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A Kinetic derivation of diffuse interface fluid models

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We present a full derivation of capillary fluid equations from the kinetic theory of dense gases. These equations involve van der Waals' gradient energy, Korteweg's tensor, Dunn and Serrin's heat flux as well as viscous and heat dissipative fluxes. Starting from macroscopic equations obtained from the kinetic theory of dense gases, we use a new second order expansion of the pair distribution function in order to derive the diffuse interface model. The capillary extra terms and the capillarity coefficient are then associated with intermolecular forces and the pair interaction potential.

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I. INTRODUCTION

Diffuse interface methods describe liquid-gas interfaces as transition zones with smooth variations of physical properties. Second gradient diffuse interface fluid models, also termed capillary fluids, have been successfully used to describe liquid-vapor interfaces, capillary waves, near critical points, three phase contact lines, as well as droplets formation and nucleation [1–7]. The second gradient theory has been extended to binary fluids by Cahn and Hilliard allowing to model spinodal decomposition [8]. Diffuse interface models may likewise be used in the supercritical domain allowing a smooth transition from supercritical to subcritical conditions [9]. These models are also compatible with the limiting free boundary problem when the interface thickness goes to zero [5].

The thermodynamics of diffuse interface models has been built by van der Waals [1] using a gradient squared term in the free energy and the corresponding capillary tensor has been derived by Korteweg [2]. The proper heat flux has been obtained by Dunn and Serrin in the framework of rational thermodynamics [10]. These equations have alternatively been obtained from Hamiltonian considerations by Gavriluk and Shugrin [11] and some of their mathematical properties are discussed by and Gavriluk and Gouin [12] and Benzoni et al. [13].

Aside from mechanical, thermodynamical, or mathematical arguments, it is also important to investigate capillary fluids *at the molecular level*. Statistical mechanics of equilibrium systems that are highly inhomogeneous on the scale of length of intermolecular forces has notably been used to investigate liquid-gas interfaces by Ono and Kondo [14], Evans [15], and Rowlinson and Widom [3]. The links between capillary phenomena 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, 14, 15].

Focusing on nonequilibrium models, the kinetic theory of gases has been used in various contexts in order to investigate phase transition as presented in the review paper by Frezzotti and Barbante [16]. Phase changes have

notably been investigated by employing linearized Boltzmann equations with condensation-evaporation boundary conditions [17–19]. Vlasov-Enskog type equations have been used to investigate more deeply spatial aspects of phase transition [20–27] as well as particulate flows [28]. Detailed molecular dynamics of Lennard-Jones fluids have further been performed by Frezzotti and Barbante and compared to capillary fluid models with a general very good agreement [7].

Focusing on the derivation of capillary fluids equations from the kinetic theory, a notable achievement was that of Rocard who derived the capillary force acting locally in a fluid using a Taylor expansion of the two point distribution function [29]. Rocard then recovered the Korteweg tensor and the capillary coefficient. In a remarkable study, a minimum kinetic model has also been introduced by Takata and Noguchi [24] with nonideal effect 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 a Cahn-Hilliard type equation in an isothermal framework. To the best of the author's knowledge, however, a full derivation of nonisothermal capillary fluid equations from the kinetic theory of dense gases is still missing is the object of this work.

The kinetic theory of dense gases is based on a generalized Boltzmann equation for the one-particle distribution function [30–36]. Such a Boltzmann type equation is derived from the two first equations of the BBGKY hierarchy using cluster expansions and Bogoliubov's functional property. A key point in the generalized Boltzmann equation, allowing the derivation of capillary fluids, is that the distribution functions are evaluated *at different spatial positions*. In particular, models starting from the classical Boltzmann equation may lead to Burnett type contributions but not to capillary fluids. The macroscopic equations are then obtained in the kinetic framework through an asymptotic expansion in terms of a uniformity parameter analogous to that of the Chapman-Enskog method. The resulting macroscopic equations are found to be of Navier-Stokes-Fourier type with density dependent transport coefficients [30–36].

An examination of the asymptotic expansions then indicates that second order corrections arising from the pair

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distribution function should be taken into account. A new second order expansion of the pair distribution function is then introduced and lead to the capillary fluid equations. The capillary energy, the Korteweg tensor, the Dunn and Serrin heat flux are exactly recovered after lengthy calculations as well as an expression of the capillary coefficient due to van der Waals and Rayleigh. The capillary terms as well as the capillarity coefficient are related with intermolecular forces and the pair interaction potential.

The equations governing capillary fluids are presented in Section II. The kinetic theory of dense gases and the associated new asymptotics are described in Section III. A full derivation of capillary fluid equations from the kinetic theory is then given in Section IV.

II. DIFFUSE INTERFACE FLUIDS

We summarize in this section the equations governing fluids with diffuse interfaces also termed capillary fluids. These equations involve van der Waals' energy [1], Korteweg's tensor [2] and Dunn and Serrin's heat flux [10]. Incidentally, there exists another type of diffuse interface models of more empirical nature, namely mult fluids, typically obtained through averaging processes, that lay outside the scope of this work. We further discuss a failure of rational thermodynamics—the thermodynamics of irreversible processes—for such *nonlinear* systems of equations governing capillarity fluids, with the apparition of a gradients' product term in the rate of entropy production leading to an artificial alternative for the expression of transport fluxes.

A. Van der Waals free energy

The free energy per unit volume \mathcal{A} in a second gradient theory is in the form

$$\mathcal{A} = \mathcal{A}^0 + \frac{1}{2}\varkappa|\nabla\rho|^2, \quad (1)$$

where \mathcal{A}^0 denotes the bulk free energy per unit volume, ρ the mass density, ∇ the usual differential operator and \varkappa the capillary coefficient. The superscript 0 is used to denote standard bulk phase thermodynamic properties that do not involve gradients. The free energy \mathcal{A}^0 only depends on the densities ρ and the absolute temperature T whereas the gradient squared term $\frac{1}{2}\varkappa|\nabla\rho|^2$ in \mathcal{A} represents the excess free energy of the interfacial region [1–3, 8]. We will assume in the following that the capillarity coefficient \varkappa is constant for the sake of simplicity.

Denoting by $a = \mathcal{A}/\rho$ the free energy per unit mass, T the absolute temperature, s the entropy per unit mass, p the pressure, and $\nu = 1/\rho$ the volume per

unit mass, we have the classical thermodynamic relation $da^0 = -s^0dT - p^0d\nu$. Differentiating (1), we then obtain

$$da = -s^0dT - (p^0 - \frac{1}{2}\varkappa|\nabla\rho|^2)d\nu + \frac{\varkappa\nabla\rho \cdot d\nabla\rho}{\rho}, \quad (2)$$

where d denotes the differentiation operator. This shows that the entropy s and the pressure p are given by

$$s = s^0, \quad p = p^0 - \frac{1}{2}\varkappa|\nabla\rho|^2. \quad (3)$$

The equality of the entropy s with the bulk entropy s^0 is in agreement with van der Waals derivation [1–3, 8]. Denoting by e the energy per unit mass and using the thermodynamic relation $e = a + Ts$ we also get

$$e = e^0 + \frac{1}{2}\frac{\varkappa}{\rho}|\nabla\rho|^2, \quad (4)$$

and we denote by $\mathcal{E} = \rho e$ the energy per unit volume and $\mathcal{E}^c = \frac{1}{2}\varkappa|\nabla\rho|^2$ its capillary part. The generalized Gibbs relation is finally in the form

$$Tds = de - \frac{p}{\rho^2}d\rho - \frac{1}{\rho}\varkappa\nabla\rho \cdot d\nabla\rho. \quad (5)$$

We will deduce from (5) an entropy balance equation and next discuss entropy production and the structure of the momentum and energy fluxes.

In order to illustrate the impact of the van der Waals capillary energy, consider an equilibrium planar liquid-gas interface. The structure of the interface may be obtained by extremalizing the integral of entropy while energy and mass are conserved [1, 3, 6]. Denoting by l and g the indices of the liquid and its vapor at equilibrium, we have $T_l = T_g$, $p_l = p_g$, and $g_l = g_g$, where g is the Gibbs function $g = a + p/\rho$. Denoting by z the normal coordinate, the interface is found to be isotherm and such that $\frac{1}{2}\varkappa(d\rho/dz)^2 = \mathcal{A} - \mathcal{A}_g - g_g(\rho - \rho_g)$ and the density $\rho(z)$ may then be obtained by numerical integration [1, 3, 37]. The function $\mathcal{A} - \mathcal{A}_g - g_g(\rho - \rho_g)$ is the difference between \mathcal{A} and its bi-tangent line, since $\mathcal{A}_l = \mathcal{A}_g - g_g(\rho_l - \rho_g)$ from the equality of pressures and since $\partial_\rho\mathcal{A} = g$ at constant temperature. Approximating the excess function $\mathcal{A} - \mathcal{A}_g - g_g(\rho - \rho_g)$ as $\bar{A}(\rho - \rho_l)^2(\rho - \rho_g)^2$, where \bar{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 $\bar{z} = (\varkappa/2\bar{A})^{1/2}/(\rho_l - \rho_g)$. Detailed numerical simulations also show that the error function erf yields more accurate fits to actual density profiles than the hyperbolic tangent [38].

