assuming that \mathbf{w} is symmetric, and for any isotropic function $\gamma(z)$ we have

$$\int [\gamma(z) \mathbf{w} : \mathbf{z}^{\otimes 2} \mathbf{v} : \mathbf{z}^{\otimes 2}] d\mathbf{z} = \frac{1}{15} \int z^4 \gamma(z) d\mathbf{z} [\mathbf{w} : \mathbf{v} + \mathbf{w} : \mathbf{v}^t + \text{tr}(\mathbf{w}) \text{tr}(\mathbf{v}) \mathbf{I}], \quad (\text{F4})$$

where $\text{tr}(\mathbf{w})$ denote the trace of a tensor \mathbf{w} .

Moreover, for any third rank tensor \mathbf{A}_{ijk} independent of \mathbf{z} and for any isotropic function $\gamma(z)$ we have

$$\int [\gamma(z) z_i \mathbf{A} : \mathbf{z}^{\otimes 3}] d\mathbf{z} = \frac{1}{15} \int z^4 \gamma(z) d\mathbf{z} \left(\sum_l \mathbf{A}_{lll} + \sum_l \mathbf{A}_{lll} + \sum_l \mathbf{A}_{lll} \right), \quad (\text{F5})$$

where $\mathbf{A} : \mathbf{z}^{\otimes 3}$ is the total contraction of \mathbf{A} with the tensor product $\mathbf{z}^{\otimes 3} = \mathbf{z} \otimes \mathbf{z} \otimes \mathbf{z}$ given by $\mathbf{A} : \mathbf{z}^{\otimes 3} = \sum_{ijk} \mathbf{A}_{ijk} z_i z_j z_k$. As a typical application, for any third-order gradient tensor like $\nabla^2 \mathbf{v}$ independent of \mathbf{z} and for any isotropic function $\gamma(z)$ we have

$$\int \gamma(z) \mathbf{z} [\nabla^2 \mathbf{v} : (\mathbf{z} \otimes \mathbf{z} \otimes \mathbf{z})] d\mathbf{z} = \frac{1}{15} \int z^4 \gamma(z) d\mathbf{z} [\Delta \mathbf{v} + 2 \nabla (\nabla \cdot \mathbf{v})], \quad (\text{F6})$$

where $\nabla^2 \mathbf{v} : \mathbf{z}^{\otimes 3}$ is the total contraction of $\nabla^2 \mathbf{v}$ with the tensor product $\mathbf{z}^{\otimes 3} = \mathbf{z} \otimes \mathbf{z} \otimes \mathbf{z}$ given by $\nabla^2 \mathbf{v} : \mathbf{z}^{\otimes 3} = \sum_{ijk} \partial_{r_j} \partial_{r_k} v_i z_i z_j z_k$.

We now investigate various differential relations used in the derivation of the capillary fluid equations. The following relation is established for scalar functions $n_i(\mathbf{r})$ and $n_j(\mathbf{r})$, $i, j \in \mathfrak{S}$, of $\mathbf{r} \in \mathbb{R}^3$ after integrations by parts

$$\nabla \cdot (n_i \nabla^2 n_j) = \nabla \cdot (n_i \Delta n_j \mathbf{I} + \nabla n_i \cdot \nabla n_j \mathbf{I} - \nabla n_i \otimes \nabla n_j), \quad (\text{F7})$$

where ∇n_i is the gradient of n_i , $\Delta n_i = \nabla \cdot \nabla n_i$ the Laplacian, and $\nabla^2 n_i$ the Hessian matrix with components $\partial_{r_k} \partial_{r_l} n_i$ for $1 \leq k, l \leq 3$.

In addition, for any scalar functions $n_i(\mathbf{r})$ and $n_j(\mathbf{r})$, $i, j \in \mathfrak{S}$, and any vector function $\mathbf{v}(\mathbf{r})$ of $\mathbf{r} \in \mathbb{R}^3$ one may establish after a few integration by parts that

$$\nabla \cdot (n_i \nabla \cdot \mathbf{v} \nabla n_j) = \nabla \cdot [n_i \nabla \mathbf{v} \cdot \nabla n_j + (\nabla n_i \cdot \nabla n_j \mathbf{I} + n_i \Delta n_j \mathbf{I} - \nabla n_j \otimes \nabla n_i - n_i \nabla^2 n_j) \cdot \mathbf{v}]. \quad (\text{F8})$$

