Smoothed particle hydrodynamics model for phase separating fluid mixtures. I. General equations

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We present a thermodynamically consistent discrete fluid particle model for the simulation of a recently proposed set of hydrodynamic equations for a phase separating van der Waals fluid mixture [P. Español and C.A.P. Thieulot, J. Chem. Phys. **118**, 9109 (2003)]. The discrete model is formulated by following a discretization procedure given by the smoothed particle hydrodynamics (SPH) method within the thermodynamically consistent general equation for the nonequilibrium reversible-irreversible coupling (GENERIC) framework. Each fluid particle carries information on the mass, momentum, energy, and the mass fraction of the different components. The discrete model allows one to simulate nonisothermal dynamic evolution of phase separating fluids with surface tension effects while respecting the first and second laws of thermodynamics exactly.

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I. INTRODUCTION

The dynamics of phase separation in liquid mixtures plays an important role in many industrial and technological processes. There is a continuing interest in the understanding of the dynamics of these fluids in situations where a quench from high temperature to low temperature leads to the formation of domains of coexisting phases, with interfaces that are subject to surface tension [1]. These fluid domains can interact diffusively and hydrodynamically, coalesce and break up, leading to a variety of scaling laws depending on the leading mechanism involved [2].

The hydrodynamic equations governing fluid mixtures have been known for a long time [3,4], but for *phase separating* fluid mixtures the presence of interfaces and the intricate interplay between thermodynamics, hydrodynamics, and surface tension has deferred the presentation of the hydrodynamic equations until quite recently. A very fruitful approach has been the so-called diffuse interface model in which phenomenologically introduced free energies depending on the gradients of the density fields lead to a reasonable description for phase separation [5–7]. Another recent very interesting derivation of hydrodynamic equations for binary mixtures has been done in the context of kinetic theory [8]. In a recent work, we have provided a microscopic basis for a thermodynamically consistent set of diffuse interface hydrodynamic equations for a phase separating fluid mixture [9]. The microscopic derivation based on projection operators has the advantage over phenomenological derivations that the different thermodynamic variables and, in particular, the internal energy, have a well-defined meaning in terms of microscopic variables, allowing to dispel some ambiguities that may appear in phenomenological treatments. In the process, we also derived molecular expressions for the transport coefficients in terms of Green-Kubo formulas. The microscopic derivation of the hydrodynamic equations for phase separat-

ing fluids makes use of the van der Waals assumption that the molecular potential has a short range hard core part and a long range attractive tail. This results in a macroscopic theory that has the thermodynamic behavior predicted by the equation of state of van der Waals. Even though the van der Waals model is very simple, it captures the qualitative features of phase separation and, some times, it can even be quantitative [1].

The objective of the present paper is to formulate a fluid particle model that is the discrete counterpart of the continuum hydrodynamic equations of Ref. [9]. The discrete model thus allows for a numerical simulation of the continuum equations. Our approach is based on the smooth-particle hydrodynamics (SPH) methodology that enables one to discretize the equations of hydrodynamics on a set of points (fluid particles) that move following the flow in a Lagrangian way [10]. SPH is particularly appealing for the treatment of free surfaces which are advected by the flow with little numerical diffusion. One of the nice features of SPH is that it can accommodate very easily the modeling of extra physical and chemical effects and deal with irregular, flexible or deformable boundaries [11]. Nugent and Posch have applied this methodology for the simulation of a fluid with liquid-vapor phase separation [12]. We emphasize that there are many different ways of writing the hydrodynamic equations of Ref. [9] just by recursing to the chain rule of differentiation. A naive application of the SPH rules for discretization of the continuum equations does not lead in general to a fluid particle model that is thermodynamically consistent. By this we mean a model that respects the mass, momentum and energy conservation laws *exactly* and has a *rigorous* nondecreasing behavior of the entropy. In order to find what is the right combination of terms in the continuum equations that leads to a satisfactory discrete model, we resort to the general equation for the nonequilibrium reversible-irreversible coupling (GENERIC) formalism [13]

that has been proved successful in the formulation of fluid particle models for simple Newtonian fluids [14–16]. The GENERIC framework is a very elegant nonequilibrium thermodynamic formalism that embodies the first and second laws of thermodynamics in a natural way. It allows for a transparent account of the Poisson structure of the reversible part of the dynamics and the fluctuation-dissipation theorem inherent to the irreversible part of the dynamics [13]. In this paper we use it as a methodological tool which helps us in finding the correct *structure* of the fluid particle equations, and suggest the appropriate combination of terms in the continuum equations to be discretized.

The method we present has a close connection with recent developments in the many-body dissipative particle dynamics (DPD) [17–20]. The original DPD model [21,22] produces an equation of state that is quadratic in the density, and can never display a phase separation. Pagonabarraga and Frenkel have proposed a DPD model for nonideal fluids where a nontrivial free energy is introduced, and this allows one the treatment of fluids that can phase separate [17]. The model has been further studied by simulations [19,18], and interesting pendant drop simulations have been conducted [20]. However, the DPD model (including its many-body counterpart) has several limitations: it is an isothermal model, the inherent thermal fluctuations of the model are not well controlled, and the connection with the macroscopic transport is obscure. These problems have been solved in a formulation of the DPD equations called smoothed dissipative particle dynamics, which is thermodynamically consistent and that allows for arbitrary equations of state [16]. The model has a very close connection with SPH. Actually, the bottom line of Ref. [16] is that DPD, when properly formulated, is nothing else but SPH plus thermal fluctuations. The present work is the generalization of Ref. [16] to the multicomponent case.

II. THE HYDRODYNAMIC EQUATIONS FOR A PHASE SEPARATING MIXTURE

In this section, we summarize the main results of Ref. [9] which is the starting point for the present work. The main motivation of Ref. [9] has been to extend to nonequilibrium situations the van der Waals ideas for the description of equilibrium states of fluid mixtures. According to the van der Waals picture, phase transitions and surface tension effects in mixtures can be understood by assuming that the potential of interaction $\phi_{i_\alpha j_\beta}$ between molecules of species α, β can be expressed as the sum of two contributions,

$$\phi_{ij}^{\alpha\beta} = \hat{\phi}^{\alpha\beta}(\mathbf{q}_{i_\alpha} - \mathbf{q}_{j_\beta}) + \bar{\phi}^{\alpha\beta}(\mathbf{q}_{i_\alpha} - \mathbf{q}_{j_\beta}), \quad (1)$$

where, $\mathbf{q}_{i_\alpha}$ is the position of the ith molecule of species α, $\hat{\phi}^{\alpha\beta}(r) \geq 0$ is a short range repulsive (hard core) part and $\bar{\phi}^{\alpha\beta}(r) \leq 0$ is a long range attractive tail [1].

In a nonequilibrium situation, the state x of a fluid mixture of r species, is described by the set of time and space dependent hydrodynamic fields. These are the number density $n_{\mathbf{r}}^\alpha$ of species α, with $\alpha = 1, \cdots, r$, the momentum density $\mathbf{g_r}$ of the full mixture, and the internal energy density $\hat{\epsilon}_{\mathbf{r}}$. The mo-

lecular definition of the internal energy density field contains only the short range part $\hat{\phi}$ of the potential of Eq. (1). In this way, the total energy of the system written in terms of the hydrodynamic variables is given by

$$E[x] = \int d\mathbf{r} \left(\frac{\mathbf{g_r}^2}{2\rho_{\mathbf{r}}} + \hat{\epsilon}_{\mathbf{r}} \right) + \frac{1}{2} \sum_{\alpha\beta} \int d\mathbf{r} d\mathbf{r}' n_{\mathbf{r}}^\alpha n_{\mathbf{r}'}^\beta \bar{\phi}_{\mathbf{r}\mathbf{r}'}^{\alpha\beta}, \quad (2)$$

where we have introduced the total mass density field as

$$\rho_{\mathbf{r}} = m_\alpha n_{\mathbf{r}}^\alpha, \quad (3)$$

m_α being the mass of a single molecule of species α, and we are summing over the repeated species index α (Einstein convention on species index). In Eq. (2), $\bar{\phi}_{\mathbf{r}\mathbf{r}'}^{\alpha\beta} = \bar{\phi}^{\alpha\beta}(\mathbf{r} - \mathbf{r}')$ is the long range part of the potential of interaction between two molecules of species α and β located at $\mathbf{r}$ and $\mathbf{r}'$, respectively. In this paper, variables with a hat as in $\hat{A}$ are related to the hard core potential while variables with an overline as in $\bar{A}$ are related to the long range potential.

The entropy functional in the van der Waals approximation has the following form for a mixture of species:

$$S[x] = \int d\mathbf{r} \, \hat{s}(\{n_{\mathbf{r}}^\alpha\}, \hat{\epsilon}_{\mathbf{r}}), \quad (4)$$

where $\hat{s}(\{n^\alpha\}, \hat{\epsilon})$ is the entropy density function of a system of molecules *which are interacting with only the short range part of the potential $\hat{\phi}^{\alpha\beta}$*, as a function of the densities $\{n^\alpha\}$ and the internal energy $\hat{\epsilon}$. That the entropy functional contains only the short range part of the potential is a nontrivial result that follows from the van der Waals assumption in Eq. (1). In order to fix ideas, we can assume that the functional form of $\hat{s}(\{n^\alpha\}, \hat{\epsilon})$ is given by the excluded volume entropy (see Appendix A),

$$\hat{s}(\{n^\alpha\}, \hat{\epsilon}) = \sum_\alpha n^\alpha \left[\frac{D+2}{2} - \ln\left(\frac{n_\alpha \lambda_\alpha^D}{1 - nb} \right) \right], \quad (5)$$

where the thermal wavelength is

$$\lambda_\alpha = \sqrt{\frac{h^2}{2\pi m_\alpha k_B \hat{T}}}. \quad (6)$$

Here, h, k_B are the Planck and Boltzmann constants, and D is the space dimension. The temperature as a function of the hard core internal energy is given by

$$\hat{T} = \frac{2\hat{\epsilon}}{Dk_B n}. \quad (7)$$

In these equations we have introduced the total number density $n = \Sigma_\alpha n^\alpha$, and the excluded volume parameter $b = (1/n)\Sigma_\alpha n^\alpha b_\alpha$, where b_α is the excluded volume of molecules of type α.