B. Equations of capillary fluids

Using the pressure p and the energy per unit mass e given by (3) and (4), the equations governing capillary

fluids may be written [5, 6]

$$\partial_t \rho + \nabla \cdot (\rho \mathbf{v}) = 0, \quad (6)$$

$$\partial_t (\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) + \nabla \cdot \mathcal{P} = 0, \quad (7)$$

$$\begin{aligned} \partial_t (\rho (e + \frac{1}{2} |\mathbf{v}|^2)) + \nabla \cdot (\rho \mathbf{v} (e + \frac{1}{2} |\mathbf{v}|^2)) \\ + \nabla \cdot (\mathcal{Q} + \mathcal{P} \cdot \mathbf{v}) = 0, \end{aligned} \quad (8)$$

where \mathbf{v} denotes the fluid velocity, \mathcal{P} the pressure tensor, and \mathcal{Q} the total heat flux. The transport fluxes \mathcal{P} and \mathcal{Q} contain capillary and dissipative terms

$$\mathcal{P} = p\mathbf{I} + \varkappa \nabla \rho \otimes \nabla \rho - \varkappa \rho \Delta \rho \mathbf{I} + \mathcal{P}^{\text{NS}}, \quad (9)$$

$$\mathcal{Q} = \varkappa \rho \nabla \cdot \mathbf{v} \nabla \rho + \mathcal{Q}^{\text{NS}}, \quad (10)$$

where \mathbf{I} denotes the three dimensional unit tensor, \mathcal{P}^{NS} the viscous pressure tensor, $\Delta = \nabla \cdot \nabla$ the Laplacian operator, and \mathcal{Q}^{NS} the Fourier heat flux [5, 6]. The dissipative fluxes \mathcal{P}^{NS} and \mathcal{Q}^{NS} are classically of Navier-Stokes type [34, 35, 39–41]

$$\mathcal{P}^{\text{NS}} = -\mathbf{v} \nabla \cdot \mathbf{v} \mathbf{I} - \eta (\nabla \mathbf{v} + \nabla \mathbf{v}^t - \frac{2}{3} \nabla \cdot \mathbf{v} \mathbf{I}), \quad (11)$$

$$\mathcal{Q}^{\text{NS}} = -\lambda \nabla T, \quad (12)$$

where \mathbf{v} denotes the volume viscosity, η the shear viscosity and λ the thermal conductivity.

We may decompose the total pressure tensor \mathcal{P} and heat flux \mathcal{Q} in the form $\mathcal{P} = p^0 \mathbf{I} + \mathcal{P}^{\text{NS}} + \mathcal{P}^{\text{C}}$ and $\mathcal{Q} = \mathcal{Q}^{\text{NS}} + \mathcal{Q}^{\text{C}}$ so that the Korteweg's tensor \mathcal{P}^{C} and the Dunn and Serrin's heat flux \mathcal{Q}^{C} solely arise from capillarity

$$\mathcal{P}^{\text{C}} = -\frac{1}{2} \varkappa |\nabla \rho|^2 \mathbf{I} + \varkappa \nabla \rho \otimes \nabla \rho - \varkappa \rho \Delta \rho \mathbf{I}, \quad (13)$$

$$\mathcal{Q}^{\text{C}} = \varkappa \rho \nabla \cdot \mathbf{v} \nabla \rho. \quad (14)$$

The capillary part of the pressure $p^{\text{C}} = -\frac{1}{2} \varkappa |\nabla \rho|^2$ has been included in the Korteweg tensor (13). Both capillary fluxes (13) and (14) will have to be recovered from the kinetic theory as well as the capillary energy per unit volume \mathcal{E}^{C} . Such capillary fluids models have been successfully used for the study of many phase change problems including complex liquid-gas interfaces with topological changes [4–7, 9].

C. A Failure of rational thermodynamics

Using Gibbs relation (5) and the governing equations (6)–(8), the rate of entropy production may be written after some algebra

$$\begin{aligned} \rho (\partial_t s + \mathbf{v} \cdot \nabla s) + \nabla \cdot \left(\frac{\mathcal{Q}}{T} - \frac{\varkappa \rho \nabla \cdot \mathbf{v} \nabla \rho}{T} \right) = \\ - \frac{1}{T} \left(\mathcal{P} - p\mathbf{I} - \varkappa \nabla \rho \otimes \nabla \rho + \varkappa \rho \Delta \rho \mathbf{I} \right) : \nabla \mathbf{v} \\ - \left(\mathcal{Q} - \varkappa \rho \nabla \cdot \mathbf{v} \nabla \rho \right) \cdot \frac{\nabla T}{T^2}, \end{aligned} \quad (15)$$

where $\mathbf{v} : \mathbf{w}$ denotes the full contraction between any two tensors \mathbf{v} and \mathbf{w} . Proceeding as in the thermodynamics of irreversible processes [5, 6, 42], also termed rational thermodynamics, and using the Curie principle, we recover from (15) that $\mathcal{P} - p^0 \mathbf{I} - \mathcal{P}^{\text{C}}$ is given by (11) and similarly that $\mathcal{Q} - \mathcal{Q}^{\text{C}}$ is given by (12) and we have recovered both fluxes \mathcal{P} and \mathcal{Q} , including their capillary part (13) and (14).

However, the situation is more complex than it may appear since *there is a term in (15) involving the product of two gradients*, namely

$$\frac{\varkappa \rho \nabla \cdot \mathbf{v} \nabla \rho \cdot \nabla T}{T^2}. \quad (16)$$

Considering this terms as *a temperature gradient term* and regrouping it in the corresponding sum $-(\mathcal{Q} - \rho \nabla \cdot \mathbf{v} \varkappa \nabla \rho) \cdot \nabla T / T^2$, as in (15), we recover Korteweg's tensor and Dunn and Serrin's heat flux. However, using $\nabla \cdot \mathbf{v} = \nabla \mathbf{v} : \mathbf{I}$, this gradients' product term (16) *could* also be considered as *a velocity derivative term*, and one may rewrite the rate of entropy production as

$$\begin{aligned} \rho (\partial_t s + \mathbf{v} \cdot \nabla s) + \nabla \cdot \left(\frac{\mathcal{Q}}{T} - \frac{\varkappa \rho \nabla \cdot \mathbf{v} \nabla \rho}{T} \right) = -\mathcal{Q} \cdot \frac{\nabla T}{T^2} \\ - \frac{1}{T} \left(\mathcal{P} - p\mathbf{I} - \varkappa \nabla \rho \otimes \nabla \rho + \varkappa \rho \Delta \rho \mathbf{I} \right. \\ \left. - \varkappa \rho \nabla \rho \cdot \nabla \log T \mathbf{I} \right) : \nabla \mathbf{v}. \end{aligned} \quad (17)$$

Writting again that the proportionality of fluxes and gradients, we obtain *different fluxes* in an alternative *unphysical* form

$$\begin{aligned} \mathcal{P}' = p\mathbf{I} + \varkappa \nabla \rho \otimes \nabla \rho - \varkappa \rho \Delta \rho \mathbf{I} \\ + \varkappa \rho \nabla \rho \cdot \nabla \log T \mathbf{I} + \mathcal{P}^{\text{NS}}, \end{aligned} \quad (18)$$

$$\mathcal{Q}' = \mathcal{Q}^{\text{NS}}, \quad (19)$$

as overlooked in the literature [43, 44].

Rational thermodynamics, that is usually a faithful tool for linear-like problems, is here unable to determine unambiguously the proper transport fluxes. As quoted by de Groot and Mazur, the methods of rational thermodynamics are essentially valid for linear relations between fluxes and gradients [42]. For nonlinear like capillary fluids, there is a failure of rational thermodynamics in the sense that a simple algebraic reordering of the entropy production rate seems to lead to different physical fluxes and thus to different physics. We thus conclude that *only finer physical theories* may determine unambiguously the proper fluxes and equations. The correct expressions (9)(10) have been obtained in particular by Gavriluk and Shugrin [11] from Hamilton's principle, they have remarkable mathematical properties [12, 13], and are derived in this work from the kinetic theory of dense gases.

III. A DENSE GAS KINETIC MODEL

A kinetic theory describing moderately dense gases is summarized in this section as well as the corresponding macroscopic dense fluid equations. The traditional first order expansion in terms of a uniformity parameter is presented and a new second order expansion of the *pair correlation function* is introduced, as required by the capillary terms.

A. Kinetic framework

We consider a single dense gas and the associated BBGKY hierarchy governing multiple-particle distribution functions [34, 35, 45]. Assuming for the sake of simplicity that there are no external forces acting on the particles, the two first equations of the BBGKY hierarchy are in the form

$$\partial_t f_1 + \mathbf{c}_1 \cdot \nabla_{\mathbf{r}_1} f_1 = \int \theta_{12} f_2 d\mathbf{x}_2, \quad (20)$$

$$\partial_t f_2 + \mathbf{c}_1 \cdot \nabla_{\mathbf{r}_1} f_2 + \mathbf{c}_2 \cdot \nabla_{\mathbf{r}_2} f_2 = \int (\theta_{13} + \theta_{23}) f_3 d\mathbf{x}_3, \quad (21)$$

where ∂_t denotes the time derivative operator, \mathbf{r}_i the spatial coordinates of the i th particle, \mathbf{c}_i the velocity of the i th particle, f_k the k -particle(s) distribution function, $\nabla_{\mathbf{r}_i}$ 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 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 $d\mathbf{r}_i d\mathbf{c}_i$. When there is no ambiguity, we will also denote by \mathbf{r} and \mathbf{c} the vectors \mathbf{r}_1 and \mathbf{c}_1 and by ∇ the differential operator $\nabla_{\mathbf{r}_1}$. The differential operator θ_{ij} is given by

$$\theta_{ij} = \frac{1}{m} \nabla_{\mathbf{r}_i} \varphi_{ij} \cdot \nabla_{\mathbf{c}_i} + \frac{1}{m} \nabla_{\mathbf{r}_j} \varphi_{ij} \cdot \nabla_{\mathbf{c}_j}, \quad (22)$$

where m denotes the particle mass and φ_{ij} the interaction potential between the i th and j th particles that only depends on the intermolecular distance $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$. The traditional one-particle distribution function is thus $f_1 = f_1(\mathbf{x}_1, t) = f_1(\mathbf{r}_1, \mathbf{c}_1, t)$ and the particle pair distribution function $f_2 = f_2(\mathbf{x}_1, \mathbf{x}_2, t)$ and is symmetric $f_2(\mathbf{x}_1, \mathbf{x}_2, t) = f_2(\mathbf{x}_2, \mathbf{x}_1, t)$. The triplet particle distribution function f_3 is assumed to be zero in this work for the sake of simplicity. These equations are the two first equations of the BBGKY hierarchy that has been derived independently by Bogoliubov [46], Born and Green [47], Kirkwood [48], and introduced by Yvon [49], and we refer to the literature [34, 35, 45] for more details.