where $\nabla \mathbf{v}$ is the gradient matrix and $\nabla \cdot \mathbf{v}$ the divergence of \mathbf{v} . Similarly, one may establish the following identity

$$\nabla \cdot [n_i n_j \nabla (\nabla \cdot \mathbf{v})] = \nabla \cdot (n_i \nabla \mathbf{v} \cdot \nabla n_j + n_j \nabla \mathbf{v} \cdot \nabla n_i - n_i \nabla \mathbf{v}' \cdot \nabla n_j - n_j \nabla \mathbf{v}' \cdot \nabla n_i + n_i n_j \Delta \mathbf{v}), \quad (\text{F9})$$

where $\nabla \mathbf{v}'$ denotes the transpose of the gradient matrix.

Denoting then by \mathcal{F}_i any vector function of $\mathbf{r} \in \mathbb{R}^3$, it is also obtained after a few integration by parts that

$$\nabla \cdot (\nabla^2 n_j \cdot \mathcal{F}_i) = \nabla \cdot (\Delta n_j \mathcal{F}_i + \nabla \mathcal{F}_i \cdot \nabla n_j - \nabla n_j \cdot \nabla \mathcal{F}_i), \quad (\text{F10})$$

and letting $n_i = 1$ in the (F9) we finally obtain that

$$\nabla \cdot [n_j \nabla (\nabla \cdot \mathcal{F}_i)] = \nabla \cdot (\nabla \mathcal{F}_i \cdot \nabla n_j - \nabla \mathcal{F}_i' \cdot \nabla n_j + n_j \Delta \mathcal{F}_i). \quad (\text{F11})$$

APPENDIX G: OTHER BOGOLIUBOV DEVIATION TERMS

We complete in this Appendix the estimates of the deviations arising from the differences $f_{ij}^{\text{Bo}} - f_{ij}^{\text{sy}}$ by investigating the pressure tensor \mathcal{P} and the heat fluxes \mathcal{Q}_1^{p} and \mathcal{Q}_2^{p} .

The corrections for the pressure tensor $\delta^{\text{Bo}} \mathcal{P} = \delta^{\text{Bo}} \mathcal{P}^{\text{p}}$ are first written in the form

$$\delta^{\text{Bo}} \mathcal{P} = - \sum_{i,j \in \mathcal{G}} \frac{1}{2} \int \frac{\varphi'_{ij}(r_{ij})}{r_{ij}} \mathbf{r}_{ij} \otimes \mathbf{r}_{ij} (f_{ij}^{(0),\text{Bo}} - f_{ij}^{(0),\text{sy}})(\mathbf{r}_i^\alpha, \mathbf{r}_j^\alpha) d\alpha d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j,$$

where we have denoted for convenience $\mathbf{r}_i^\alpha = \mathbf{r}_i - (1 - \alpha)\mathbf{r}_{ij}$ and $\mathbf{r}_j^\alpha = \mathbf{r}_i + \alpha\mathbf{r}_{ij}$ and have left implicit the dependence of $f_{ij}^{(0),\text{Bo}} - f_{ij}^{(0),\text{sy}}$ on the velocities \mathbf{c}_i and \mathbf{c}_j . We may thus write that

$$\delta^{\text{Bo}} \mathcal{P} = - \sum_{i,j \in \mathcal{G}} \int \frac{1}{4} \frac{\varphi'_{ij}(r_{ij})}{r_{ij}} \mathbf{r}_{ij} \otimes \mathbf{r}_{ij} [\partial_{(\mathbf{r}_i, \mathbf{r}_j)}^2 f_{ij}^{(0),\text{Bo}} : (\delta \mathbf{r}_i^\alpha, \delta \mathbf{r}_j^\alpha)^{\otimes 2} - \partial_{\mathbf{r}_i, \mathbf{r}_j}^2 f_{ij}^{(0),\text{sy}} : (-\mathbf{r}_{ij} + \alpha \mathbf{r}_{ij}, \alpha \mathbf{r}_{ij})^{\otimes 2}] d\alpha d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j,$$

where $\delta \mathbf{r}_i^\alpha = \mathbf{r}_i^\alpha - \mathbf{r}_i = \mathbf{r}'_i - (1 - \alpha)\mathbf{r}'_{ij} - \mathbf{r}_i$ and $\delta \mathbf{r}_j^\alpha = \mathbf{r}_j^\alpha - \mathbf{r}_i = \mathbf{r}'_i + \alpha \mathbf{r}'_{ij} - \mathbf{r}_i = \mathbf{r}'_j - (1 - \alpha)\mathbf{r}'_{ij} - \mathbf{r}_i$. Using the identity