The main result of Ref. [9] is the following set of hydrodynamic equations for a fluid mixture:

$$\partial_t n^\alpha = -\,\boldsymbol{\nabla}\cdot\mathbf{v}n^\alpha + \boldsymbol{\nabla}\cdot\left(\sum_\beta D^{\alpha\beta}\hat{T}\boldsymbol{\nabla}\left(\frac{\hat{\mu}^\beta}{\hat{T}}\right)\right)$$

$$-\,\boldsymbol{\nabla}\cdot\left(S^\alpha\hat{T}^2\,\boldsymbol{\nabla}\left(\frac{1}{\hat{T}}\right)\right) - \boldsymbol{\nabla}\cdot\left(\sum_\beta D^{\alpha\beta}\bar{\mathbf{F}}^\beta\right),$$

$$\partial_t\mathbf{g} = -\,\boldsymbol{\nabla}\cdot(\mathbf{g}\cdot\mathbf{v}) - \boldsymbol{\nabla}\hat{P} - \boldsymbol{\nabla}\cdot\hat{\boldsymbol{\Pi}} + \sum_\alpha n^\alpha\bar{\mathbf{F}}^\alpha,$$

$$\partial_t\hat{\epsilon} = -\,\boldsymbol{\nabla}\cdot(\mathbf{v}\hat{\epsilon}) - \hat{P}\boldsymbol{\nabla}\cdot\mathbf{v} - \hat{\Pi}:\boldsymbol{\nabla}\,\mathbf{v}$$

$$+\,\boldsymbol{\nabla}\cdot\left(\sum_\alpha S^\alpha\hat{T}^2\,\boldsymbol{\nabla}\left(\frac{\hat{\mu}^\alpha}{\hat{T}}\right)\right) - \boldsymbol{\nabla}\cdot\left(\hat{\kappa}\hat{T}^2\,\boldsymbol{\nabla}\left(\frac{1}{\hat{T}}\right)\right)$$

$$-\sum_{\alpha\beta}\left[\hat{T}\boldsymbol{\nabla}\left(\frac{\hat{\mu}^\alpha}{\hat{T}}\right) - \bar{\mathbf{F}}^\alpha\right]\cdot D^{\alpha\beta}\bar{\mathbf{F}}^\beta - \boldsymbol{\nabla}\cdot\left(\sum_\alpha S^\alpha\bar{\mathbf{F}}^\alpha\hat{T}\right)$$

$$-\sum_\alpha S^\alpha\bar{\mathbf{F}}^\alpha\cdot\boldsymbol{\nabla}\hat{T}. \tag{8}$$

The quantities appearing in these equations are enumerated and defined in what follows. The temperature $\hat{T}$, chemical potential $\hat{\mu}^\alpha$ of species α, and pressure $\hat{P}$ are defined in the usual way [23] from the entropy density $\hat{s}$ introduced after Eq. (4), this is

$$\frac{1}{\hat{T}} = \frac{\partial}{\partial\hat{\epsilon}}\hat{s}(\{n^\alpha\},\hat{\epsilon}),$$

$$\frac{\hat{\mu}^\alpha}{\hat{T}} = -\frac{\partial}{\partial n^\alpha}\hat{s}(\{n^\alpha\},\hat{\epsilon}),$$

$$\hat{P} = \hat{T}\hat{s} - \hat{\epsilon} + \sum_\alpha n^\alpha\mu^\alpha. \tag{9}$$

These intensive quantities become field quantities in Eq. (8) when evaluated at the local values of $\{n_\mathbf{r}^\alpha\}, \hat{\epsilon}_\mathbf{r}$. It is quite remarkable that the equations of state appearing in the hydrodynamic equations (8) are those of the hard core system. This is a direct consequence of the functional form of the entropy functional in Eq. (4). The viscous stress tensor in Eq. (8) has a usual form [3]

$$\hat{\boldsymbol{\Pi}} = -\,\hat{\eta}\left(\boldsymbol{\nabla}\cdot\mathbf{v} + \boldsymbol{\nabla}\cdot\mathbf{v}^T - \frac{2}{3}\boldsymbol{\nabla}\cdot\mathbf{v}\mathbf{1}\right) - \hat{\zeta}\boldsymbol{\nabla}\cdot\mathbf{v}\mathbf{1}. \tag{10}$$

The shear and bulk viscosities are $\hat{\eta}$ and $\hat{\zeta}$, respectively. The rest of transport coefficients $D^{\alpha\beta}, S^\alpha, \hat{\kappa}$ in Eqs. (8) are related to mass diffusion, cross effects, and heat conductivity, respectively. These transport coefficients are defined in terms of Green-Kubo formulas and correspond to a mixture of molecules interacting with the hard core potentials only [9]. From these Green-Kubo formulas it is shown that not all the transport coefficients are independent, but the following relations hold:

$$\sum_\alpha m_\alpha D_\mathbf{r}^{\alpha\beta} = 0,$$

$$\sum_\alpha m_\alpha S_\mathbf{r}^\alpha = 0. \tag{11}$$

These properties ensure that the mass density $\rho = \Sigma_\alpha m_\alpha n^\alpha$ obeys the continuity equation, expressing total mass conservation.

The remaining quantity appearing in Eqs. (8) is the long range force $\bar{\mathbf{F}}_\mathbf{r}^\alpha$, which is defined by

$$\bar{\mathbf{F}}_\mathbf{r}^\alpha = \sum_\beta\int d\mathbf{r}'\,\bar{\mathbf{F}}_{\mathbf{rr}'}^{\alpha\beta}n_{\mathbf{r}'}^\beta, \tag{12}$$

and $\bar{\mathbf{F}}_{\mathbf{rr}'}^{\alpha\beta}$ is the long range attractive force that a molecule of specie β at $\mathbf{r}'$ exerts on a molecule of specie α at $\mathbf{r}$.

As it can be appreciated, the hydrodynamic equations (8) are those of a hard core fluid in which the long range part of the potential is treated in mean field in the sense of Eq. (12).

III. A CHANGE OF VARIABLES

Our aim in this section is to use as independent hydrodynamic variables the set $y = \{n_\mathbf{r}^\alpha, \mathbf{g}_\mathbf{r}, u_\mathbf{r}\}$, instead of $x = \{n_\mathbf{r}^\alpha, \mathbf{g}_\mathbf{r}, \hat{\epsilon}_\mathbf{r}\}$. The internal energy $u_\mathbf{r}$ is defined as

$$u_\mathbf{r} = \hat{\epsilon}_\mathbf{r} - \frac{1}{2}\sum_{\alpha\beta}a_{\alpha\beta}n_\mathbf{r}^\alpha n_\mathbf{r}^\beta, \tag{13}$$

where the positive constants $a_{\alpha\beta}$ are

$$a_{\alpha\beta} = -\int d\mathbf{r}\,\bar{\phi}_{\mathbf{rr}'}^{\alpha\beta}. \tag{14}$$

The internal energy $u_\mathbf{r}$ contains not only the internal energy due to the hardcore part of the potential, but also the *local* contribution due to the long range part of the potential. The basic reason for preferring this set of variables y can be made clear by looking at the energy and entropy functionals, written as functionals of the set of variables. The energy functional is

$$E[y] = \int d\mathbf{r}\left(\frac{\mathbf{g}_\mathbf{r}^2}{2\rho_\mathbf{r}} + u_\mathbf{r}\right) - \frac{1}{4}\int d\mathbf{r}d\mathbf{r}'[n_\mathbf{r}^\alpha - n_{\mathbf{r}'}^\alpha][n_\mathbf{r}^\beta - n_{\mathbf{r}'}^\beta]\bar{\phi}_{\mathbf{rr}'}^{\alpha\beta}. \tag{15}$$

The last term represents purely nonlocal terms due to the long range potential. Actually, a Taylor expansion of the density fields around $\mathbf{r}$ leads to a familiar form

$$E[y] = \int d\mathbf{r}\left(\frac{\mathbf{g}_\mathbf{r}^2}{2\rho_\mathbf{r}} + u_\mathbf{r}\right) + \frac{1}{2}\sum_{\alpha\beta}c_{\alpha\beta}\int d\mathbf{r}\,\boldsymbol{\nabla}\,n_\mathbf{r}^\alpha\cdot\boldsymbol{\nabla}\,n_\mathbf{r}^\beta, \tag{16}$$

where the positive constants $c_{\alpha\beta}$ are given by

$$c_{\alpha\beta} = -\frac{1}{6}\int d\mathbf{s}\,s^2\bar{\phi}^{\alpha\beta}(\mathbf{s}). \tag{17}$$

The last term in the energy functional represents the energy cost due to spatially varying density fields, and is an important contribution in those regions where the system displays

interfaces. This term leads to the usual expressions for the surface tension coefficient [1]. In particular, the coefficients $c_{\alpha\beta}$ govern the overall strength of surface tension. We will not make use of the gradient approximation (16) until the very end of the development, as discussed in Sec. VIII.

The entropy functional in the variables y takes the form

$$S[y] = \int d\mathbf{r} s(\{n^\alpha\}, u_\mathbf{r}),\qquad (18)$$

where we have introduced the van der Waals entropy density as (see Appendix A)

$$s(\{n_\mathbf{r}^\alpha\}, u_\mathbf{r}) = \hat{s}\left(\{n_\mathbf{r}^\alpha\}, u_\mathbf{r} + \frac{1}{2}\sum_{\alpha\beta} a_{\alpha\beta} n^\alpha n^\beta\right).\qquad (19)$$

We introduce the temperature, chemical potential, and pressure according to the usual thermodynamic definitions

$$\frac{1}{T} = \frac{\partial s}{\partial u},$$

$$\frac{\mu^\alpha}{T} = -\frac{\partial s}{\partial n^\alpha},$$

$$P = Ts - u + \sum_\alpha n^\alpha \mu^\alpha.\qquad (20)$$

For the case that the hard core entropy $\hat{s}$ is given by the excluded volume entropy in Eq. (5), the functional form of the intensive parameters in Eqs. (20) is

$$T(\{n^\alpha\}, u) = = \frac{2}{Dk_B \sum_\alpha n^\alpha}\left(u + \frac{1}{2}n^2 a\right),$$

$$\mu^\alpha(\{n^\alpha\}, u) = k_B T\left(\ln \frac{n^\alpha \lambda_\alpha^D}{1 - bn} + \frac{n^\alpha \lambda_\alpha^D}{1 - bn}\right) - 2\sum_\beta a_{\alpha\beta} n^\beta,$$

$$P(\{n^\alpha\}, u) = \frac{nk_B T}{1 - nb} - n^2 a,\qquad (21)$$

where the attractive parameter a is defined through $n^2 a = \sum_{\alpha\beta} a_{\alpha\beta} n^\alpha n^\beta$. It is apparent that these equations of state correspond to a van der Waals fluid mixture containing both, excluded volume terms and attractive terms. While the hard-core equations of state do not exhibit phase transitions, the equations of state (21) do describe phase transitions. Therefore, the rational for changing variables in the hydrodynamic equations is that in the variables y, the effects of intrinsic phase separation and the surface tension effects are clearly separated. It proves convenient to introduce the following definitions:

$$\bar{\mathbf{F}}_\mathbf{r}^\alpha = -\nabla \bar{\phi}_\mathbf{r}^\alpha,\qquad (22)$$

with

$$\bar{\phi}_\mathbf{r}^\alpha = \int d\mathbf{r}' n_{\mathbf{r}'}^\beta \bar{\phi}_{\mathbf{r}\mathbf{r}'}^{\alpha\beta}.\qquad (23)$$