The aim of this work being the derivation of the macroscopic equations governing diffuse interface fluids, we will only use a simplified version of the kinetic theory of moderately dense gases. In particular, triple collisions are not been taken into account, although they may indeed be included in the model, and some of the difficulties

associated with dense gases are not detailed like bound states, divergences with quadruple collisions in three dimensions, or long time tails for time correlation functions and we refer to the literature [30–36].

B. Macroscopic equations

The gas number density n_1 is given by

$$n_1(\mathbf{r}_1, t) = \int f_1(\mathbf{r}_1, \mathbf{c}_1, t) d\mathbf{c}_1, \quad (23)$$

and will also be denoted by n when there is no ambiguity, and the pair number density n_2 reads

$$n_2(\mathbf{r}_1, \mathbf{r}_2, t) = \int f_2(\mathbf{r}_1, \mathbf{c}_1, \mathbf{r}_2, \mathbf{c}_2, t) d\mathbf{c}_1 d\mathbf{c}_2. \quad (24)$$

The mass density is $\rho = mn$ and the gas velocity \mathbf{v} reads

$$\rho \mathbf{v}(\mathbf{r}_1, t) = \int m \mathbf{c}_1 f_1(\mathbf{r}_1, \mathbf{c}_1, t) d\mathbf{c}_1. \quad (25)$$

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

$$e = e^{\text{K}} + e^{\text{P}}, \quad (26)$$

where e^{K} is the kinetic part that originates from the peculiar motion of the particles whereas e^{P} is the potential part due to the pair interaction potential [34, 35]. We will denote by $\mathcal{E} = \rho e$ and $\mathcal{E}^{\text{P}} = \rho e^{\text{P}}$ the corresponding energy densities per unit volume. The internal energy density e^{K} and the potential part e^{P} may be written

$$\rho e^{\text{K}} = \int \frac{1}{2} m |\mathbf{c}_1 - \mathbf{v}|^2 f_1(\mathbf{r}_1, \mathbf{c}_1, t) d\mathbf{c}_1, \quad (27)$$

$$\rho e^{\text{P}} = \int \frac{1}{2} \varphi_{12}(r_{12}) n_2(\mathbf{r}_1, \mathbf{r}_2, t) d\mathbf{r}_2, \quad (28)$$

where the interaction potential φ_{12} only depends on $r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|$.

The general macroscopic equations in unclosed form are further obtained by taking appropriate moments of (20) and (21). The mass conservation equation is obtained by integrating (20) with respect to \mathbf{c}_1 and reads

$$\partial_t \rho + \nabla \cdot (\rho \mathbf{v}) = 0. \quad (29)$$

The momentum equation, obtained by multiplying (20) by $m \mathbf{c}_1$ and integrating with respect to \mathbf{c}_1 , is found in the form

$$\partial_t (\rho \mathbf{v}) + \nabla \cdot (\rho \mathbf{v} \otimes \mathbf{v}) + \nabla \cdot (\mathcal{P}^{\text{K}} + \mathcal{P}^{\text{P}}) = 0, \quad (30)$$

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

$$\mathcal{P}^{\text{K}}(\mathbf{r}_1, t) = \int m \mathbf{c}_1 \otimes \mathbf{c}_1 f_1(\mathbf{r}_1, \mathbf{c}_1, t) d\mathbf{c}_1, \quad (31)$$

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

$$\mathcal{P}^p(\mathbf{r}_1, t) = -\frac{1}{2} \int \frac{\varphi'_{12}(r_{12})}{r_{12}} \mathbf{r}_{12} \otimes \mathbf{r}_{12} n_2(\mathbf{r}_1 - (1 - \alpha)\mathbf{r}_{12}, \mathbf{r}_1 + \alpha\mathbf{r}_{12}, t) d\alpha d\mathbf{r}_{12}, \quad (32)$$

where 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 particles due to intermolecular forces [34, 35].

The energy conservation equation is next derived in several steps. One first multiply (20) by $\frac{1}{2}m|\mathbf{c}_1|^2$ and integrate with respect to \mathbf{c}_1 in order to obtain a balance equation for the kinetic part e^k of the internal energy. The balance equation for the potential part of the energy e^p is then obtained by multiplying the two point distribution function equation (21) by the potential energy $\frac{1}{2}\varphi_{12}(r_{12})$ and integrating with respect to \mathbf{c}_1 , \mathbf{c}_2 , and $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$. A balance equation for the kinetic energy $\frac{1}{2}|\mathbf{v}|^2$ is also obtained by taking the scalar prod-

uct of (30) by \mathbf{v} and added to the previous equations. After lengthy calculations, the governing equation for $e + \frac{1}{2}|\mathbf{v}|^2 = e^k + e^p + \frac{1}{2}|\mathbf{v}|^2$ is found in the form

$$\partial_t(\rho(e + \frac{1}{2}|\mathbf{v}|^2)) + \nabla \cdot (\rho(e + \frac{1}{2}|\mathbf{v}|^2)) + \nabla \cdot (\mathcal{Q}^k + \mathcal{Q}^p + (\mathcal{P}^k + \mathcal{P}^p) \cdot \mathbf{v}) = 0, \quad (33)$$

where

$$\mathcal{Q}^k(\mathbf{r}_1, t) = \frac{1}{2} \int m|\mathbf{c}_1 - \mathbf{v}|^2 (\mathbf{c}_1 - \mathbf{v}) f_1(\mathbf{r}_1, \mathbf{c}_1, t) d\mathbf{c}_1, \quad (34)$$

and $\mathcal{Q}^p = \mathcal{Q}_1^p + \mathcal{Q}_2^p$ with

$$\mathcal{Q}_1^p(\mathbf{r}_1, t) = \frac{1}{2} \int \varphi_{12}(r_{12}) (\mathbf{c}_1 - \mathbf{v}) f_2(\mathbf{r}_1, \mathbf{c}_1, \mathbf{r}_2, \mathbf{c}_2, t) d\mathbf{c}_1 d\mathbf{r}_2 d\mathbf{c}_2, \quad (35)$$

$$\mathcal{Q}_2^p(\mathbf{r}_1, t) = -\frac{1}{4} \int \frac{\varphi'_{12}(r_{12})}{r_{12}} \mathbf{r}_{12} \mathbf{r}_{12} \cdot (\mathbf{c}_1 - \mathbf{v} + \mathbf{c}_2 - \mathbf{v}) f_2(\mathbf{r}_1 - (1 - \alpha)\mathbf{r}_{12}, \mathbf{c}_1, \mathbf{r}_1 + \alpha\mathbf{r}_{12}, \mathbf{c}_2, t) d\alpha d\mathbf{c}_1 d\mathbf{r}_{12} d\mathbf{c}_2, \quad (36)$$

and the scalar α must be integrated over $(0, 1)$. 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 molecules. The first potential part \mathcal{Q}_1^p represents the flow of potential energy carried by the molecules and \mathcal{Q}_2^p represents the flux of energy associated with long range forces and thermal agitation. More specifically, the scalar product of \mathcal{Q}_2^p with a normal vector to a surface element represents the work per unit time done on molecules on one side, that move with their peculiar motion, by the molecules on the other side, and both fluxes \mathcal{Q}_1^p and \mathcal{Q}_2^p only depend on the peculiar velocities $\mathbf{c}_1 - \mathbf{v}$ and $\mathbf{c}_2 - \mathbf{v}$.

C. Generalized Boltzmann equation

The kinetic theory of dense gases involves a generalized Boltzmann equation for the one-particle distribution function f_1 that may be derived by using cluster expansions and Bogoliubov's method [30–36]. To this aim, the two point distribution function f_2 is written in the form

$$f_2 = \mathfrak{S}_{12} f_1(\mathbf{x}_1, t) f_1(\mathbf{x}_2, t), \quad (37)$$

where the combined streaming operator \mathfrak{S}_{12} is given by

$$\mathfrak{S}_{12} = \exp(-t\mathfrak{H}_{12}) \exp(t\mathfrak{H}_1) \exp(t\mathfrak{H}_2). \quad (38)$$

The operator \mathfrak{H}_i denotes the Hamiltonian operator of the i th particle alone $\mathfrak{H}_i = \mathbf{c}_i \cdot \nabla_{\mathbf{r}_i}$ whereas

$$\mathfrak{H}_{12} = \mathbf{c}_1 \cdot \nabla_{\mathbf{r}_1} + \mathbf{c}_2 \cdot \nabla_{\mathbf{r}_2} - \theta_{12},$$

denotes the Hamiltonian operator for the particle pair. In the expression (37) the contribution arising from triple distribution products or more [32, 35] have been neglected for the sake of simplicity. The streaming operators $\exp(t\mathfrak{H}_s)$ form Abelian one parameter groups of operators and correspond to the streaming of systems of s particle under the influence of the Hamiltonian \mathfrak{H}_s . It has also been assumed that the initial distribution is a product of uncorrelated distributions $f_2(\mathbf{x}_1, \mathbf{x}_2, 0) = f_1(\mathbf{x}_1, 0) f_1(\mathbf{x}_2, 0)$. A fundamental assumption in the model is that the operator $\mathfrak{S}_{12}(\mathbf{x}_1, \mathbf{x}_2, t)$ as a finite limit $\mathfrak{S}_{12}^\infty(\mathbf{x}_1, \mathbf{x}_2)$ as t is large with respect to the collision time and we refer to Choh and Uhlenbeck [30], Andrews [31], García Colín et al. [32], Ferziger and Kaper [35], and Dorfman and van Beijeren [36], for more details.

The generalized Boltzmann equation governing the one-particle distribution function f_1 is then in the form

$$\partial_t f_1 + \mathbf{c}_1 \cdot \nabla_{\mathbf{r}_1} f_1 = J(f_1, f_1), \quad (39)$$

where

$$J(f_1, f_1) = \int \theta_{12} \mathfrak{S}_{12}^\infty f_1(\mathbf{x}_1) f_1(\mathbf{x}_2) d\mathbf{x}_2. \quad (40)$$

A key point in (39) is that the particles are taken at different positions \mathbf{r}_1 and \mathbf{r}_2 and Taylor expansion will be required in order to localize the collision operator.