$$\int_0^1 (a + \alpha b)(c + \alpha d) d\alpha = \left(a + \frac{1}{2}b\right) \left(c + \frac{1}{2}d\right) + \frac{1}{12}bd,$$

with $\delta \mathbf{r}_i^\alpha = \delta \mathbf{r}_i - \mathbf{r}'_{ij} + \alpha \mathbf{r}'_{ij}$ and $\delta \mathbf{r}_j^\alpha = \delta \mathbf{r}_i + \alpha \mathbf{r}'_{ij}$, and integrating with respect to α , it is obtained that

$$\begin{aligned} \delta^{\text{Bo}} \mathcal{P} = & - \sum_{i,j \in \mathcal{G}} \int \frac{1}{4} \frac{\varphi'_{ij}(r_{ij})}{r_{ij}} \mathbf{r}_{ij} \otimes \mathbf{r}_{ij} \left[\partial_{(\mathbf{r}_i, \mathbf{r}_j)}^2 f_{ij}^{(0),\text{Bo}} : \left(\delta \mathbf{r}_i - \frac{1}{2}\mathbf{r}'_{ij}, \delta \mathbf{r}_i + \frac{1}{2}\mathbf{r}'_{ij} \right)^{\otimes 2} \right. \\ & - \partial_{(\mathbf{r}_i, \mathbf{r}_j)}^2 f_{ij}^{(0),\text{sy}} : \left(-\frac{1}{2}\mathbf{r}_{ij}, \frac{1}{2}\mathbf{r}_{ij} \right)^{\otimes 2} \\ & + \frac{1}{12} \partial_{(\mathbf{r}_i, \mathbf{r}_j)}^2 f_{ij}^{(0),\text{Bo}} : \left(\frac{1}{2}\mathbf{r}'_{ij}, \frac{1}{2}\mathbf{r}'_{ij} \right)^{\otimes 2} \\ & \left. - \frac{1}{12} \partial_{(\mathbf{r}_i, \mathbf{r}_j)}^2 f_{ij}^{(0),\text{sy}} : \left(\frac{1}{2}\mathbf{r}_{ij}, \frac{1}{2}\mathbf{r}_{ij} \right)^{\otimes 2} \right] d\alpha d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j. \end{aligned}$$

The dominant correction terms in $\delta^{\text{Bo}} \mathcal{P}$ may then be split into $\delta^{\text{Bo}} \mathcal{P}_1$ and $\delta^{\text{Bo}} \mathcal{P}_2$ with

$$\begin{aligned} \delta^{\text{Bo}} \mathcal{P}_1 = & - \sum_{i,j \in \mathcal{G}} \int \frac{1}{4} \frac{\varphi'_{ij}(r_{ij})}{r_{ij}} \mathbf{r}_{ij} \otimes \mathbf{r}_{ij} g_{ij} f_i^{(0)} f_j^{(0)} \left\{ \frac{\partial_{\mathbf{r}_i}^2 n_i}{n_i} : \left[\left(\delta \mathbf{r}_i - \frac{1}{2}\mathbf{r}'_{ij} \right)^{\otimes 2} - \left(-\frac{1}{2}\mathbf{r}_{ij} \right)^{\otimes 2} \right] \right. \\ & \times 2 \frac{\partial_{\mathbf{r}_i} n_i}{n_i} \cdot \left(\delta \mathbf{r}_i - \frac{1}{2}\mathbf{r}'_{ij} \right) \frac{\partial_{\mathbf{r}_j} n_j}{n_j} \cdot \left(\delta \mathbf{r}_i + \frac{1}{2}\mathbf{r}'_{ij} \right) - 2 \frac{\partial_{\mathbf{r}_i} n_i}{n_i} \cdot \left(-\frac{1}{2}\mathbf{r}_{ij} \right) \frac{\partial_{\mathbf{r}_j} n_j}{n_j} \cdot \left(+\frac{1}{2}\mathbf{r}_{ij} \right) \\ & \left. + \frac{\partial_{\mathbf{r}_j}^2 n_j}{n_j} : \left[\left(\delta \mathbf{r}_i + \frac{1}{2}\mathbf{r}'_{ij} \right)^{\otimes 2} - \left(\frac{1}{2}\mathbf{r}_{ij} \right)^{\otimes 2} \right] \right\} d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j, \end{aligned}$$