We split $\bar{\phi}_\mathbf{r}^\alpha = \underline{\phi}_\mathbf{r}^\alpha + \tilde{\phi}_\mathbf{r}^\alpha$ and $\bar{\mathbf{F}}_\mathbf{r}^\alpha = \underline{\mathbf{F}}_\mathbf{r}^\alpha + \tilde{\mathbf{F}}_\mathbf{r}^\alpha$, where

$$\underline{\phi}_\mathbf{r}^\alpha = -\sum_\beta a_{\alpha\beta} n_\mathbf{r}^\beta,$$

$$\tilde{\phi}_\mathbf{r}^\alpha = -\sum_\beta \int d\mathbf{r}' (n_\mathbf{r}^\beta - n_{\mathbf{r}'}^\beta) \bar{\phi}_{\mathbf{r}\mathbf{r}'}^{\alpha\beta},$$

$$\underline{\mathbf{F}}_\mathbf{r}^\alpha = -\nabla \underline{\phi}_\mathbf{r}^\alpha,$$

$$\tilde{\mathbf{F}}_\mathbf{r}^\alpha = -\nabla \tilde{\phi}_\mathbf{r}^\alpha.\qquad (24)$$

It is a simple, although tedious exercise to write the hydrodynamic equations for the set of variables y. The result is

$$\partial_t n_\mathbf{r}^\alpha = -\nabla \cdot \mathbf{v} n^\alpha + \nabla \cdot \left(\sum_\beta D_\mathbf{r}^{\alpha\beta} T_\mathbf{r} \Upsilon_\mathbf{r}^\beta\right) - \nabla \cdot \left(S_\mathbf{r}^\alpha T_\mathbf{r}^2 \nabla \frac{1}{T_\mathbf{r}}\right),$$

$$\partial_t \mathbf{g} = -\nabla \cdot (\mathbf{g}\mathbf{v}) - \nabla P - \nabla \cdot \hat{\mathbf{\Pi}} + \sum_\alpha n^\alpha \tilde{\mathbf{F}}^\alpha,$$

$$\partial_t u_\mathbf{r} = -\nabla \cdot (\mathbf{v}u) - P\nabla \cdot \mathbf{v} - \hat{\mathbf{\Pi}} : \nabla \mathbf{v} - \sum_{\alpha\beta} \tilde{\phi}_\mathbf{r}^\alpha \nabla \cdot (D_\mathbf{r}^{\beta\alpha} T_\mathbf{r} \Upsilon_\mathbf{r}^\beta)$$

$$+ \sum_{\alpha\beta} \nabla \cdot (D_\mathbf{r}^{\alpha\beta} T_\mathbf{r} (\underline{\phi}_\mathbf{r}^\alpha + \tilde{\phi}_\mathbf{r}^\alpha) \Upsilon_\mathbf{r}^\beta) + \nabla \cdot \left(\sum_\beta S_\mathbf{r}^\beta T_\mathbf{r}^2 \Upsilon_\mathbf{r}^\beta\right)$$

$$+ \sum_\alpha \tilde{\phi}_\mathbf{r}^\alpha \nabla \cdot \left(S_\mathbf{r}^\alpha T_\mathbf{r}^2 \nabla \frac{1}{T_\mathbf{r}}\right) - \nabla \cdot \left(\sum_\alpha S_\mathbf{r}^\alpha T_\mathbf{r}^2\right)$$

$$\times (\underline{\phi}_\mathbf{r}^\alpha + \tilde{\phi}_\mathbf{r}^\alpha) \nabla \frac{1}{T_\mathbf{r}}\right) - \nabla \cdot \left(\kappa_\mathbf{r} T_\mathbf{r}^2 \nabla \frac{1}{T_\mathbf{r}}\right),\qquad (25)$$

where

$$\Upsilon_\mathbf{r}^\beta = \nabla \frac{\mu^\beta}{T_\mathbf{r}} + \nabla \frac{\tilde{\phi}_\mathbf{r}^\beta}{T_\mathbf{r}} - (\underline{\phi}_\mathbf{r}^\beta + \tilde{\phi}_\mathbf{r}^\beta) \nabla \frac{1}{T_\mathbf{r}}.\qquad (26)$$

We should remark that the equations of state μ^α, T, P that appear in these equations are the van der Waals equations of state for a mixture, Eqs. (21).

IV. CONTINUUM FLUID PARTICLES

As a starting point for the derivation of discrete equations for fluid particles, we first make the following observations concerning the continuum equations. Consider the reversible part of the dynamics of Eqs. (25), which is obtained by simply zeroing the transport coefficients,

$$\frac{\partial n^\alpha}{\partial t}\bigg|_{\text{rev}} = -\nabla \cdot (\mathbf{v} n^\alpha),$$

$$\frac{\partial \mathbf{g}}{\partial t}\bigg|_{\text{rev}} = -\nabla \cdot (\mathbf{g}\mathbf{v}) - \nabla P + \sum_\alpha n^\alpha \tilde{\mathbf{F}}^\alpha,$$

$$\left.\frac{\partial u}{\partial t}\right|_{\text{rev}} = -\,\boldsymbol{\nabla}\cdot(\mathbf{v}u) - P\,\boldsymbol{\nabla}\cdot\mathbf{v}. \tag{27}$$

As we want to formulate a model for discrete fluid particles that move following the flow, it seems natural to write the above equations in a Lagrangian way:

$$\left.\frac{dn^{\alpha}}{dt}\right|_{\text{rev}} = -\,n^{\alpha}\boldsymbol{\nabla}\cdot\mathbf{v},$$

$$\left.\frac{d\mathbf{g}}{dt}\right|_{\text{rev}} = -\,\mathbf{g}\cdot\boldsymbol{\nabla}\cdot\mathbf{v} - \boldsymbol{\nabla}P + \sum_{\alpha}n^{\alpha}\widetilde{\mathbf{F}}^{\alpha},$$

$$\left.\frac{du}{dt}\right|_{\text{rev}} = -\,u\boldsymbol{\nabla}\cdot\mathbf{v} - P\,\boldsymbol{\nabla}\cdot\mathbf{v}, \tag{28}$$

where d/dt is the usual substantial time derivative, expressing how quantities change as one follows the flow field. Note that the above equations are for *density* fields. However, we want to use *extensive* variables to specify the state of our discrete fluid particles. For this reason, let us consider the Jacobian $\mathcal{J}$ of the transformation relating Eulerian coordinates $\mathbf{r}$ with Lagrangian coordinates $\mathbf{R}(\mathbf{r},t)$. The Lagrangian coordinate obeys the equation $\dot{\mathbf{R}}(t)=\mathbf{v}(\mathbf{R},t)$ with initial condition $\mathbf{R}(0)=\mathbf{r}$. This equation of motion implies that the time derivative of the Jacobian is given by $\dot{\mathcal{J}}=\mathcal{J}\boldsymbol{\nabla}\cdot\mathbf{v}$. This equation allows to interpret the Jacobian as a "volume field" $\mathcal{V}_{\mathbf{r}}$, because the divergence of the velocity field provides the relative rate of change of a little volume element that moves following the flow. We next introduce an extensive number field $N_{\mathbf{r}}^{\alpha}$, an extensive momentum field $\mathbf{P}_{\mathbf{r}}$, and an extensive energy field $U_{\mathbf{r}}$ through

$$N_{\mathbf{r}}^{\alpha} = \mathcal{V}_{\mathbf{r}}n_{\mathbf{r}}^{\alpha},$$

$$\mathbf{P}_{\mathbf{r}} = \mathcal{V}_{\mathbf{r}}\mathbf{g}_{\mathbf{r}},$$

$$U_{\mathbf{r}} = \mathcal{V}_{\mathbf{r}}u_{\mathbf{r}}. \tag{29}$$

It is simple to compute the substantial derivatives of the extensive fields and to arrive at the set of reversible equations

$$\left.\frac{dN_{\mathbf{r}}^{\alpha}}{dt}\right|_{\text{rev}} = 0,$$

$$\left.\frac{d\mathbf{P}_{\mathbf{r}}}{dt}\right|_{\text{rev}} = -\,\mathcal{V}_{\mathbf{r}}\boldsymbol{\nabla}P_{\mathbf{r}} + \sum_{\alpha}N_{\mathbf{r}}^{\alpha}\widetilde{\mathbf{F}}_{\mathbf{r}}^{\alpha},$$

$$\left.\frac{dU_{\mathbf{r}}}{dt}\right|_{\text{rev}} = P_{\mathbf{r}}\frac{d\mathcal{V}_{\mathbf{r}}}{dt}. \tag{30}$$

These equations admit a very suggestive physical interpretation in terms of the dynamics of "fluid particles." According to this interpretation, we can follow "extensive portions" of the fluid as it flows. These portions have a volume that changes according to $\dot{\mathcal{V}}_{\mathbf{r}}=\mathcal{V}_{\mathbf{r}}\boldsymbol{\nabla}\cdot\mathbf{v}$ and have a number $N_{\mathbf{r}}^{\alpha}$ of molecules of species α that do not change as far as the re-

versible part of the dynamics is concerned. The force on these "portions" is entirely due to pressure forces and interfacial forces, and the change of its internal energy content is simply due to the reversible work done on that portion.

Note that, due to the properties (11), the full evolution (reversible and irreversible) of the mass density field in Eq. (3) is

$$\frac{d\rho}{dt} = -\,\rho\,\boldsymbol{\nabla}\cdot\mathbf{v}. \tag{31}$$

The continuity equation states that the relative rate of change of the density along the flow is equal to (minus) the relative rate of change of the volume element. If we introduce an extensive mass field as $M_{\mathbf{r}}=V_{\mathbf{r}}\rho_{\mathbf{r}}=\Sigma_{\alpha}m_{\alpha}N_{\mathbf{r}}^{\alpha}$, we obtain

$$\frac{d}{dt}M_{\mathbf{r}} = 0. \tag{32}$$

This implies that the mass of an infinitesimal fluid element that moves with the flow does not change.

V. DISCRETE FLUID PARTICLE MODEL FOR MIXTURES

Now we move towards the formulation of a discrete model that mimics the continuum hydrodynamic equations (30). The fluid is represented by a discrete set of N_T fluid particles, located at positions $\mathbf{r}_i$ that move with velocities $\mathbf{v}_i$ that are supposed to be an approximation of the continuum velocity field $\mathbf{v}(\mathbf{r},t)$ at $\mathbf{r}=\mathbf{r}_i$. Every fluid particle i is considered as a small moving thermodynamic subsystem. The extensive variables that characterize this thermodynamic system are the number N_i^{α} of molecules of species α, within the fluid particle, the volume $\mathcal{V}_i$ and the internal energy U_i. The volume $\mathcal{V}_i$ is a function of the positions of the neighboring fluid particles and it is not an independent variable. The thermodynamic behavior of the fluid particle is completely characterized by the entropy function $S_i=S(\{N_i^{\alpha}\},\mathcal{V}_i,U_i)$. The total mass $m=\Sigma_{\alpha}m^{\alpha}N_i^{\alpha}$ of each fluid particle is assumed to be constant and equal for all fluid particles. According to Eq. (32), this is a reasonable assumption. Therefore, the state of our discrete model is entirely specified by the set of variables $x=\{\mathbf{r}_i,\mathbf{v}_i,N_i^{\alpha},U_i,i=1,\ldots,N_T\}$. Note that the constancy of the mass of each fluid particle implies that the variables N_i^{α} are not all independent.