D. Chapman-Enskog expansion

The asymptotic method that leads to the macroscopic fluid equations in the kinetic theory of dense gases is analogous to that of Chapman-Enskog. The distribution f_1 is expanded as a power series in terms of a *uniformity parameter* μ which is a measure of the gradients of the macroscopic variables. Such an expansion is valid in the hydrodynamic stage where f_1 only depends on time through the macroscopic variables n , \mathbf{v} and T . The macroscopic variables, on the other hand, are governed by the hydrodynamic equations [30–36].

In the Navier-Stokes regime, the one particle distribution is expanded in the form

$$f_1 = f_1^{(0)} + \mu f_1^{(1)} + \mathcal{O}(\mu^2), \quad (41)$$

in terms of the uniformity parameter μ . The case where $\mu = 0$ corresponds to a *local* uniform state and this implies a first order expansion for $f_1(\mathbf{r}'_1, \mathbf{c}_1)$ around $(\mathbf{r}_1, \mathbf{c}_1)$ with $\delta\mathbf{r}_1 = \mathbf{r}'_1 - \mathbf{r}_1$ in the form

$$f_1(\mathbf{r}'_1, \mathbf{c}_1) = f_1^{(0)}(\mathbf{r}_1, \mathbf{c}_1) + \mu(f_1^{(1)}(\mathbf{r}_1, \mathbf{c}_1) + \nabla f_1^{(0)}(\mathbf{r}_1, \mathbf{c}_1) \cdot \delta\mathbf{r}_1) + \mathcal{O}(\mu^2). \quad (42)$$

The collision operator is correspondingly expanded as

$$J(f_1, f_1) = J_0(f_1^{(0)}, f_1^{(0)}) + \mu J_1(f_1^{(1)}, \nabla f_1^{(0)}) + \mathcal{O}(\mu^2), \quad (43)$$

where J_0 is the usual Boltzmann collision operator whereas J_1 contains bilinear collision operators localized around $\mathbf{r} = \mathbf{r}_1$ [31, 32, 35].

At zeroth order, it is obtained that $J_0(f_1^{(0)}, f_1^{(0)}) = 0$ and $f_1^{(0)}$ is taken to be the local Maxwellian

$$f_1^{(0)} = n \left(\frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \exp\left(-\frac{m|\mathbf{c}_1 - \mathbf{v}|^2}{2k_B T}\right), \quad (44)$$

where n , \mathbf{v} and T are the local number density, fluid velocity and temperature, following Enskog's method of expansion. In particular, the Maxwellian distribution is such that the local value of the complete internal energy density is recovered with $f_1^{(0)}$ thereby defining the local temperature [32, 35]. The zeroth order expansion $f_2^{(0)}$ of the pair distribution function f_2 is then in the form [32, 35, 50]

$$f_2^{(0)}(\mathbf{x}_1, \mathbf{x}_2, t) = f_1^{(0)}(\mathbf{r}_1, \mathbf{c}_1, t) f_1^{(0)}(\mathbf{r}_1, \mathbf{c}_2, t) g_2(\mathbf{r}_{12}), \quad (45)$$

where g_2 denotes the equilibrium correlation function

$$g_2(r_{12}) = \exp\left(-\frac{\varphi_{12}(r_{12})}{k_B T(\mathbf{r}_1)}\right), \quad (46)$$

keeping in mind that the macroscopic unknowns are locally uniform at zeroth order. At zeroth order, the Euler fluid equations are then recovered [30–36], using (44)(45) and the macroscopic equations of Section III B.

At first order, in the Navier-Stokes regime, taking into account the operator decomposition (43), the integral equation for the perturbed distribution function $f_1^{(1)}$ is in the form

$$\partial_t f_1^{(0)} + \mathbf{c}_1 \cdot \nabla_{\mathbf{r}_1} f_1^{(0)} - J_1(f_1^{(0)}, \nabla_{\mathbf{r}_1} f_1^{(0)}) = J_0(f_1^{(0)}, f_1^{(1)}) + J_0(f_1^{(1)}, f_1^{(0)}), \quad (47)$$

and the time derivative is evaluated with Euler equations. This first order equation is similar to the classical first order equations except that there are extra gradient terms $J_1(f_1^{(0)}, \nabla_{\mathbf{r}_1} f_1^{(0)})$ arising from the Taylor expansion of $f_1(\mathbf{x}_2, t)$ in the collision operator. The distribution $f_1^{(0)}$ is then uniquely determined by imposing Enskog type constraints so that the true value of the local macroscopic variables n , \mathbf{v} and T (or equivalently e) are determined by $f_1^{(0)}$ alone [32, 35]. The resulting macroscopic equations are of Navier-Stokes-Fourier type [30–36], with fluxes in the classical form (11)(12). The resulting expressions of the transport coefficients in dense gases, however, are highly complex [30–36].

E. Pressure and internal energy

Using the zeroth order expressions of the one and two point distribution functions (44) and (45), the pressure is found in the form

$$p = nk_B T - \frac{n^2}{6} \int \varphi'_{12}(r_{12}) r_{12} g_2(r_{12}) d\mathbf{r}_{12}. \quad (48)$$

Integrating by part the integral in (48), we obtain that

$$\begin{aligned} \int \varphi'_{12}(r_{12}) r_{12} g_2(r_{12}) d\mathbf{r}_{12} &= 4\pi \int \varphi'_{12}(r_{12}) r_{12}^3 g_2(r_{12}) dr_{12} \\ &= 12\pi k_B T \int \mathfrak{f}_{12} r_{12}^2 dr_{12}, \end{aligned}$$

where \mathfrak{f}_{12} is the Mayer function

$$\mathfrak{f}_{12} = \exp\left(-\frac{\varphi_{12}}{k_B T}\right) - 1. \quad (49)$$

The internal energy is obtained with a similar procedure as

$$e = \frac{3}{2} nk_B T + \frac{1}{2} n^2 \int \varphi_{12}(r_{12}) g_2(r_{12}) d\mathbf{r}_{12}. \quad (50)$$

In order to recover the van der Waals equation of state, we may further assume that the interaction potential φ_{12} is such that

$$\varphi_{12}(r_{12}) = \begin{cases} +\infty & \text{if } 0 \leq r_{12} \leq \sigma, \\ \varphi_{12}(r_{12}) < \infty & \text{if } \sigma < r_{12}, \end{cases} \quad (51)$$

for some positive collision diameter σ . One may also assume that φ_{12} is attractive $\varphi_{12} < 0$ for $2\sigma < r_{12}$, and increases towards zero as $r_{12} \rightarrow \infty$. We may then recover the van der Waals equation of state by decomposing the integral $\int f_{12} dr_{12}$ in two zones [51–53]. More specifically, one may write that

$$\int f_{12} r_{12}^2 dr_{12} = \int_0^{2\sigma} f_{12} r_{12}^2 dr_{12} + \int_{2\sigma}^{\infty} f_{12} r_{12}^2 dr_{12},$$

use $f_{12} = -1$ over $(0, 2\sigma)$, linearize the Mayer function $f_{12} \approx -\varphi_{12}/k_{\text{B}}T$ for $2\sigma < r_{12}$, to get that

$$2\pi k_{\text{B}}T \int f_{12} dr_{12} \approx -4k_{\text{B}}T \frac{4\pi\sigma^3}{3} + 2\pi \int_{2\sigma}^{\infty} \varphi(\mathbf{r}_{12}) r_{12}^2 dr_{12},$$

and the corresponding pressure law reads

$$p = nk_{\text{B}}T + n^2 k_{\text{B}}T \frac{16\pi\sigma^3}{3} - n^2 2\pi \int_{2\sigma}^{\infty} \varphi(\mathbf{r}_{12}) r_{12}^2 dr_{12}.$$

Assuming then that the volume occupied by the particles is small $nk_{\text{B}}T \frac{4\pi\sigma^3}{3} \ll 1$ we obtain the state law

$$p = \frac{nk_{\text{B}}T}{1 - bn} - an^2, \quad (52)$$

with

$$b = 4 \frac{4\pi\sigma^3}{3}, \quad a = 2\pi \int_{2\sigma}^{\infty} \varphi(\mathbf{r}_{12}) r_{12}^2 dr_{12},$$

and the van der Waals equation of state has been recovered using the traditional method of statistical physics [51–53].

F. A new second order expansion

The scaling of the generalized Boltzman equation (39) associated with the expansion (41) in the hydrodynamic regime may be written as

$$\mu(\partial_t f_1 + \mathbf{c}_1 \cdot \nabla_{\mathbf{r}_1} f_1) = \int \theta_{12} f_2 d\mathbf{x}_2. \quad (53)$$

This shows that a second order expansion of f_2 , that leads to extra terms of order $\mathcal{O}(\mu^2)$, should formally be taken into account in the macroscopic governing equations in a Navier-Stokes regime, keeping in mind that f_1 is developed with a first order term $\mathcal{O}(\mu)$ in the left hand side. A second order expansion of the pair particle distribution f_2 is thus required and will yield the capillary terms in the macroscopic equations.