and

$$\begin{aligned} \delta^{\text{Bo}} \mathcal{P}_2 = & - \sum_{i,j \in \mathfrak{S}} \int \frac{1}{48} \frac{\phi'_{ij}(r_{ij})}{r_{ij}} \mathbf{r}_{ij} \otimes \mathbf{r}_{ij} g_{ij} f_i^{(0)} f_j^{(0)} \left\{ \frac{\partial_{\mathbf{r}_i}^2 n_i}{n_i} : \left[\left(\frac{1}{2} \mathbf{r}'_{ij} \right)^{\otimes 2} - \left(\frac{1}{2} \mathbf{r}_{ij} \right)^{\otimes 2} \right] \right. \\ & \times 2 \frac{\partial_{\mathbf{r}_i} n_i}{n_i} \cdot \left(\frac{1}{2} \mathbf{r}'_{ij} \right) \frac{\partial_{\mathbf{r}_j} n_j}{n_j} \cdot \left(\frac{1}{2} \mathbf{r}'_{ij} \right) - 2 \frac{\partial_{\mathbf{r}_i} n_i}{n_i} \cdot \left(\frac{1}{2} \mathbf{r}_{ij} \right) \frac{\partial_{\mathbf{r}_j} n_j}{n_j} \cdot \left(\frac{1}{2} \mathbf{r}_{ij} \right) + \frac{\partial_{\mathbf{r}_j}^2 n_j}{n_j} : \left[\left(\frac{1}{2} \mathbf{r}'_{ij} \right)^{\otimes 2} \right. \\ & \left. \left. - \left(\frac{1}{2} \mathbf{r}_{ij} \right)^{\otimes 2} \right] \right\} d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j, \end{aligned}$$

and both contributions vanish from the integral relations Eq. (D12) and the hard potential approximation that yields $\delta \mathbf{r}_i = 0$ and $\mathbf{r}'_{ij} = \mathbf{r}_{ij}$. The remaining corrections then necessarily involve derivatives of $\tilde{f}_i^{(0)}$ or $\tilde{f}_j^{(0)}$ and are thus negligible when assuming Eqs. (6.19) and (6.20).

Proceeding as for the energy \mathcal{E} , the difference $\delta^{\text{Bo}} \mathcal{Q}_1^{\text{p}}$ in the first potential part of the heat flux \mathcal{Q}_1^{p} is obtained in the form

$$\delta^{\text{Bo}} \mathcal{Q}_1^{\text{p}} = \sum_{i,j \in \mathfrak{S}} \int \frac{1}{4} \phi_{ij}(\mathbf{c}_i - \mathbf{v}) \left[\partial_{(\mathbf{r}_i, \mathbf{r}_j)}^2 f_{ij}^{(0), \text{Bo}} : (\delta \mathbf{r}_i, \delta \mathbf{r}_j)^{\otimes 2} - \partial_{\mathbf{r}_j}^2 f_{ij}^{(0), \text{sy}} : \mathbf{r}_{ij}^{\otimes 2} \right] d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j,$$

and all the main contributions associated with second-order density derivatives vanish since they are odd with respect to the velocities $\mathbf{c}_i - \mathbf{v}$ and the remaining terms may then be estimated to be negligible as for $\delta^{\text{Bo}} \mathcal{E}$ in the regime under consideration, Eqs. (6.19) and (6.20).

Proceeding as for the pressure tensor \mathcal{P} , the Bogoliubov correction $\delta^{\text{Bo}} \mathcal{Q}_2^{\text{p}}$ in the first potential part of the heat flux \mathcal{Q}_2^{p} is obtained in the form

$$\delta^{\text{Bo}} \mathcal{Q}_2^{\text{p}} = - \sum_{i,j \in \mathfrak{S}} \frac{1}{8} \int \frac{\phi'_{ij}(r_{ij})}{r_{ij}} \mathbf{r}_{ij} \mathbf{r}_{ij} \cdot (\mathbf{c}_i - \mathbf{v} + \mathbf{c}_j - \mathbf{v}) \times (f_{ij}^{(0), \text{Bo}} - f_{ij}^{(0), \text{sy}})(\mathbf{r}_i^\alpha, \mathbf{r}_j^\alpha) d\alpha d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j,$$