The main problem now is to formulate the equations of motion for the state variables characterizing the fluid particles. We follow here a strategy analogous to the one used for the derivation of the equations of motion for fluid particles in simple liquids [16]. The idea is to formulate the equations according to the thermodynamically consistent GENERIC framework. We refer to Ref. [16] for an introduction to the GENERIC framework as applied to fluid particles and to the details of the procedure.

Two basic building blocks of the GENERIC framework are the total energy and entropy of the system, expressed in terms of the state variables. The total energy and total entropy of the discrete model are postulated by analogy with the continuum expressions (15) and (18), this is

$$E(x) = \sum_i \frac{m_i}{2} \mathbf{v}_i^2 + \sum_i U_i - \frac{1}{4} \sum_{\alpha\beta} \sum_{ij} (N_i^\alpha - N_j^\alpha)(N_i^\beta - N_j^\beta) \bar{\phi}_{ij}^{\alpha\beta},$$

$$S(x) = \sum_i S(\{N_i^\alpha\}, U_i, \mathcal{V}_i). \tag{33}$$

In the definition of the total entropy we use the van der Waals expression (A5) for the functional form of the fluid particle entropy.

We need for future reference the derivatives of the energy and entropy functions with respect to the state variables, which are

$$\begin{pmatrix} \dfrac{\partial E}{\partial \mathbf{r}_j} \\[4pt] \dfrac{\partial E}{\partial \mathbf{v}_j} \\[4pt] \dfrac{\partial E}{\partial N_j^\alpha} \\[4pt] \dfrac{\partial E}{\partial U_j} \end{pmatrix} = \begin{pmatrix} \dfrac{1}{2} \sum_{\alpha\beta} \sum_k (N_j^\alpha - N_k^\alpha)(N_j^\beta - N_k^\beta) \bar{\mathbf{F}}_{jk}^{\alpha\beta} \\[4pt] m\mathbf{v}_j \\[4pt] \tilde{\phi}_j^\alpha \\[4pt] 1 \end{pmatrix},$$

$$\tag{34}$$

$$\begin{pmatrix} \dfrac{\partial S}{\partial \mathbf{r}_j} \\[4pt] \dfrac{\partial S}{\partial \mathbf{v}_j} \\[4pt] \dfrac{\partial S}{\partial N_j^\alpha} \\[4pt] \dfrac{\partial S}{\partial U_j} \end{pmatrix} = \begin{pmatrix} \sum_k \dfrac{P_k}{T_k} \dfrac{\partial \mathcal{V}_k}{\partial \mathbf{r}_j} \\[4pt] 0 \\[4pt] -\dfrac{\mu_j^\alpha}{T_j} \\[4pt] \dfrac{1}{T_j} \end{pmatrix}. \tag{35}$$

The long range force $\bar{\mathbf{F}}_{jk}^{\alpha\beta}$ is (minus) the gradient of the long range potential $\bar{\phi}_{jk}^{\alpha\beta}$. We have defined $\tilde{\phi}_i^\alpha$ in Eq. (34) as being the discretized equivalent of the continuous variable $\tilde{\phi}_{\mathbf{r}}^\alpha$ in Eq. (24), this is

$$\tilde{\phi}_i^\alpha = -\sum_{\beta k} (N_i^\beta - N_k^\beta) \bar{\phi}_{ik}^{\beta\alpha}. \tag{36}$$

VI. THE REVERSIBLE PART OF THE DYNAMICS

According to the GENERIC framework, [13,16], the reversible part of the dynamics is given by $\dot{x}|_{\mathrm{rev}} = L \partial E / \partial x$, where L is a reversible operator. This operator is antisymmetric and satisfies the degeneracy property $L \partial S / \partial x = 0$, ensuring that the reversible part of the dynamics does not produce entropy. In our discrete problem, the operator L becomes a matrix L_{ij}, and the antisymmetry of L, takes the form $L_{ij} = -L_{ji}^T$. The reversible dynamics is given by

$$\begin{pmatrix} \dot{\mathbf{r}}_i \\[4pt] \dot{\mathbf{v}}_i \\[4pt] \dot{N}_i^\alpha \\[4pt] \dot{U}_i \end{pmatrix}\Bigg|_{\mathrm{rev}} = \sum_j L_{ij} \begin{pmatrix} \dfrac{\partial E}{\partial \mathbf{r}_j} \\[4pt] \dfrac{\partial E}{\partial \mathbf{v}_j} \\[4pt] \dfrac{\partial E}{\partial N_j^\beta} \\[4pt] \dfrac{\partial E}{\partial U_j} \end{pmatrix}. \tag{37}$$

It is important to note that when calculating the product of the L_{ij} with $\partial E / \partial x_j$ the summation over the number of species is implied when dealing with the variable N_j^α.

We want to ensure that $\dot{\mathbf{r}}_i = \mathbf{v}_i$ as an expression of the Lagrangian nature of the model. Also, Eq. (30) suggests to request $\dot{N}_i^\alpha = 0$. The simplest ansatz for L satisfying these requirements and the antisymmetry is

$$L_{ij} \rightarrow \begin{pmatrix} 0 & \mathbf{1}\frac{\delta_{ij}}{m} & 0 & 0 \\[6pt] -\mathbf{1}\frac{\delta_{ij}}{m} & A_{ij} & 0 & B_{ij} \\[6pt] 0 & 0 & 0 & 0 \\[6pt] 0 & -B_{ij}^T & 0 & 0 \end{pmatrix}, \tag{38}$$

where A_{ij}, B_{ij} are yet unknown. We can fix B_{ij} by requiring the GENERIC degeneracy $L \partial S / \partial x = 0$, which leads to

$$-\sum_j \frac{P_j}{mT_j} \frac{\partial \mathcal{V}_j}{\partial \mathbf{r}_i} + \sum_j B_{ij} \frac{1}{T_j} = 0. \tag{39}$$

A simple way to satisfy this condition is

$$B_{ij} = \frac{P_j}{m} \frac{\partial \mathcal{V}_j}{\partial \mathbf{r}_i}. \tag{40}$$

Therefore our ansatz for L is

$$L_{ij} \rightarrow \begin{pmatrix} 0 & \mathbf{1}\frac{\delta_{ij}}{m} & 0 & 0 \\[6pt] -\mathbf{1}\frac{\delta_{ij}}{m} & A_{ij} & 0 & \frac{P_j}{m}\frac{\partial \mathcal{V}_j}{\partial \mathbf{r}_i} \\[6pt] 0 & 0 & 0 & 0 \\[6pt] 0 & -\frac{P_i}{m}\frac{\partial \mathcal{V}_i}{\partial \mathbf{r}_j} & 0 & 0 \end{pmatrix}, \tag{41}$$

where we still must determine A_{ij}.

Equations (34), (37), and (41) combine to produce the following set of reversible dynamic equations:

$$\dot{\mathbf{r}}_i|_{\mathrm{rev}} = \mathbf{v}_i,$$

$$\dot{\mathbf{v}}_i|_{\mathrm{rev}} = \sum_j \frac{P_j}{m} \frac{\partial \mathcal{V}_j}{\partial \mathbf{r}_i} + \sum_j A_{ij} m\mathbf{v}_j - \frac{1}{2m} \sum_{\alpha\beta} \sum_k (N_i^\alpha - N_k^\alpha)$$

$$\times (N_i^\beta - N_k^\beta) \bar{\mathbf{F}}_{ik}^{\alpha\beta},$$

$$\dot{N}_i^\alpha|_{\mathrm{rev}} = 0,$$

$$\dot{U}_i\big|_{\text{rev}} = -\sum_j \frac{P_i}{m}\frac{\partial \mathcal{V}_i}{\partial \mathbf{r}_j} m\mathbf{v}_j = -P_i\dot{\mathcal{V}}_i. \tag{42}$$

By comparing the momentum equation with the continuum equation in (30), it is apparent that we should require simply $A_{ij}=0$. In this way, each term in Eqs. (42) is a discrete counterpart of a corresponding term in Eqs. (30).

At this point we must specify the volume $\mathcal{V}_i$ of the fluid particle i as a function of the position of the fluid particles. There are several possibilities for defining a volume. One of them is through the Voronoi tessellation [15]. The strategy we follow in this paper defines the volume in terms of a weight function [16]. A bell-shaped function $W(r)$ of finite support h and normalized to unity is introduced

$$\int d\mathbf{r}\, W(r) = 1. \tag{43}$$

The density of the fluid particle i is defined through

$$d_i = \sum_j W(|\mathbf{r}_i - \mathbf{r}_j|). \tag{44}$$

Note that when there are many particles j around i, the sum in Eq. (44) will be large, and the density associated to i will be correspondingly large. The volume is defined as the inverse of the density, i.e., $\mathcal{V}_i = d_i^{-1}$. With such a definition for the volume, the reversible part of the discrete dynamics will be finally

$$\dot{\mathbf{r}}_i\big|_{\text{rev}} = \mathbf{v}_i,$$

$$m\dot{\mathbf{v}}_i\big|_{\text{rev}} = \sum_j \left[\frac{P_i}{d_i^2} + \frac{P_j}{d_j^2}\right] F_{ij}\mathbf{r}_{ij} - \frac{1}{2}\sum_{\alpha\beta}\sum_k (N_i^\alpha - N_k^\alpha)$$
$$\times (N_i^\beta - N_k^\beta)\bar{\mathbf{F}}_{ik}^{\alpha\beta},$$

$$\dot{N}_i^\alpha\big|_{\text{rev}} = 0,$$

$$\dot{U}_i\big|_{\text{rev}} = -\frac{P_i}{d_i^2}\sum_j F_{ij}\mathbf{r}_{ij}\cdot\mathbf{v}_{ij}, \tag{45}$$

where we have used that the time derivative of the volume is given by

$$\dot{\mathcal{V}}_i = \sum_j F_{ij}\mathbf{r}_{ij}\cdot\mathbf{v}_{ij}, \tag{46}$$

$$F_{ij} = F(|\mathbf{r}_i - \mathbf{r}_j|)$$

$$\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j,$$

$$\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j, \tag{47}$$

and we have introduced the function $F(r)$ through

$$\nabla W(r) = -\mathbf{r}F(r). \tag{48}$$

VII. IRREVERSIBLE PART OF THE DYNAMICS

In order to formulate the irreversible part of the dynamics for the discrete fluid particle model, we will follow the SPH methodology. Note that all the irreversible terms of the continuum equations (25) contain second space derivatives. In Appendix C we show how second derivatives of functions and products of functions can be discretized. Of course, the continuum hydrodynamic equations can be written in many different ways, just by using the chain rule and making different groupings of the terms. Accordingly, there are many different possibilities to write the discretized version. However, even though the discrete versions are good approximations to the continuum equations, they do not necessarily carry over the exact conservation of mass, momentum, and energy, nor do they exactly satisfy the second law. Our purpose in this section is to write a set of discrete equations that, simultaneously, are good approximations to the irreversible part of the continuum equations and exactly satisfy the requirement of thermodynamic consistency. The strategy we follow combines the powerful machinery of the GENERIC formalism, that produces the correct *structure* of the equations, with the SPH methodology, that allows to input the information given by the continuum equations into the discrete equations.