In order to obtain a second order expansion of f_2 , we first have to consider the one point distribution function f_1 . The distribution f_1 is expanded in the form

$$f_1 = f_1^{(0)} + \mu f_1^{(1)} + \mu^2 f_1^{(2)}, \quad (54)$$

and this yields an expansion of $f_1(\mathbf{r}'_1, \mathbf{c}_1)$ around $\mathbf{x}_1 = (\mathbf{r}_1, \mathbf{c}_1)$ with $\delta\mathbf{r}_1 = \mathbf{r}'_1 - \mathbf{r}_1$

$$\begin{aligned} f_1(\mathbf{r}'_1, \mathbf{c}_1) &= f_1^{(0)}(\mathbf{r}_1, \mathbf{c}_1) + \mu(f_1^{(1)}(\mathbf{r}_1, \mathbf{c}_1) + \nabla f_1^{(0)}(\mathbf{r}_1, \mathbf{c}_1) \cdot \delta\mathbf{r}_1) \\ &\quad + \mu^2(f_1^{(2)}(\mathbf{r}_1, \mathbf{c}_1) + \nabla f_1^{(1)}(\mathbf{r}_1, \mathbf{c}_1) \cdot \delta\mathbf{r}_1 + \frac{1}{2} \nabla^2 f_1^{(0)}(\mathbf{r}_1, \mathbf{c}_1) : \delta\mathbf{r}_1 \otimes \delta\mathbf{r}_1). \end{aligned}$$

We now remark that both $f_1^{(2)}$ and $\nabla f_1^{(1)}$ are *Burnett type terms* and should be discarded in a Navier-Stokes regime. Keeping only the $\nabla^2 f_1^{(0)}$ second order terms, we obtain a *new second order expansion* of f_1

$$f_1(\mathbf{r}'_1, \mathbf{c}_1) = f_1^{(0)}(\mathbf{r}_1, \mathbf{c}_1) + \mu(f_1^{(1)}(\mathbf{r}_1, \mathbf{c}_1) + \nabla f_1^{(0)}(\mathbf{r}_1, \mathbf{c}_1) \cdot \delta\mathbf{r}_1) + \mu^2 \frac{1}{2} \nabla^2 f_1^{(0)}(\mathbf{r}_1, \mathbf{c}_1) : \delta\mathbf{r}_1 \otimes \delta\mathbf{r}_1, \quad (55)$$

that does not contain Burnett type terms in the classical sense. The second order expansion of f_2 is then obtained from that of f_1 (55) with the nonequilibrium expression

$$f_2(\mathbf{x}_1, \mathbf{x}_2, t) = f_1^{(0)}(\mathbf{x}_1, t) f_1^{(0)}(\mathbf{x}_2, t) g_2(r_{12}), \quad (56)$$

where $g_2(r_{12})$ is the correlation function. In order to derive the modified macroscopic equations, the new expansion of f_2 must then be used with the general balance equations established in Section III B. Note that only the extra terms arising from the second order terms of f_2 must be taken into account, and this is the object of the next section.

Although a nonequilibrium correlation function g_2 could in principle also be used, and could eventually depend on $T(\mathbf{r}_2)$, we will nevertheless use the correlation function (46) as if the temperature is locally uniform. There is indeed no clear expression for a nonequilibrium correlation function at interfaces and many solutions have been proposed, e.g., using an average temperature, or the center of mass temperature, or solving integral equations [3, 54, 55]. In addition, temperature variations during phase change are modest at variance with large density variations. Using a locally uniform correlation function g_2 will imply that the capillary coefficient is independent of temperature in agreement with

the van der Waals and Rayleigh expressions obtained in the following and further corresponds to the simplified model presented in Section II.

IV. DERIVATION OF CAPILLARY FLUID EQUATIONS

In this section, we derive the capillary fluid equations from the dense gas kinetic theory described in Section III. The method combines the dense fluid macroscopic equations obtained in Section III B as well as the new second order expansion of f_2 . The second order terms in f_2 are obtained from (56) and (55) and will yield the extra terms associated with capillarity. This method has intuitively

$$\begin{aligned} n_2(\mathbf{r}_1 - (1 - \alpha)\mathbf{r}_{12}, \mathbf{r}_1 + \alpha\mathbf{r}_{12}, t) &\approx (n(\mathbf{r}_1) - (1 - \alpha)\nabla n(\mathbf{r}_1) \cdot \mathbf{r}_{12} + \frac{1}{2}(1 - \alpha)^2 \nabla^2 n(\mathbf{r}_1) : (\mathbf{r}_{12} \otimes \mathbf{r}_{12})) \\ &\times (n(\mathbf{r}_1) + \alpha \nabla n(\mathbf{r}_1) \cdot \mathbf{r}_{12} + \frac{1}{2}\alpha^2 \nabla^2 n(\mathbf{r}_1) : (\mathbf{r}_{12} \otimes \mathbf{r}_{12})) \times g_2(r_{12}). \end{aligned}$$

Extracting the terms with two derivatives, the relevant integrands involves the factors

$$\begin{aligned} &-\alpha(1 - \alpha)(\nabla n(\mathbf{r}_1) \cdot \mathbf{r}_{12})^2 \\ &+ \frac{1}{2}((1 - \alpha)^2 + \alpha^2)n(\mathbf{r}_1)\nabla^2 n(\mathbf{r}_1) : (\mathbf{r}_{12} \otimes \mathbf{r}_{12}). \end{aligned}$$

Incidentally, the n^2 term is already taken into account in the state law (48) and the odd terms yield zero contributions in \mathcal{P}^{ex} but contribute in the dissipative fluxes [32, 35].

Focusing on the first integrand, we note that

$$(\nabla n(\mathbf{r}_1) \cdot \mathbf{r}_{12})^2 = \nabla n(\mathbf{r}_1) \otimes \nabla n(\mathbf{r}_1) : (\mathbf{r}_{12} \otimes \mathbf{r}_{12}),$$

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

$$\mathbf{p}_1 = \frac{1}{12} \int \frac{\varphi'_{12}(r_{12})}{r_{12}} \mathbf{r}_{12} \otimes \mathbf{r}_{12} (\nabla n \otimes \nabla n : (\mathbf{r}_{12} \otimes \mathbf{r}_{12})) d\mathbf{r}_{12}.$$

We may now use the identity (A3) from Appendix in order to perform the integrations over $\mathbf{r}_{12} \in \mathbb{R}^3$, and we obtain that

$$\mathbf{p}_1 = \frac{\varkappa}{6} (2\nabla n \otimes \nabla n + |\nabla n|^2 \mathbf{I}),$$

where the capillarity coefficient is defined as

$$\begin{aligned} \varkappa &= \frac{1}{30} \int \varphi'_{12}(r_{12}) g_2(r_{12}) r_{12}^3 d\mathbf{r}_{12}, \\ &= \frac{2\pi}{15} \int \varphi'_{12}(r_{12}) g_2(r_{12}) r_{12}^5 dr_{12}. \end{aligned} \quad (57)$$

been introduced by Rocard who determined the force resulting from intermolecular potentials and the Korteweg pressure tensor [29] and is used systematically in this work.

A. The Korteweg tensor

We consider the tensor \mathcal{P}^{p} arising from the interaction potential (32) and look for the *extra terms* with *two spatial derivatives* \mathcal{P}^{ex} arising from the second order expansion of the distribution function $f_2(\mathbf{x}_1, \mathbf{x}_2, t) = f_1^{(0)}(\mathbf{x}_1, t) f_1^{(0)}(\mathbf{x}_2, t) g_2(r_{12})$. We use Taylor expansions and keep only the extra terms associated with two derivatives in the governing equations. The relevant integrand factor in (32) is expanded in the form

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

$$\mathbf{p}_2 = -\frac{n}{6} \int \frac{\varphi'_{12}(r_{12})}{r_{12}} \mathbf{r}_{12} \otimes \mathbf{r}_{12} (\nabla^2 n : (\mathbf{r}_{12} \otimes \mathbf{r}_{12})) d\mathbf{r}_{12}.$$

Using again the identity (A3) in order to perform the integrations over $\mathbf{r}_{12} \in \mathbb{R}^3$, we obtain that

$$\mathbf{p}_2 = -\frac{\varkappa}{3} (2n \nabla^2 n + n \Delta n \mathbf{I}).$$

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

$$\mathcal{P}^{\text{ex}} = \frac{\varkappa}{6} (2\nabla n \otimes \nabla n + |\nabla n|^2 \mathbf{I} - 4n \nabla^2 n - 2n \Delta n \mathbf{I}).$$

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

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

Expressing the divergence of the Hessian matrix contribution $n \nabla^2 n$ with the help of differential identity (A5), we indeed obtain the simplified pressure tensor

$$\bar{\mathcal{P}}^{\text{ex}} = \varkappa \left(\nabla n \otimes \nabla n - \frac{1}{2} |\nabla n|^2 \mathbf{I} - n \Delta n \mathbf{I} \right). \quad (58)$$

Introducing the mass based capillary coefficient $\varkappa_m = \varkappa/m^2$ and using $\rho = mn$ we may rewrite the extra pressure tensor $\nabla \cdot \bar{\mathcal{P}}^{\text{ex}}$ as

$$\bar{\mathcal{P}}^{\text{ex}} = \varkappa_m \left(\nabla \rho \otimes \nabla \rho - \frac{1}{2} |\nabla \rho|^2 \mathbf{I} - \rho \Delta \rho \mathbf{I} \right), \quad (59)$$

that *coincides* with the Korteweg tensor $\bar{\mathcal{P}}^{\text{ex}} = \mathcal{P}^{\text{C}}$ given in (13).

B. The capillarity coefficient

The capillary coefficient has been found in the form (57) where $g_2(r_{12}) = \exp(-\varphi/k_{\text{B}}T)$. We may integrate by part the integral in (57) to get that

$$\varkappa = \frac{1}{6}k_{\text{B}}T \int \mathfrak{f}_{12} r_{12}^2 d\mathbf{r}_{12} = \frac{2\pi}{3}k_{\text{B}}T \int \mathfrak{f}_{12} r_{12}^4 dr_{12}, \quad (60)$$

where \mathfrak{f}_{12} is the Mayer function (49).

We may now simplify (60) in order to recover the van der Waals and Rayleigh capillarity coefficient. To this aim, we assume that the interaction potential is like (51). We simplify then the integral in (60) by neglecting the integral over $(0, \sigma)$ and by linearizing \mathfrak{f}_{12} into $\mathfrak{f}_{12} \approx -\varphi_{12}/k_{\text{B}}T$ for $r_{12} > \sigma$, and we obtain that

$$\varkappa = -\frac{1}{6} \int_{r_{12} > \sigma} \varphi_{12} r_{12}^2 d\mathbf{r}_{12}, \quad (61)$$

that coincides with the expression of van der Waals and Rayleigh [3]. Incidentally, considering for instance the attractive part of a Lennard-Jones potential $4\varepsilon(\sigma/r_{12})^6$, where ε is the potential well depth, the integral over $(0, \sigma)$ is $k_{\text{B}}T\sigma^5/5$ and that over $(\sigma, +\infty)$ is $4\varepsilon\sigma^5$ and their ratio is $k_{\text{B}}T/\varepsilon \ll 1$ since $k_{\text{B}}T/\varepsilon$ is typically of order unity.