where we have denoted for convenience $\mathbf{r}_i^\alpha = \mathbf{r}_i - (1 - \alpha)\mathbf{r}_{ij}$ and $\mathbf{r}_j^\alpha = \mathbf{r}_i + \alpha\mathbf{r}_{ij}$ and have left implicit the dependence of $f_{ij}^{(0), \text{Bo}} - f_{ij}^{(0), \text{sy}}$ on the velocities \mathbf{c}_i and \mathbf{c}_j . We may thus write that

$$\begin{aligned} \delta^{\text{Bo}} \mathcal{Q}_2^{\text{p}} = & - \sum_{i,j \in \mathfrak{S}} \int \frac{1}{8} \frac{\phi'_{ij}(r_{ij})}{r_{ij}} \mathbf{r}_{ij} \cdot (\mathbf{c}_i - \mathbf{v} + \mathbf{c}_j - \mathbf{v}) \left[\partial_{(\mathbf{r}_i, \mathbf{r}_j)}^2 f_{ij}^{(0), \text{Bo}} : (\delta \mathbf{r}_i^\alpha, \delta \mathbf{r}_j^\alpha)^{\otimes 2} \right. \\ & \left. - \partial_{(\mathbf{r}_i, \mathbf{r}_j)}^2 f_{ij}^{(0), \text{sy}} : (-\mathbf{r}_{ij} + \alpha \mathbf{r}_{ij}, \alpha \mathbf{r}_{ij})^{\otimes 2} \right] d\alpha d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j, \end{aligned}$$

where $\delta \mathbf{r}_i^\alpha = \mathbf{r}_i^\alpha - \mathbf{r}_i = \mathbf{r}'_i - (1 - \alpha)\mathbf{r}'_{ij} - \mathbf{r}_i$ and $\delta \mathbf{r}_j^\alpha = \mathbf{r}_j^\alpha - \mathbf{r}_i = \mathbf{r}'_i + \alpha \mathbf{r}'_{ij} - \mathbf{r}_i = \mathbf{r}'_j - (1 - \alpha)\mathbf{r}'_{ij} - \mathbf{r}_i$. We may now proceed as for the pressure tensor using the identity $\int_0^1 (a + \alpha b)(c + \alpha d) d\alpha = (a + \frac{1}{2}b)(c + \frac{1}{2}d) + \frac{1}{12}bd$ to integrate with respect to α , and it is obtained that

$$\begin{aligned} \delta^{\text{Bo}} \mathcal{Q}_2^{\text{p}} = & - \sum_{i,j \in \mathfrak{S}} \frac{1}{8} \int \frac{\phi'_{ij}(r_{ij})}{r_{ij}} \mathbf{r}_{ij} \cdot (\mathbf{c}_i - \mathbf{v} + \mathbf{c}_j - \mathbf{v}) \\ & \times \left[\partial_{(\mathbf{r}_i, \mathbf{r}_j)}^2 f_{ij}^{(0), \text{Bo}} : \left(\delta \mathbf{r}_i - \frac{1}{2} \mathbf{r}'_{ij}, \delta \mathbf{r}_i + \frac{1}{2} \mathbf{r}'_{ij} \right)^{\otimes 2} - \partial_{(\mathbf{r}_i, \mathbf{r}_j)}^2 f_{ij}^{(0), \text{sy}} : \left(-\frac{1}{2} \mathbf{r}_{ij}, \frac{1}{2} \mathbf{r}_{ij} \right)^{\otimes 2} \right. \\ & \left. + \frac{1}{12} \partial_{(\mathbf{r}_i, \mathbf{r}_j)}^2 f_{ij}^{(0), \text{Bo}} : \left(\frac{1}{2} \mathbf{r}'_{ij}, \frac{1}{2} \mathbf{r}'_{ij} \right)^{\otimes 2} - \frac{1}{12} \partial_{(\mathbf{r}_i, \mathbf{r}_j)}^2 f_{ij}^{(0), \text{sy}} : \left(\frac{1}{2} \mathbf{r}_{ij}, \frac{1}{2} \mathbf{r}_{ij} \right)^{\otimes 2} \right] d\alpha d\mathbf{c}_i d\mathbf{r}_{ij} d\mathbf{c}_j. \end{aligned}$$

The dominant terms with respect to the density gradients then vanish being odd with respect to velocities $\mathbf{c}_i - \mathbf{v}$ and $\mathbf{c}_j - \mathbf{v}$ and the remaining part involving the gradients of $\tilde{f}_i^{(0)}$ are negligible in the regime under consideration, Eqs. (6.19) and (6.20).

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