Viscous and diffusive processes are independent of each other, so we study them separately in the following two sections.

A. The viscous part of irreversible dynamics

The viscous processes appear in Eqs. (25) through the viscous stress tensor $\hat{\mathbf{\Pi}}$. These terms are exactly the same as those encountered in a simple fluid and their discretization according to the SPH/GENERIC methodology has been given in Ref. [16], i.e.,

$$\dot{N}_i^\alpha\big|_{\text{visc}} = 0,$$

$$\dot{\mathbf{P}}_{i\,\text{visc}} = -\left(\frac{D+2}{D}\hat{\eta} - \hat{\zeta}\right)\sum_j \frac{F_{ij}}{d_i d_j}\mathbf{v}_{ij} - (2+D)$$
$$\times\left(\hat{\zeta} + \frac{D-2}{D}\hat{\eta}\right)\sum_j \frac{F_{ij}}{d_i d_j}\mathbf{e}_{ij}\mathbf{e}_{ij}\cdot\mathbf{v}_{ij},$$

$$\dot{U}_i\big|_{\text{visc}} = \left(\frac{\frac{D+2}{D}\hat{\eta}}{2} - \frac{\hat{\zeta}}{2}\right)\sum_j \frac{F_{ij}}{d_i d_j}\mathbf{v}_{ij}^2 + \frac{D+2}{2}$$
$$\times\left(\hat{\zeta} + \frac{D-2}{D}\hat{\eta}\right)\sum_j \frac{F_{ij}}{d_i d_j}(\mathbf{e}_{ij}\cdot\mathbf{v}_{ij})^2. \tag{49}$$

B. The diffusive part of irreversible dynamics

We start by formulating within the GENERIC framework the irreversible diffusive part of the dynamics of the discrete model. In GENERIC the irreversible part of the dynamics takes the form [13,16]

$$\dot{x}_{\text{irr}} = M(x)\frac{\partial S(x)}{\partial x}, \tag{50}$$

where the matrix $M(x)$ is a symmetric and positive semidefinite matrix of "transport coefficients" that is directly related

to the amplitude of the thermal fluctuations $d\tilde{x}$ in the system. The fluctuation-dissipation theorem states that the variance of the thermal fluctuations is proportional to $M(x)$, this is

$$d\tilde{x}d\tilde{x} = 2k_B M(x)dt. \tag{51}$$

This equation can be taken as a definition of $M(x)$ in terms of the thermal noise. One can even make an analogy between the "projected current" appearing in the microscopic expression of the matrix $M(x)$ in terms of Green-Kubo formulas [24], and the stochastic terms $d\tilde{x}$ [25]. In this paper, we will follow the "noise route to dissipation," which means that we first postulate the noise terms $d\tilde{x}$ and afterwards we construct the dissipative matrix M through the fluctuation-dissipation theorem (51). The resulting M matrix will automatically be symmetric and positive semidefinite, ensuring that the irreversible terms of the dynamics lead to positive entropy production. If, in addition, the noise vector satisfies the orthogonality condition $(\partial E/\partial x)d\tilde{x}=0$, then the irreversible part of the dynamics will conserve exactly the energy of the system [25].

Our aim is to propose a noise vector $d\tilde{x}$ $=\{d\tilde{\mathbf{r}}_i, d\tilde{\mathbf{v}}_i, d\tilde{N}_i^\alpha, d\tilde{U}_i\}$ such that its dyadic product produces a dissipative matrix M through Eq. (51) which, in turn, when applied on $\partial S/\partial x$ produces discrete counterparts of the continuum diffusive terms in (25) (those terms containing the transport coefficients $\hat{\kappa}, D^{\alpha\beta}, S^\alpha$). In this purely diffusive problem, we are dealing with fluid particles at rest that exchange mass and energy. For this reason, we simply set $d\tilde{\mathbf{r}}_i=0, d\tilde{\mathbf{v}}_i=0$. The orthogonality condition $(\partial E/\partial x)d\tilde{x}=0$ takes the form

$$\sum_i \left(d\tilde{U}_i + \sum_\alpha \tilde{\phi}_i^\alpha d\tilde{N}_i^\alpha \right) = 0. \tag{52}$$

The noise terms $d\tilde{U}_i, d\tilde{N}_i^\alpha$ should be given in terms of independent increments of Wiener processes. These noises are formulated by resorting to an intuitive idea that proves to be very fruitful. We introduce an "elementary process" $d\tilde{J}_{ij}^\beta$ associated to a random interchange of molecules of type β between fluid particles i, j, and an "elementary process" $d\tilde{Q}_{ij}$ associated to a random interchange of energy. These elementary processes are statistically independent of each other. Physically, we expect that when there is a random interchange of particles between two fluid particles, there is also an energy transfer between particles. This will lead to "cross effects" in the final equations. Therefore, we postulate that the noise terms $d\tilde{U}_i, d\tilde{N}_i^\alpha$ have the following structure:

$$d\tilde{N}_i^\alpha = \sum_{j\beta} O_{ij}^{\alpha\beta} d\tilde{J}_{ij}^\beta + \sum_j T_{ij}^\alpha d\tilde{Q}_{ij},$$

$$d\tilde{U}_i = \sum_{j\alpha} R_{ij}^\alpha d\tilde{J}_{ij}^\alpha + \sum_j C_{ij} d\tilde{Q}_{ij}$$

$$- \sum_{j\alpha} \left(\frac{1}{2}(\tilde{\phi}_i^\alpha - \tilde{\phi}_j^\alpha) - \frac{1}{2}(\underline{\phi}_i^\alpha + \underline{\phi}_j^\alpha) \right)$$

$$\times \left(\sum_\beta O_{ij}^{\alpha\beta} d\tilde{J}_{ij}^\beta + T_{ij}^\alpha d\tilde{Q}_{ij} \right), \tag{53}$$

where $O_{ij}^{\alpha\beta}, T_{ij}^\alpha, R_{ij}^\alpha, C_{ij}$, are the actual amount of quantity exchanged in every elementary process. The last term in the energy noise $d\tilde{U}_i$ has been introduced in order to fulfill the orthogonality (52). The factors of $1/2$ have been introduced after setting them first as undetermined and then checking that the value $1/2$ is the most sensible one. The term $\underline{\phi}_i^\alpha$ $=-\sum_\beta a^{\alpha\beta} N_i^\beta$ is the discrete counterpart of $\phi_{\mathbf{r}}^\alpha$ in Eq. (24).

In order to fulfill mass and energy conservation, we require the following symmetry properties for the coefficients of the Wiener processes:

$$O_{ij}^{\alpha\beta} = O_{ji}^{\alpha\beta},$$

$$T_{ij}^\alpha = T_{ji}^\alpha,$$

$$R_{ij}^\alpha = R_{ji}^\alpha,$$

$$C_{ij} = C_{ji}, \tag{54}$$

and the following symmetries of the Wiener processes themselves:

$$d\tilde{J}_{ij}^\beta = -d\tilde{J}_{ji}^\beta,$$

$$d\tilde{Q}_{ij} = -d\tilde{Q}_{ji}. \tag{55}$$

With these symmetries, it is easily seen that the orthogonality conditions (52) (implying energy conservation) and $\sum_i d\tilde{N}_i^\alpha$ $=0$ (implying mass conservation) are satisfied.

The Wiener processes satisfy the following Ito rules, compatible with the symmetries (55)

$$d\tilde{J}_{ii'}^\alpha d\tilde{J}_{jj'}^\beta = \delta^{\alpha\beta}[\delta_{ij}\delta_{i'j'} - \delta_{ij'}\delta_{i'j}]dt,$$

$$d\tilde{Q}_{ii'}d\tilde{Q}_{jj'} = [\delta_{ij}\delta_{i'j'} - \delta_{ij'}\delta_{i'j}]dt,$$

$$d\tilde{Q}_{ii'}d\tilde{J}_{jj'}^\alpha = 0. \tag{56}$$

With these properties, we can now compute the dyadic product $d\tilde{x}d\tilde{x}$ of the noises (53). It will have the following four components: $d\tilde{N}_i^\alpha d\tilde{N}_j^\beta$, $d\tilde{N}_i^\alpha d\tilde{U}_j$, $d\tilde{U}_i d\tilde{N}_j^\alpha$, and $d\tilde{U}_i d\tilde{U}_j$ which are computed explicitly in Appendix B.

Once we use the derivative of the entropy function in Eq. (35), the equation of motion (50) takes the form

$$\dot{N}_i^\alpha|_{\text{diff}} = -\sum_{j\beta} \frac{d\tilde{N}_i^\alpha d\tilde{N}_j^\beta}{2k_B dt} \frac{\mu_j^\beta}{T_j} + \sum_j \frac{d\tilde{N}_i^\alpha d\tilde{U}_j}{2k_B dt} \frac{1}{T_j},$$

$$\dot{U}_i|_{\text{diff}} = -\sum_{j\beta} \frac{d\tilde{U}_i d\tilde{N}_j^\beta}{2k_B dt} \frac{\mu_j^\beta}{T_j} + \sum_j \frac{d\tilde{U}_i d\tilde{U}_j}{2k_B dt} \frac{1}{T_j}. \tag{57}$$