We will use in the following the van der Waals and Rayleigh expression of the capillarity coefficient (61) that is independent of temperature and number density.

C. The energy density

We first investigate the extra terms \mathcal{E}^{ex} arising from the energy density \mathcal{E}^{P} of potential origin (28) that involves an integral of the two point distribution function f_2 . Expanding the two point distribution function $f_2 = f_1(\mathbf{x}_1, t)f_1(\mathbf{x}_2, t)g_2(r_{12})$ around $\mathbf{r}_2 = \mathbf{r}_1 + \mathbf{r}_{12}$, the relevant extra term involving two derivatives is in the form

$$\mathcal{E}^{\text{ex}} = \frac{1}{2} \int \varphi(r_{12})n(\mathbf{r}_1)\frac{1}{2}\nabla^2 n(\mathbf{r}_1):(\mathbf{r}_{12} \otimes \mathbf{r}_{12})d\mathbf{r}_{12}.$$

After some algebra, using the van der Waals and Rayleigh expression (61) for the capillarity coefficient, the resulting extra volumetric energy density \mathcal{E}^{ex} is found to be

$$\mathcal{E}^{\text{ex}} = -\frac{1}{2}\varkappa n \Delta n. \quad (62)$$

In order to simplify (62) we may use the identity

$$\mathcal{E}^{\text{ex}} = -\frac{1}{2}\varkappa n \Delta n = \frac{1}{2}\varkappa |\nabla n|^2 - \frac{1}{2}\nabla \cdot (\varkappa n \nabla n),$$

in order to recover an energy density in the form

$$\bar{\mathcal{E}}^{\text{ex}} = \frac{1}{2}\varkappa |\nabla n|^2,$$

provided we take into account the residual $-\frac{1}{2}\nabla \cdot (\varkappa n \nabla n)$. By changing the energy density from $\mathcal{E}^{\text{ex}} = -\frac{1}{2}\varkappa n \Delta n$ into $\bar{\mathcal{E}}^{\text{ex}} = \frac{1}{2}\varkappa |\nabla n|^2$ we have indeed to add an extra corrector term to the energy equation in the form

$$\Xi = -\frac{1}{2} \left(\partial_t \nabla \cdot (\varkappa n \nabla n) + \nabla \cdot (\nabla \cdot (\varkappa n \nabla n) \mathbf{v}) \right).$$

We may rewrite this corrector as the divergence of a corrector flux by using the mass conservation equation $\partial_t n = -\nabla \cdot (n\mathbf{v})$ and moreover that the capillarity \varkappa is constant. After some algebra, the corrector term Ξ is rewritten as $\Xi = \nabla \cdot \mathbf{q}_0$ where

$$\mathbf{q}_0 = \frac{1}{2}\varkappa \nabla (n \nabla \cdot (n\mathbf{v})) - \frac{1}{2}\varkappa \nabla \cdot (n \nabla n) \mathbf{v}. \quad (63)$$

Therefore, the extra flux \mathbf{q}_0 must be taken into account, in addition to the extra terms involving two spatial derivatives that will arise from \mathcal{Q}_1^{P} and \mathcal{Q}_2^{P} . For future use in the next section, we may further develop the extra flux \mathbf{q}_0 in the form

$$\begin{aligned} \mathbf{q}_0 &= \varkappa n \nabla \cdot \mathbf{v} \nabla n + \frac{1}{2}\varkappa n^2 \nabla (\nabla \cdot \mathbf{v}) + \frac{1}{2}\varkappa n (\nabla \mathbf{v})^t \cdot \nabla n \\ &+ \frac{1}{2}\varkappa \left(\nabla n \otimes \nabla n + n \nabla^2 n - |\nabla n|^2 \mathbf{I} - n \Delta n \mathbf{I} \right) \mathbf{v}. \end{aligned} \quad (64)$$

The change of energy density from $\mathcal{E}^{\text{ex}} = -\frac{1}{2}\varkappa n \Delta n$ into $\bar{\mathcal{E}}^{\text{ex}} = \frac{1}{2}\varkappa |\nabla n|^2$ has not been discussed in a satisfactory way in the literature. It has been advocated in previous work that \mathcal{E}^{ex} may be transformed into $\bar{\mathcal{E}}^{\text{ex}}$ by integrating by part 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. At variance, in this work, *by properly taking into account the correction heat flux* \mathbf{q}_0 , we clarify the *local* change of energy density from \mathcal{E}^{ex} to $\bar{\mathcal{E}}^{\text{ex}}$.

D. The Dunn and Serrin heat flux

In order to evaluate the extra heat flux \mathcal{Q}^{ex} arising from the second order expansion of f_2 in \mathcal{Q}_1^{P} and \mathcal{Q}_2^{P} and using (56), we need to evaluate the gradients of $f_1^{(0)}$. After some algebra we note that

$$\frac{\nabla f_1^{(0)}}{f_1^{(0)}} = \frac{m}{k_{\text{B}}T} (\mathbf{c}_1 - \mathbf{v}) \cdot \nabla \mathbf{v} + \frac{\nabla n}{n} - \left(\frac{3}{2} - \frac{m|\mathbf{c}_1 - \mathbf{v}|^2}{2k_{\text{B}}T} \right) \frac{\nabla T}{T},$$

where all gradients are of course evaluated at \mathbf{r}_1 and similarly that

$$\begin{aligned} \frac{\nabla^2 f_1^{(0)}}{f_1^{(0)}} &= \frac{\nabla f_1^{(0)} \otimes \nabla f_1^{(0)}}{(f_1^{(0)})^2} - \frac{m}{k_B T} \nabla \mathbf{v} \cdot \nabla \mathbf{v} + \frac{m}{k_B T} (\mathbf{c}_1 - \mathbf{v}) \cdot \nabla^2 \mathbf{v} + \frac{\nabla^2 n}{n} - \frac{\nabla n \otimes \nabla n}{n^2} - \frac{m}{k_B T^2} ((\mathbf{c}_1 - \mathbf{v}) \cdot \nabla \mathbf{v}) \otimes \nabla T \\ &\quad - \frac{m}{k_B T^2} \nabla T \otimes ((\mathbf{c}_1 - \mathbf{v}) \cdot \nabla \mathbf{v}) - \left(\frac{3}{2} - \frac{m|\mathbf{c}_1 - \mathbf{v}|^2}{2k_B T} \right) \frac{\nabla^2 T}{T} + \left(\frac{3}{2} - \frac{m|\mathbf{c}_1 - \mathbf{v}|^2}{k_B T} \right) \frac{\nabla T \otimes \nabla T}{T^2}. \end{aligned}$$

With \mathcal{Q}_1^p given by (35), we need to select integrands obtained from a Taylor expansion of $f_1^{(0)}(\mathbf{x}_1) f_1^{(0)}(\mathbf{x}_2)$ that involve the peculiar velocity of the first particle $\mathbf{c}_1 - \mathbf{v}$ as well as two spatial derivatives and that are even in \mathbf{r}_{12} . It appears, however, that there are not such terms in the Taylor expansion of $f_1^{(0)}(\mathbf{r}_1, \mathbf{c}_1, t) f_1^{(0)}(\mathbf{r}_2, \mathbf{c}_2, t)$ in such a way that there is no extra capillary heat flux arising from \mathcal{Q}_1^p .

On the other hand, with \mathcal{Q}_2^p given by (36), from the isotropy of space and velocity space, we need to select the integrands in the Taylor expansion of

$$f_1^{(0)}(\mathbf{r}_1 - (1 - \alpha)\mathbf{r}_{12}, \mathbf{c}_1, t) f_1^{(0)}(\mathbf{r}_1 + \alpha\mathbf{r}_{12}, \mathbf{c}_2, t),$$

that involve two derivatives, are even with respect to \mathbf{r}_{12} , and odd with respect to either $\mathbf{c}_1 - \mathbf{v}$ or $\mathbf{c}_2 - \mathbf{v}$. We first focus of integrands having such properties arising from the cross products of two first order derivatives of $f_1^{(0)}$ at

different points. These integrands are

$$\begin{aligned} & - \alpha(1 - \alpha) \frac{m}{k_B T} (\mathbf{c}_1 - \mathbf{v}) \cdot \nabla \mathbf{v} \cdot \mathbf{r}_{12} \frac{\nabla n \cdot \mathbf{r}_{12}}{n} \\ & - \alpha(1 - \alpha) \frac{m}{k_B T} (\mathbf{c}_2 - \mathbf{v}) \cdot \nabla \mathbf{v} \cdot \mathbf{r}_{12} \frac{\nabla n \cdot \mathbf{r}_{12}}{n}, \end{aligned}$$

as well as other integrands still including the factor $\alpha(1 - \alpha)$ and proportional to

$$\begin{aligned} & \frac{m}{k_B T} (\mathbf{c}_1 - \mathbf{v}) \cdot \nabla \mathbf{v} \cdot \mathbf{r}_{12} \left(\frac{3}{2} - \frac{m|\mathbf{c}_2 - \mathbf{v}|^2}{2k_B T} \right) \frac{\nabla T \cdot \mathbf{r}_{12}}{T} \\ & + \frac{m}{k_B T} (\mathbf{c}_2 - \mathbf{v}) \cdot \nabla \mathbf{v} \cdot \mathbf{r}_{12} \left(\frac{3}{2} - \frac{m|\mathbf{c}_1 - \mathbf{v}|^2}{2k_B T} \right) \frac{\nabla T \cdot \mathbf{r}_{12}}{T}. \end{aligned}$$

These later integrands yield vanishing contributions since

$$\int \left(\frac{3}{2} - \frac{m|\mathbf{c}_1 - \mathbf{v}|^2}{2k_B T} \right) f_1^{(0)} d\mathbf{c}_1 = 0.$$