Let us focus first on the equation for $\dot{N}_i^\alpha$. By using the dyadic products of Appendix B we obtain the explicit equations

$$\dot{N}_i^\alpha|_{\text{diff}} = \frac{1}{2k_B}\sum_j \left(\sum_\gamma O_{ij}^{\alpha\gamma}R_{ij}^\gamma + T_{ij}^\alpha C_{ij}\right)\left(\frac{1}{T_i} - \frac{1}{T_j}\right)$$

$$- \frac{1}{2k_B}\sum_{j\beta} \left(\sum_\gamma O_{ij}^{\alpha\gamma}O_{ij}^{\beta\gamma} + T_{ij}^\alpha T_{ij}^\beta\right)\left(\frac{\tilde{\phi}_i^\beta}{T_i} - \frac{\tilde{\phi}_j^\beta}{T_j}\right)$$

$$+ \frac{1}{4k_B}\sum_{j\beta} \left(\sum_\gamma O_{ij}^{\alpha\gamma}O_{ij}^{\beta\gamma} + T_{ij}^\alpha T_{ij}^\beta\right)(\tilde{\phi}_i^\beta + \tilde{\phi}_j^\beta)\left(\frac{1}{T_i} - \frac{1}{T_j}\right)$$

$$+ \frac{1}{4k_B}\sum_{j\beta} \left(\sum_\gamma O_{ij}^{\alpha\gamma}O_{ij}^{\beta\gamma} + T_{ij}^\alpha T_{ij}^\beta\right)(\underline{\phi}_i^\beta + \underline{\phi}_j^\beta)\left(\frac{1}{T_i} - \frac{1}{T_j}\right)$$

$$- \frac{1}{2k_B}\sum_{j\beta} \left(\sum_\gamma O_{ij}^{\alpha\gamma}O_{ij}^{\beta\gamma} + T_{ij}^\alpha T_{ij}^\beta\right)\left(\frac{\mu_i^\beta}{T_i} - \frac{\mu_j^\beta}{T_j}\right). \quad (58)$$

These equations have a very specific form regarding the potentials and temperatures. At the end of the day, we want Eq. (58) to be a discrete version of the continuum equations. Consider the density equations in Eqs. (25) for the case that no viscous processes are present in the system. The structure of Eqs. (58) suggests to rewrite the continuum equation for the densities in the following equivalent way:

$$\partial_t n^\alpha|_{\text{diff}} = -\nabla\left(S^\alpha T^2 \nabla\frac{1}{T}\right) + \nabla\left(\sum_\beta D^{\alpha\beta}T\nabla\frac{\tilde{\phi}^\beta}{T}\right)$$

$$- \nabla\left(\sum_\beta D^{\alpha\beta}T\tilde{\phi}^\beta \nabla\frac{1}{T}\right) - \nabla\left(\sum_\beta D^{\alpha\beta}T\underline{\phi}^\beta \nabla\frac{1}{T}\right)$$

$$+ \nabla\left(\sum_\beta D^{\alpha\beta}T\nabla\frac{\mu^\beta}{T}\right), \quad (59)$$

where, somehow, we have a direct correspondence between the discrete and continuum terms. Now, we are in the position to discretize Eq. (59) with the SPH formulas for second derivatives given in Appendix C. The result is

$$\dot{N}_{i\,\text{diff}}^\alpha = \sum_j \frac{F_{ij}}{d_i d_j}(S_i^\alpha T_i^2 + S_j^\alpha T_j^2)\left(\frac{1}{T_i} - \frac{1}{T_j}\right) - \sum_{j\beta}\frac{F_{ij}}{d_i d_j}(D_i^{\alpha\beta}T_i$$

$$+ D_j^{\alpha\beta}T_j)\left(\frac{\tilde{\phi}_i^\beta}{T_i} - \frac{\tilde{\phi}_j^\beta}{T_j}\right) + \sum_{j\beta}\frac{F_{ij}}{d_i d_j}(D_i^{\alpha\beta}T_i + D_j^{\alpha\beta}T_j)$$

$$\times \frac{1}{2}(\tilde{\phi}_i^\beta + \tilde{\phi}_j^\beta)\left(\frac{1}{T_i} - \frac{1}{T_j}\right) + \sum_{j\beta}\frac{F_{ij}}{d_i d_j}(D_i^{\alpha\beta}T_i + D_j^{\alpha\beta}T_j)$$

$$\times \frac{1}{2}(\underline{\phi}_i^\beta + \underline{\phi}_j^\beta)\left(\frac{1}{T_i} - \frac{1}{T_j}\right) - \sum_{j\beta}\frac{F_{ij}}{d_i d_j}(D_i^{\alpha\beta}T_i + D_j^{\alpha\beta}T_j)$$

$$\times \left(\frac{\mu_i^\beta}{T_i} - \frac{\mu_j^\beta}{T_j}\right). \quad (60)$$

By comparing Eqs. (58) and (60), we should have the following identifications:

$$\frac{1}{2k_B}\left(\sum_\gamma O_{ij}^{\alpha\gamma}R_{ij}^\gamma + T_{ij}^\alpha C_{ij}\right) = \frac{F_{ij}}{d_i d_j}(S_i^\alpha T_i^2 + S_j^\alpha T_j^2),$$

$$\frac{1}{2k_B}\left(\sum_\gamma O_{ij}^{\alpha\gamma}O_{ij}^{\beta\gamma} + T_{ij}^\alpha T_{ij}^\beta\right) = \frac{F_{ij}}{d_i d_j}(D_i^{\alpha\beta}T_i + D_j^{\alpha\beta}T_j). \quad (61)$$

Therefore, we have connected the amplitude of the thermal noises with the transport coefficients of the fluid. This connection involves geometrical objects (F_{ij}, d_i, d_j) reminiscent of the way in which spatial derivatives are discretized. In principle, we would need to solve the system of equations (63) in order to obtain the noise amplitudes O, R, T, C. This would be necessary if we would like to formulate a stochastic model with explicit thermal noise. The construction of the stochastic model is outside the scope of this paper.

We now turn to the energy equation in Eq. (57). The introduction in this equation of the dyadic products $d\tilde{U}_i d\tilde{N}_j^\beta$ and $d\tilde{U}_i d\tilde{U}_j$ computed in the Appendix B leads to a plethora of terms. Let us discuss first the *RRCC* term of $d\tilde{U}_i d\tilde{U}_j$. It leads to the following contribution to the energy equation:

$$\frac{1}{2k_B}\sum_j \left(\sum_\gamma R_{ij}^\gamma R_{ij}^\gamma + C_{ij}C_{ij}\right)\left(\frac{1}{T_i} - \frac{1}{T_j}\right)dt. \quad (62)$$

The structure of this equation reminds the structure of the conduction term in Eqs. (25). The conduction term is the only one depending on the thermal conductivity κ. According to the rules of discretization given in Appendix C the discretized version of the conduction term is

$$\sum_j \frac{F_{ij}}{d_i d_j}(\kappa_i T_i^2 + \kappa_j T_j^2)\left(\frac{1}{T_i} - \frac{1}{T_j}\right), \quad (63)$$

which, by comparison with Eq. (62) allows one to make the following identification:

$$\frac{1}{2k_B}\left(\sum_\gamma R_{ij}^\gamma R_{ij}^\gamma + C_{ij}C_{ij}\right) = \frac{F_{ij}}{d_i d_j}(\kappa_i T_i^2 + \kappa_j T_j^2). \quad (64)$$

After a lengthy algebra one computes the energy equation in Eq. (57) once the dyadic expressions (B1) are inserted and the identifications (63) and (64) have been made. The result is presented in Eqs. (65a). We present in Eq. (65b) the diffusive part of the energy equation (25) written in such a way that the term by term correspondence between Eqs. (65a) and (65b) is apparent.

$$\dot{U}_{i\text{diff}} = \sum_j \frac{F_{ij}}{d_i d_j}(\kappa_i T_i^2 + \kappa_j T_j^2)\left(\frac{1}{T_i} - \frac{1}{T_j}\right) - \sum_\alpha \sum_j \tilde{\phi}_i^\alpha \frac{F_{ij}}{d_i d_j}(S_i^\alpha T_i^2 + S_j^\alpha T_j^2)\left(\frac{1}{T_i} - \frac{1}{T_j}\right) + \sum_\alpha \sum_j \frac{F_{ij}}{d_i d_j}(S_i^\alpha T_i^2 + S_j^\alpha T_j^2)(\tilde{\phi}_i^\alpha + \tilde{\phi}_j^\alpha)$$

$$\times\left(\frac{1}{T_i} - \frac{1}{T_j}\right) + \sum_\alpha \sum_j \frac{F_{ij}}{d_i d_j}(S_i^\alpha T_i^2 + S_j^\alpha T_j^2)(\underline{\phi}_i^\alpha + \underline{\phi}_j^\alpha)\left(\frac{1}{T_i} - \frac{1}{T_j}\right) - \sum_{\alpha\beta} \tilde{\phi}_i^\alpha \sum_j \frac{F_{ij}}{d_i d_j}(D_i^{\alpha\beta}T_i + D_j^{\alpha\beta}T_j)\frac{(\tilde{\phi}_i^\beta + \tilde{\phi}_j^\beta)}{2}\left(\frac{1}{T_i} - \frac{1}{T_j}\right)$$

$$+ \sum_{\alpha\beta} \sum_j \frac{F_{ij}}{d_i d_j}(D_i^{\alpha\beta}T_i + D_j^{\alpha\beta}T_j)\frac{(\tilde{\phi}_i^\alpha + \tilde{\phi}_j^\alpha)}{2}\frac{(\tilde{\phi}_i^\beta + \tilde{\phi}_j^\beta)}{2}\left(\frac{1}{T_i} - \frac{1}{T_j}\right)$$

$$- \sum_{\alpha\beta} \tilde{\phi}_i^\alpha \sum_j \frac{F_{ij}}{d_i d_j}(D_i^{\alpha\beta}T_i + D_j^{\alpha\beta}T_j)\frac{(\underline{\phi}_i^\beta + \underline{\phi}_j^\beta)}{2}\left(\frac{1}{T_i} - \frac{1}{T_j}\right) + \sum_{\alpha\beta} \sum_j \frac{F_{ij}}{d_i d_j}(D_i^{\alpha\beta}T_i + D_j^{\alpha\beta}T_j)\frac{(\tilde{\phi}_i^\alpha + \tilde{\phi}_j^\alpha)}{2}$$

$$\times(\underline{\phi}_i^\beta + \underline{\phi}_j^\beta)\left(\frac{1}{T_i} - \frac{1}{T_j}\right) + \sum_{\alpha\beta} \sum_j \frac{F_{ij}}{d_i d_j}(D_i^{\alpha\beta}T_i + D_j^{\alpha\beta}T_j)\frac{(\underline{\phi}_i^\alpha + \underline{\phi}_j^\alpha)}{2}\frac{(\underline{\phi}_i^\beta + \underline{\phi}_j^\beta)}{2}\left(\frac{1}{T_i} - \frac{1}{T_j}\right)$$

$$- \sum_j \sum_\alpha \frac{F_{ij}}{d_i d_j}(S_i^\alpha T_i^2 + S_j^\alpha T_j^2)\left(\frac{\mu_i^\alpha}{T_i} - \frac{\mu_j^\alpha}{T_j}\right) + \sum_{\alpha\beta} \tilde{\phi}_i^\alpha \sum_j \frac{F_{ij}}{d_i d_j}(D_i^{\alpha\beta}T_i + D_j^{\alpha\beta}T_j)\left(\frac{\mu_i^\beta}{T_i} - \frac{\mu_j^\beta}{T_j}\right) - \sum_{\alpha\beta} \sum_j \frac{F_{ij}}{d_i d_j}(D_i^{\alpha\beta}T_i$$

$$+ D_j^{\alpha\beta}T_j)\frac{(\tilde{\phi}_i^\alpha + \tilde{\phi}_j^\alpha)}{2}\left(\frac{\mu_i^\beta}{T_i} - \frac{\mu_j^\beta}{T_j}\right) - \sum_{\alpha\beta} \sum_j \frac{F_{ij}}{d_i d_j}(D_i^{\alpha\beta}T_i + D_j^{\alpha\beta}T_j)\frac{(\underline{\phi}_i^\alpha + \underline{\phi}_j^\alpha)}{2}\left(\frac{\mu_i^\beta}{T_i} - \frac{\mu_j^\beta}{T_j}\right) - \sum_\alpha \sum_j \frac{F_{ij}}{d_i d_j}(S_i^\alpha T_i^2 + S_j^\alpha T_j^2)$$

$$\times\left(\frac{\tilde{\phi}_i^\alpha}{T_i} - \frac{\tilde{\phi}_j^\alpha}{T_j}\right) + \sum_{\alpha\beta} \tilde{\phi}_i^\alpha \sum_j \frac{F_{ij}}{d_i d_j}(D_i^{\alpha\beta}T_i + D_j^{\alpha\beta}T_j)\left(\frac{\tilde{\phi}_i^\beta}{T_i} - \frac{\tilde{\phi}_j^\beta}{T_j}\right) - \sum_{\alpha\beta} \sum_j \frac{F_{ij}}{d_i d_j}(D_i^{\alpha\beta}T_i + D_j^{\alpha\beta}T_j)\frac{(\tilde{\phi}_i^\alpha + \tilde{\phi}_j^\alpha)}{2}\left(\frac{\tilde{\phi}_i^\beta}{T_i} - \frac{\tilde{\phi}_j^\beta}{T_j}\right)$$

$$- \sum_{\alpha\beta} \sum_j \frac{F_{ij}}{d_i d_j}(D_i^{\alpha\beta}T_i + D_j^{\alpha\beta}T_j)\frac{(\underline{\phi}_i^\alpha + \underline{\phi}_j^\alpha)}{2}\left(\frac{\tilde{\phi}_i^\beta}{T_i} - \frac{\tilde{\phi}_j^\beta}{T_j}\right), \tag{65a}$$

$$\partial_t u_{\text{diff}} = -\nabla \cdot \left(\hat{\kappa}T^2 \nabla \frac{1}{T}\right) + \sum_\alpha \tilde{\phi}^\alpha \nabla \cdot \left(S^\alpha T^2 \nabla \frac{1}{T}\right) - 2\nabla \cdot \left(\sum_\alpha S^\alpha T^2 \tilde{\phi}^\alpha \nabla \frac{1}{T}\right) - 2\nabla \cdot \left(\sum_\alpha S^\alpha T^2 \underline{\phi}^\alpha \nabla \frac{1}{T}\right)$$

$$+ \sum_{\alpha\beta} \tilde{\phi}^\alpha \nabla \cdot \left(D^{\alpha\beta}T\tilde{\phi}^\beta \nabla \frac{1}{T}\right) - \sum_{\alpha\beta} \nabla \cdot \left(D^{\alpha\beta}T\tilde{\phi}^\alpha\tilde{\phi}^\beta \nabla \frac{1}{T}\right) + \sum_{\alpha\beta} \tilde{\phi}^\alpha \nabla \cdot \left(D^{\alpha\beta}T\underline{\phi}^\beta \nabla \frac{1}{T}\right) - 2\sum_{\alpha\beta} \nabla \cdot \left(D^{\alpha\beta}T\underline{\phi}^\alpha\tilde{\phi}^\beta \nabla \frac{1}{T}\right)$$

$$- \sum_{\alpha\beta} \nabla \cdot \left(D^{\alpha\beta}T\underline{\phi}^\alpha\underline{\phi}^\beta \nabla \frac{1}{T}\right) + \nabla \cdot \left(\sum_\alpha S^\alpha T^2 \nabla \frac{\mu^\alpha}{T}\right) - \sum_{\alpha\beta} \tilde{\phi}^\alpha \nabla \cdot \left(D^{\alpha\beta}T \nabla \frac{\mu^\beta}{T}\right) + \sum_{\alpha\beta} \nabla \cdot \left(D^{\alpha\beta}T\tilde{\phi}^\alpha \nabla \frac{\mu^\beta}{T}\right)$$

$$+ \sum_{\alpha\beta} \nabla \cdot \left(D^{\alpha\beta}T\underline{\phi}^\alpha \nabla \frac{\mu^\beta}{T}\right) + \nabla \cdot \left(\sum_\alpha S^\alpha T^2 \nabla \frac{\tilde{\phi}^\alpha}{T}\right) - \sum_{\alpha\beta} \tilde{\phi}^\alpha \nabla \cdot \left(D^{\alpha\beta}T \nabla \frac{\tilde{\phi}^\beta}{T}\right) + \sum_{\alpha\beta} \nabla \cdot \left(D^{\alpha\beta}T\tilde{\phi}^\alpha \nabla \frac{\tilde{\phi}^\beta}{T}\right)$$

$$+ \sum_{\alpha\beta} \nabla \cdot \left(D^{\alpha\beta}T\underline{\phi}^\alpha \nabla \frac{\tilde{\phi}^\beta}{T}\right). \tag{65b}$$

In summary, by collecting Eqs. (42), (49), (60), and (65a) we obtain the final SPH equations that are a faithful representation of the continuum hydrodynamic equations (25).

VIII. DISCUSSION

We have presented a fluid particle model of the SPH type for the simulation of the continuum hydrodynamic equations for phase separating fluids derived in Ref. [9]. The model has been constructed in such a way as to fit within the thermo-dynamically consistent GENERIC framework. We want to emphasize that it is the combination of both, the GENERIC and SPH methodologies what allows us to write thermodynamically consistent discrete equations. In order to write the continuum equations in the forms (59) and (65b) and not in any other of the many possibilities allowed by the rules of differentiation, we had to know the structure of the equations. This information has been supplied by the GENERIC "noise to dissipation route," Eq. (58). But, in turn, the GENERIC route is insufficient as it tell us nothing about the

connection between the continuum and discrete equations, that is, what noise amplitudes should we take in order that the discrete equations (58) are actually an approximate discrete version of the continuum equations (59). This bit of information is supplied by the SPH methodology, closing in this way the circle.

The thermodynamic consistency of the discrete fluid particle model ensures that total mass, momentum and energy are exactly conserved while the entropy is a strictly nondecreasing function of time. The model should allow one to study liquid-vapor and miscible-immiscible phase transitions in mixtures in nonisothermal situations with full inclusion of surface tension and cross effects.

A word is in order about the interpretation of $\bar{\phi}_{ij}^{\alpha\beta}$ in the definition of the discrete energy function in Eq. (33). In principle, this object is the long range part of the potential evaluated at the distance between the fluid particles i, j. An explicit assumption in the microscopic derivation of the continuum equations is the fact that the long range potential $\bar{\phi}$ must have a range of interaction which is much larger than the size of the fluid particles [9]. Actually, the van der Waals picture is expected to be exact in the so-called Kac limit, where the range of the potential extends to infinity while its intensity goes to zero [26]. Of course, from a computational point of view, such a limit is not possible to achieve. For this reason, a different strategy is required. Instead of using the nonlocal form for the energy (15) we can use the local expression (16). The last term of the continuum energy function Eq. (16) can be written as

$$\frac{1}{2}\sum_{\alpha\beta} c_{\alpha\beta} \int d\mathbf{r}\, \boldsymbol{\nabla}\, n_{\mathbf{r}}^{\alpha} \cdot \boldsymbol{\nabla}\, n_{\mathbf{r}}^{\beta} = -\frac{1}{2}\sum_{\alpha\beta} c_{\alpha\beta} \int d\mathbf{r} n_{\mathbf{r}}^{\alpha} \boldsymbol{\nabla}^2 n_{\mathbf{r}}^{\beta}.$$

(66)

This integral can be discretized by following the SPH rule Eq. (C18) in Appendix C,

$$-\frac{1}{4}\sum_{\alpha\beta} c_{\alpha\beta}\sum_{ij} F_{ij}(N_i^{\alpha} - N_j^{\alpha})(N_i^{\beta} - N_j^{\beta}).$$

(67)

We observe that the quadratic structure of the term in Eq. (67) is exactly the same as the last term in Eq. (33). This allows us to make the identification

$$\bar{\phi}_{ij}^{\alpha\beta} = c_{\alpha\beta} F_{ij}.$$

(68)

By using the local form (67) we achieve two goals. On the one hand, we capture the most important effects of the long range part of the potential, which occur with the neighboring fluid particles. This reduces the computational load, as only the neighbors of a fluid particle need to be considered. On the other hand, we avoid the need of specifying a functional form for the long range potential, whose effects are simply parametrized with the set of constants $c_{\alpha\beta}$. Note that this way of introducing surface tension in SPH is very different from the method proposed by Nugent and Posch [12], where the surface tension arises from a mismatch of the range of different weight functions used in the model. It also differs from the continuous surface force method [11], in that there

is no need to compute curvature and normal vectors at the interface.

We would like to comment now on the Schmidt number problem in dissipative particle dynamics [27]. The Schmidt number is the ratio between the kinematic viscosity of the fluid and the self-diffusion coefficient of the *molecules* of the fluid. The Schmidt number takes a value of order 1 for gases and 10^3 for liquids. Due to the soft nature of the interactions between dissipative particles, the ratio between the kinematic viscosity and the self-diffusion coefficient of the *dissipative particles* is of order 1. At a first sight, DPD would deceptively model gas behavior only. Note, however, that a dissipative particle is usually understood as representing a cluster of molecules moving cooperatively. Therefore, the self-diffusion coefficient of the dissipative particles should be very different from the self-diffusion coefficient of the underlying molecules. In the original DPD model, there is no physical scale associated to the dissipative particles (in terms of, for example, how many molecules it represents and how much space it occupies). Therefore, the fact that the Schmidt number of DPD is of order 1 for usual values of the model parameters should be taken as a computational rather than physical statement. By properly formulating the DPD model in a thermodynamically consistent way as in Ref. [16] the fluid particles acquire mass and volume. The thermal fluctuations scale in a familiar way with the square root of the size of the fluid particles and, therefore, the self-diffusion coefficient of the fluid particle decreases accordingly with the size of the fluid particles, leading to "computational" Schmidt numbers as large as desired. A different situation occurs in other mesoscopic particle models like the multiparticle-collision or stochastic rotation model [28,29]. In that model, the "particles" can be understood as "atoms" and the merit of the model is that it simplifies its dynamics (from Lennard-Jones potentials to probabilistic rules conserving momentum and energy). The Schmidt number issue has a clear meaning there.