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 two former integrands a contribution \mathbf{q}_1 for the heat flux in the form

$$\mathbf{q}_1 = \frac{1}{12} \int \frac{\varphi'_{12}(r_{12})}{r_{12}} \mathbf{r}_{12} \mathbf{r}_{12} \cdot (\mathbf{c}_1 - \mathbf{v}) \frac{m}{k_B T} (\mathbf{c}_1 - \mathbf{v}) \cdot \nabla \mathbf{v} \cdot \mathbf{r}_{12} \frac{\nabla n \cdot \mathbf{r}_{12}}{n} f_1^{(0)}(\mathbf{r}_1, \mathbf{c}_1) f_1^{(0)}(\mathbf{r}_1, \mathbf{c}_2) g_2(r_{12}) d\mathbf{c}_1 d\mathbf{r}_{12} d\mathbf{c}_2.$$

The integration over \mathbf{c}_2 is trivial and yields a factor n , the integration over \mathbf{c}_1 is performed using the reduced velocity $(\mathbf{c}_1 - \mathbf{v})(m/2k_B T)^{1/2}$ and (A1) from Appendix, and this yields

$$\mathbf{q}_1 = \frac{n}{12} \int \frac{\varphi'_{12}(r_{12})}{r_{12}} \mathbf{r}_{12} \otimes \mathbf{r}_{12} (\nabla \mathbf{v} : (\mathbf{r}_{12} \otimes \mathbf{r}_{12})) g_2(\mathbf{r}_{12}) d\mathbf{r}_{12} \nabla n.$$

Using the differential identity (A3) we then obtain that \mathbf{q}_1 is in the form

$$\mathbf{q}_1 = \frac{\varkappa}{6} n \left(\nabla \mathbf{v} + (\nabla \mathbf{v})^t + \nabla \cdot \mathbf{v} \mathbf{I} \right) \nabla n, \quad (65)$$

with the capillary coefficient given by (57).

We now focus on contributions arising from the second order derivatives $\nabla^2 f_1^{(0)}$ in the Taylor expansion of $f_1^{(0)}(\mathbf{r}_1 - (1 - \alpha)\mathbf{r}_{12}, \mathbf{c}_1, t) f_1^{(0)}(\mathbf{r}_1 + \alpha\mathbf{r}_{12}, \mathbf{c}_2, t)$. The relevant integrands are those even with respect to \mathbf{r}_{12} and odd with respect to either $\mathbf{c}_1 - \mathbf{v}$ or $\mathbf{c}_2 - \mathbf{v}$. These integrands are first

$$\alpha^2 \frac{2m}{k_B T} (\mathbf{c}_1 - \mathbf{v}) \cdot \nabla \mathbf{v} \cdot \mathbf{r}_{12} \frac{\nabla n \cdot \mathbf{r}_{12}}{n} + (1 - \alpha)^2 \frac{2m}{k_B T} (\mathbf{c}_2 - \mathbf{v}) \cdot \nabla \mathbf{v} \cdot \mathbf{r}_{12} \frac{\nabla n \cdot \mathbf{r}_{12}}{n},$$

$$+ \alpha^2 \frac{m}{k_B T} (\mathbf{c}_1 - \mathbf{v}) \cdot \nabla^2 \mathbf{v} : (\mathbf{r}_{12} \otimes \mathbf{r}_{12}) + (1 - \alpha)^2 \frac{m}{k_B T} (\mathbf{c}_2 - \mathbf{v}) \cdot \nabla^2 \mathbf{v} : (\mathbf{r}_{12} \otimes \mathbf{r}_{12}).$$

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

$$\mathbf{q}_2 = -\frac{\varkappa}{3} n \left(\nabla \mathbf{v} + (\nabla \mathbf{v})^t + \nabla \cdot \mathbf{v} \mathbf{I} \right) \nabla n. \quad (66)$$

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

$$\mathbf{q}_3 = -\frac{1}{12} \int \frac{\varphi'_{12}(r_{12})}{r_{12}} \mathbf{r}_{12} \mathbf{r}_{12} \cdot (\mathbf{c}_1 - \mathbf{v}) \frac{m}{k_B T} (\mathbf{c}_1 - \mathbf{v}) \cdot \nabla^2 \mathbf{v} : (\mathbf{r}_{12} \otimes \mathbf{r}_{12}) f_1^{(0)}(\mathbf{r}_1, \mathbf{c}_1) f_1^{(0)}(\mathbf{r}_1, \mathbf{c}_2) g_2(\mathbf{r}_{12}) d\mathbf{c}_1 d\mathbf{r}_{12} d\mathbf{c}_2.$$

The integration over \mathbf{c}_2 yield a factor n , the integration over \mathbf{c}_1 is obtained with (A1) from Appendix so that

$$\mathbf{q}_3 = -\frac{n^2}{12} \int \frac{\varphi'_{12}(r_{12})}{r_{12}} \mathbf{r}_{12} \mathbf{r}_{12} \cdot \nabla^2 \mathbf{v} : (\mathbf{r}_{12} \otimes \mathbf{r}_{12}) g_2(\mathbf{r}_{12}) d\mathbf{r}_{12}.$$

We may then use (A4) with $\nabla^2 \mathbf{v} : (\mathbf{r}_{12} \otimes \mathbf{r}_{12} \otimes \mathbf{r}_{12}) = \mathbf{r}_{12} \cdot \nabla^2 \mathbf{v} : (\mathbf{r}_{12} \otimes \mathbf{r}_{12})$ to deduce that

$$\mathbf{q}_3 = -n^2 \frac{\varkappa}{6} \left(\Delta \mathbf{v} + 2\nabla(\nabla \cdot \mathbf{v}) \right). \quad (67)$$

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

$$-\frac{2m}{k_B T} (\mathbf{c}_1 - \mathbf{v}) \cdot \nabla \mathbf{v} \cdot \mathbf{r}_{12} \left(\frac{5}{2} - \frac{m|\mathbf{c}_1 - \mathbf{v}|^2}{2k_B T} \right) \frac{\nabla T \cdot \mathbf{r}_{12}}{T}$$

with a similar expression in terms of $(\mathbf{c}_2 - \mathbf{v})$ but these terms yield vanishing contributions since

$$\int (\mathbf{c}_1 - \mathbf{v}) \left(\frac{5}{2} - \frac{m|\mathbf{c}_1 - \mathbf{v}|^2}{2k_B T} \right) f_1^{(0)} d\mathbf{c}_1 = 0.$$

and

$$\int |\mathbf{c}_1 - \mathbf{v}|^2 \left(\frac{5}{2} - \frac{m|\mathbf{c}_1 - \mathbf{v}|^2}{2k_B T} \right) f_1^{(0)} d\mathbf{c}_1 = 0.$$

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

$$\mathcal{Q}^{\text{ex}} + \mathcal{P}^{\text{ex}} \cdot \mathbf{v} = \varkappa n \nabla \cdot \mathbf{v} \nabla n + \frac{1}{2} \varkappa n^2 \nabla(\nabla \cdot \mathbf{v}) + \frac{1}{2} \varkappa n (\nabla \mathbf{v})^t \cdot \nabla n + \frac{1}{2} \varkappa \left(\nabla n \otimes \nabla n + n \nabla^2 n - |\nabla n|^2 \mathbf{I} - n \Delta n \right) \mathbf{v}$$

$$- \frac{\varkappa}{6} n \left(\nabla \mathbf{v} + (\nabla \mathbf{v})^t + \nabla \cdot \mathbf{v} \mathbf{I} \right) \nabla n - \frac{\varkappa}{6} n^2 \left(\Delta \mathbf{v} + 2\nabla(\nabla \cdot \mathbf{v}) \right) + \frac{\varkappa}{6} \left(2\nabla n \otimes \nabla n + |\nabla n|^2 \mathbf{I} - 4n \nabla^2 n - 2n \Delta n \mathbf{I} \right) \cdot \mathbf{v}.$$

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

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

This will indeed allow the simultaneous use of the simplified heat flux $\bar{\mathcal{Q}}^{\text{ex}}$ and simplified pressure tensor $\bar{\mathcal{P}}^{\text{ex}}$. In

order to simplify the divergence of $\mathcal{Q}^{\text{ex}} + \mathcal{P}^{\text{ex}} \cdot \mathbf{v}$, the first term $\varkappa n \nabla \cdot \mathbf{v} \nabla n$ is left unchanged since it corresponds to the Dunn and Serrin heat flux, all terms proportional to \mathbf{v} are regrouped, and the differential identity (A6) is used to transform the divergence of the term $-\frac{1}{6} \varkappa n \nabla \cdot \mathbf{v} \nabla n$ in the second line that originates from $\mathbf{q}_1 + \mathbf{q}_2$. After some lengthy algebra this yields the expression

$$\nabla \cdot (\mathcal{Q}^{\text{ex}} + \mathcal{P}^{\text{ex}} \cdot \mathbf{v}) = \nabla \cdot \left(\varkappa n \nabla \cdot \mathbf{v} \nabla n - \frac{1}{3} \varkappa n \nabla \mathbf{v} \cdot \nabla n + \frac{1}{3} \varkappa n (\nabla \mathbf{v})^t \cdot \nabla n - \frac{1}{6} n^2 \Delta \mathbf{v} + \frac{1}{6} n^2 \nabla(\nabla \cdot \mathbf{v}) \right.$$

$$\left. + \varkappa \left(\nabla n \otimes \nabla n - \frac{1}{2} |\nabla n|^2 \mathbf{I} - n \Delta n \mathbf{I} \right) \cdot \mathbf{v} \right).$$

Using then the differential identity (A7), the divergence of the four last terms in the first line miraculously vanishes, and we obtain

$$\nabla \cdot (\mathcal{Q}^{\text{ex}} + \mathcal{P}^{\text{ex}} \cdot \mathbf{v}) = \nabla \cdot \left(\varkappa n \nabla \cdot \mathbf{v} \nabla n + \varkappa (\nabla n \otimes \nabla n - \frac{1}{2} |\nabla n|^2 \mathbf{I} - n \Delta n \mathbf{I}) \cdot \mathbf{v} \right),$$

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

$$\overline{\mathcal{Q}}^{\text{ex}} = \varkappa n \nabla \cdot \mathbf{v} \nabla n. \quad (68)$$

Using the mass based capillarity coefficient $\varkappa_m = \varkappa/m^2$, we thus obtain that the extra flux $\overline{\mathcal{Q}}^{\text{ex}}$ coincides with the Dunn and Serrin heat flux $\overline{\mathcal{Q}}^{\text{ex}} = \mathcal{Q}^{\text{C}}$. The full capillary fluid equations (6)–(8) with the capillary fluxes (13)(14) and the energy density (4) have finally been recovered. A key point in the simplification of the capillary heat flux was notably the use of the modified density energy $\overline{\mathcal{E}}^{\text{ex}}$ in order to compensate the complex corrections arising from \mathcal{Q}_2^{P} by similar terms arising from \mathbf{q}_0 .

E. Discussion

We have presented in the previous sections the first molecular derivation of the complete diffuse interface fluid equations in the framework of the kinetic theory of dense gases. This derivation notably includes the van der Waals gradient energy, the Korteweg tensor (9), the Dunn and Serrin heat flux (10), the van der Waals capillarity coefficient and the van der Waals equation of state. We now address the validity domain of the derivation from the kinetic theory, discuss various alternative models and address some previous work.

The derivation of the van der Waals equation of state from statistical mechanics classically requires that the volume ratio nb is small $nb \ll 1$ and makes use of the identity $(1-nb)^{-1} \approx 1+nb$ [51–53]. 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 nb is of order unity. Another derivation of the van der Waals equation of state is also possible by directly including a factor $(1-nb)^{-1}$ in the correlation function g_2 as first suggested by Sobrino [20]. This is a very interesting method that has the advantage of directly giving a factor $(1-nb)^{-1}$ in the repulsive part of the state law. However, in our framework, it would also yield such a factor in the attractive part of the equation of state as well as in the capillary coefficient without further simplifications. This is why we have preferred to use the exact equilibrium correlation function given by statistical mechanics (46) and to follow the traditional derivation of van der Waals equation of state from statistical mechanics [51–53].

Similarly, the capillary fluid equations have been derived within the kinetic theory of moderately dense gases essentially assuming that $r_0 \ll \lambda_K \ll \Lambda$, where r_0 is the

typical range of the interaction molecular potential, λ_K the mean free path, and Λ a hydrodynamic length. However, these capillary equation also apply to liquids where $r_0 \approx \lambda_K$. 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. In the same vein, even though the second order corrections have been included in a Navier-Stokes regime, the resulting equation may also be simplified by removing all dissipative terms and we then recover the inviscid capillary fluid equations.

The derivation from the kinetic theory has been performed by simplifying the capillarity coefficient \varkappa so that it is independant of T and n . The temperature dependence of the capillary coefficients could still be investigated by using a nonequilibrium correlation function g_2 . Since there is no clear expression for a nonequilibrium correlation function at interfaces, g_2 should be chosen carefully [3, 54, 55]. Preliminary analyses using the temperature at the center of mass lead to highly complex analytical calculations and new extra terms that do not reduce to the traditional thermodynamic models with variable capillarity coefficients. The dependence on n may also be investigated but would require to take into account the triplet distribution f_3 and to take into account triple collisions. Equations of states like the Redlich-Kwong equation of state [56] could eventually be recovered from a kinetic theory including the three particles distribution f_3 .

Finally, a key argument in the derivation is the use of a generalized Boltzmann equation with distribution functions are evaluated *at different spatial positions*. In particular, all analyses starting from the classical localized Boltzmann equation, however deep and interesting, *can only recover Burnett type terms but not the capillary terms*. As notably pointed out by Gorban and Karlin [57] *terms which look similar to Korteweg's stress tensor have been recognized in the Chapman-Enskog many times and Everyone can compare the Korteweg stress with Burnett's equations*. However, these Burnett's type terms traditionally involve pressure gradients or temperature gradients and are not capillary terms *that require a non-localized collision operator*. In their remarkable work, Gorban and Karlin have notably obtained the Burnett, super-Burnett as well as an infinitely accurate reduced hydrodynamic model starting from a linearized version of the ten moment Grad fluid model [57]. Nevertheless, however deep and original these results are par se, they do not lead to the capillary fluid equations. In the same vein, Huang et al.[58] have obtained Burnett type terms conducting a difficult mathematical analysis. Some of

the resulting temperature gradients terms in their limiting macroscopic equations are still incorrectly interpreted as Korteweg type terms. All these studies starting from the traditional Boltzmann equation are indeed missing the key argument of a nonlocalized collision operator. On the other hand, the Enskog-Vlasov model does include a nonlocalized Enskog like collision kernel as well as a soft long range attractive potential. This very interesting model has been used successfully to investigate many phase change problems in a kinetic framework [20–27]. In a recent paper, Piechór, after having shown that the local Korteweg tensor may be obtained from a non-local version, has proposed to use an Enskog-Vlasov kinetic equation in order to obtain the Korteweg tensor and has investigated rigorously the mathematical properties of the Enskog-Vlasov kinetic equation and collision operators [59]. Nevertheless, Piechór has only used a first order expansion of the distribution function so that only the Navier-Stokes-Fourier equations have been recovered [59]. The capillary terms indeed require the new second order expansion of f_2 introduced in Section III F. In a remarkable study, Takata and Noguchi have introduced a minimum version of the Enskog-Vlasov kinetic model in order to investigate phase transition in a van der Waals fluid [24]. Takata and Noguchi have investigated the limiting fluid for small Knudsen numbers in an isothermal framework. They have notably obtained a laplacian like capillary energy per unit mass, that yields a gradient square term after integration by part, as well as a limiting Cahn-Hilliard type model [24]. The same framework has next been used by Takata and coworkers in order to clarify the stability of uniform equilibrium states in the kinetic regime rather than that in the continuum limit [26].

Last, but not least, the remarkable numerical simulations by Barbante and Frezzotti [7] have shown a very good agreement between the solutions of the capillary fluid equations and that of a particular Enskog-Vlasov kinetic equation. This very good agreement, except in rarefied regions, is better understood knowing that the capillary fluid equations are a limiting model of kinetic equations and suggest new numerical simulations in order to deepen the analysis.

V. CONCLUSION

We have derived for the first time the full diffuse interface fluid equations from the kinetic theory of dense gases. Investigating more refine models would be of high scientific interest. This notably includes dense gas models including triple collisions so that the capillarity \varkappa would depend on the number density n . It would also be of high scientific interest to investigate the situation where the capillarity coefficient \varkappa depends on temperature T using a properly chosen nonequilibrium correlation function g_2 .

The case of gas mixtures—for which there is also a failure of rational thermodynamics—could also be investigated using similar methods. Investigating fluctuations at both the kinetic and the capillary fluid level would also be of high interest as well as boundary conditions with three phase lines. Numerical simulations would also be an outstanding tool for comparing nonlocal kinetic models and their corresponding macroscopic diffuse interface equations.

Appendix A: 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 $(\mathbf{c} - \mathbf{v})(m/2k_B T)^{1/2}$ or else the relative position $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$.

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

$$\int \mathbf{z}(\mathbf{z} \cdot \mathbf{a}) \gamma(z) d\mathbf{z} = \frac{1}{3} \int z^2 \gamma(z) d\mathbf{z} \mathbf{a}, \quad (\text{A1})$$

for any vector \mathbf{a} independent of \mathbf{z} . Similarly, we have [35]

$$\int \mathbf{z} \otimes \mathbf{z} \gamma(z) d\mathbf{z} = \frac{1}{3} \int z^2 \gamma(z) d\mathbf{z} \mathbf{I}, \quad (\text{A2})$$

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 [35]

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

as well as

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

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

$$\int \gamma(z) \mathbf{z} \otimes \mathbf{z} (\mathbf{z} \otimes \mathbf{z} : \mathbf{w}) d\mathbf{z} = \frac{1}{15} \int z^4 \gamma(z) d\mathbf{z} (\mathbf{w} + \mathbf{w}^t + \mathbf{w} : \mathbf{I} \mathbf{I}), \quad (\text{A3})$$

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} .

Finally, for any third order gradient tensor like $\nabla^2 \mathbf{v}$ independent of \mathbf{z} and for any isotropic function $\gamma(z)$ we have

$$\int \gamma(z) \mathbf{z} (\nabla^2 \mathbf{v} : (\mathbf{z} \otimes \mathbf{z} \otimes \mathbf{z})) d\mathbf{z} = \frac{1}{15} \int z^4 \gamma(z) d\mathbf{z} (\Delta \mathbf{v} + 2\nabla(\nabla \cdot \mathbf{v})), \quad (\text{A4})$$

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

We now investigate various differential relations used in the derivation of the capillary fluid equations. The following relation is established for a scalar function $n(\mathbf{r})$ of $\mathbf{r} \in \mathbb{R}^3$ after integrations by parts

$$\nabla \cdot (n \nabla^2 n) = \nabla \cdot (n \Delta n \mathbf{I} + |\nabla n|^2 \mathbf{I} - \nabla n \otimes \nabla n), \quad (\text{A5})$$

where ∇n is the gradient of n , $\Delta n = \nabla \cdot \nabla n$ the Laplacian, and $\nabla^2 n$ the Hessian matrix with components $\partial_{r_i} \partial_{r_j} n$ for $1 \leq i, j \leq 3$.

In addition, for any scalar function $n(\mathbf{r})$ 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

$$\nabla \cdot (n \nabla \cdot \mathbf{v} \nabla n) = \nabla \cdot (n \nabla \mathbf{v} \cdot \nabla n + (|\nabla n|^2 \mathbf{I} + n \Delta n \mathbf{I} - \nabla n \otimes \nabla n - n \nabla^2 n) \cdot \mathbf{v}). \quad (\text{A6})$$

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

$$\frac{1}{2} \nabla \cdot (n^2 \nabla(\nabla \cdot \mathbf{v})) = \nabla \cdot (n \nabla \mathbf{v} \cdot \nabla n - n \nabla \mathbf{v}^t \cdot \nabla n + \frac{1}{2} n^2 \Delta \mathbf{v}), \quad (\text{A7})$$

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

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