Another way to look at this issue is by noting that the fluid particle model of Ref. [16] is just a Lagrangian discretization of the fluctuating Navier-Stokes equations. In these continuum equations, the molecular self-diffusion coefficient does not appear and there is no way to construct a Schmidt number. Whether we are dealing with a liquid or a gas depends uniquely on the thermodynamic state we are considering, which is controllable through the equation of state in the discrete model for simple fluids. Of course, in the multicomponent model presented in this paper, we start from the continuum equations (8) involving diffusion coefficients of the different species. We can construct a nondimensional Schmidt number out of the typical time scales associated to viscous and diffusive processes. This number is a tunable parameter in the model.

In a companion paper we present the validation of the discrete model presented in this paper for the particularly simple, although nontrivial, case where only diffusive processes take place. In future work we will consider the single component case for which there is no mass diffusion. In this case, the SPH model presented should allow to discuss the dynamics of the liquid-vapor van der Waals phase transition in a similar way to that in Ref. [12].

ACKNOWLEDGMENTS

APPENDIX A: THE VAN DER WAALS ENTROPY

In this appendix we review the explicit form of the entropy of a van der Waals mixture of fluids. The classic partition function of a mixture of fluids containing N^α atoms of species α that interact with hardcore potentials is given by

$$Z = \prod_\alpha \int \frac{d^{3N^\alpha} r}{N^\alpha! \, \lambda_\alpha^{DN^\alpha}} e^{-\beta\Phi}, \quad (A1)$$

where Φ is the intermolecular potential and $\beta = (k_B \hat{T})^{-1}$ is proportional to the inverse of the temperature. In Eq. (A1) we have integrated over the momentum variables leading to the usual appearance of the thermal wavelength λ_α,

$$\lambda_\alpha = \sqrt{\frac{h^2}{2\pi m_\alpha k_B \hat{T}}}.$$

The configuration integral is very difficult to compute in general. By following the ideas of van der Waals, we can approximate this integral by assuming that due to the hardcore interaction, every molecule has only a part of the whole volume available to it, this is

$$Z = \prod_\alpha \frac{(V-v)^{N^\alpha}}{N^\alpha! \, \lambda_\alpha^{DN^\alpha}},$$

where $v = \Sigma_\alpha N_\alpha b_\alpha$ is the volume occupied by the molecules, each one having a typical molecular volume given by b_α.

The free energy $\hat{F}(\{N^\alpha\}, \beta)$ of this hardcore fluid mixture is given by $\beta\hat{F}(\{N^\alpha\}, \beta) = -\ln Z$. The hat in the free energy (and in any other quantity) expresses that this is the free energy of a hardcore molecular system. By using Stirling's approximation $\ln N^\alpha! = N^\alpha \ln N^\alpha - N^\alpha$, we arrive at the following expression for the free energy of a mixture of hardcore particles:

$$\beta\hat{F}(\{N^\alpha\}, \beta) = \sum_\alpha N^\alpha \left[\ln\left(\frac{n_\alpha \lambda_\alpha^D}{1 - \sum_{\alpha'} n_{\alpha'} b_{\alpha'}} \right) - 1 \right], \quad (A2)$$

where $n_\alpha = N^\alpha / V$ is the number density of species α. The energy is given by the thermodynamic relation

$$\hat{\mathcal{E}} = \frac{\partial \beta\hat{F}}{\partial \beta} = \frac{D}{2} \sum_\alpha N^\alpha k_B T. \quad (A3)$$

Finally, the entropy of a hardcore mixture of fluids is $\hat{S}/k_B = \beta\hat{\mathcal{E}} - \beta\hat{F}$, which explicitly reads

$$\hat{S}(\{N^\alpha\}, \hat{\mathcal{E}}) = \frac{D}{2} k_B \sum_\alpha N^\alpha - \sum_\alpha N^\alpha \left[\ln\left(\frac{n_\alpha \lambda_\alpha^D}{1 - \sum_{\alpha'} n_{\alpha'} b_{\alpha'}} \right) - 1 \right]. \quad (A4)$$

The van der Waals entropy is obtained from the hardcore entropy according to

$$S(\{N^\alpha\}, U) = \hat{S}\left(\{N^\alpha\}, U + \frac{1}{2V} \sum_{\alpha\beta} a_{\alpha\beta} N^\alpha N^\beta \right), \quad (A5)$$

where the only dependence on the energy is through the temperature in the thermal wavelength. The temperature as a function of U is now [see Eq. (A3)]

$$T = \frac{2}{Dk_B \sum_\alpha N^\alpha} \left(U + \frac{1}{2V} \sum_{\alpha\beta} a_{\alpha\beta} N^\alpha N^\beta \right). \quad (A6)$$

APPENDIX B: THE DYADIC PRODUCTS

In order to obtain the elements of the M matrix in (51) that leads to the dynamic equations (57), we need to compute the dyadic product of the stochastic noises $d\tilde{N}_i^\alpha, d\tilde{U}_i$. These noises are defined in Eq. (53) in terms of the independent increments of the Wiener processes $d\tilde{J}_{ii'}^\alpha, d\tilde{Q}_{ii'}$ that satisfy the Ito rules (56).

A standard calculation leads to

$$d\tilde{N}_i^\alpha d\tilde{N}_j^\beta = \delta_{ij} \sum_k \left(\sum_\gamma O_{ik}^{\alpha\gamma} O_{jk}^{\beta\gamma} + T_{ik}^\alpha T_{jk}^\beta \right) dt - \left(\sum_\gamma O_{ij}^{\alpha\gamma} O_{ij}^{\beta\gamma} + T_{ij}^\alpha T_{ij}^\beta \right) dt,$$

$$d\tilde{N}_i^\alpha d\tilde{U}_j = \delta_{ij} \sum_k \left(\sum_\gamma O_{ik}^{\alpha\gamma} R_{jk}^\gamma + T_{ik}^\alpha C_{jk} \right) dt - \left(\sum_\gamma O_{ij}^{\alpha\gamma} R_{ij}^\gamma + T_{ij}^\alpha C_{ij} \right) dt,$$

$$d\tilde{U}_i d\tilde{N}_i^\beta = \delta_{ij} \sum_k \left(\sum_\gamma O_{ik}^{\beta\gamma} R_{jk}^\gamma + T_{ik}^\beta C_{jk} \right) dt - \left(\sum_\gamma O_{ij}^{\beta\gamma} R_{ij}^\gamma + T_{ij}^\beta C_{ij} \right) dt - \delta_{ij} \frac{1}{2} \sum_{\alpha_2} \sum_k \left[(\tilde{\phi}_j^{\alpha_2} - \tilde{\phi}_k^{\alpha_2}) \right.$$

$$\left. - (\underline{\phi}_j^{\alpha_2} + \underline{\phi}_k^{\alpha_2}) \right] \left(\sum_\gamma O_{ik}^{\beta\gamma} O_{jk}^{\alpha_2\gamma} + T_{ik}^\beta T_{jk}^{\alpha_2} \right) dt + \frac{1}{2} \sum_{\alpha_2} \left[(\tilde{\phi}_j^{\alpha_2} - \tilde{\phi}_i^{\alpha_2}) - (\underline{\phi}_j^{\alpha_2} + \underline{\phi}_i^{\alpha_2}) \right] \left(\sum_\gamma O_{ij}^{\beta\gamma} O_{ij}^{\alpha_2\gamma} + T_{ij}^\beta T_{ij}^{\alpha_2} \right) dt,$$

$$d\tilde{U}_i d\tilde{U}_j = \delta_{ij} \sum_k \left(\sum_\gamma R_{ik}^\gamma R_{jk}^\gamma + C_{ik} C_{jk} \right) dt - \left(\sum_\gamma R_{ij}^\gamma R_{ij}^\gamma + C_{ij} C_{ij} \right) dt - \delta_{ij} \frac{1}{2} \sum_{\alpha_1} \sum_k [(\tilde{\phi}_i^{\alpha_1} - \tilde{\phi}_k^{\alpha_1})$$

$$- (\underline{\phi}_i^{\alpha_1} + \underline{\phi}_k^{\alpha_1})] \left(\sum_\gamma O_{ik}^{\alpha_1 \gamma} R_{jk}^\gamma + T_{ik}^{\alpha_1} C_{jk} \right) dt + \frac{1}{2} \sum_{\alpha_1} [(\tilde{\phi}_i^{\alpha_1} - \tilde{\phi}_j^{\alpha_1}) - (\underline{\phi}_i^{\alpha_1} + \underline{\phi}_j^{\alpha_1})] \left(\sum_{\beta_1} O_{ij}^{\alpha_1 \beta_1} R_{ij}^{\beta_1} + T_{ij}^{\alpha_1} C_{ij} \right) dt$$

$$- \delta_{ij} \frac{1}{2} \sum_{\alpha_1} \sum_k [(\tilde{\phi}_j^{\alpha_1} - \tilde{\phi}_k^{\alpha_1}) - (\underline{\phi}_j^{\alpha_1} + \underline{\phi}_k^{\alpha_1})] \left(\sum_\gamma O_{jk}^{\alpha_1 \gamma} R_{jk}^\gamma + T_{jk}^{\alpha_1} C_{ik} \right) dt + \frac{1}{2} \sum_{\alpha_1} [(\tilde{\phi}_j^{\alpha_1} - \tilde{\phi}_i^{\alpha_1}) - (\underline{\phi}_j^{\alpha_1} + \underline{\phi}_i^{\alpha_1})]$$

$$\times \left(\sum_{\beta_1} O_{ij}^{\alpha_1 \beta_1} R_{ij}^{\beta_1} + T_{ij}^{\alpha_1} C_{ij} \right) dt + \delta_{ij} \frac{1}{4} \sum_{\alpha_1 \alpha_2} \sum_k [(\tilde{\phi}_i^{\alpha_1} - \tilde{\phi}_k^{\alpha_1}) - (\underline{\phi}_i^{\alpha_1} + \underline{\phi}_k^{\alpha_1})]$$

$$\times [(\tilde{\phi}_j^{\alpha_2} - \tilde{\phi}_k^{\alpha_2}) - (\underline{\phi}_j^{\alpha_2} + \underline{\phi}_k^{\alpha_2})] \left(\sum_\gamma O_{ik}^{\alpha_1 \gamma} O_{jk}^{\alpha_2 \gamma} + T_{ik}^{\alpha_1} T_{jk}^{\alpha_2} \right) dt - \frac{1}{4} \sum_{\alpha_1 \alpha_2} [(\tilde{\phi}_i^{\alpha_1} - \tilde{\phi}_j^{\alpha_1}) - (\underline{\phi}_i^{\alpha_1} + \underline{\phi}_j^{\alpha_1})]$$

$$\times [(\tilde{\phi}_j^{\alpha_2} - \tilde{\phi}_i^{\alpha_2}) - (\underline{\phi}_j^{\alpha_2} + \underline{\phi}_i^{\alpha_2})] \left(\sum_\gamma O_{ij}^{\alpha_1 \gamma} O_{ij}^{\alpha_2 \gamma} + T_{ij}^{\alpha_1} T_{ij}^{\alpha_2} \right) dt. \tag{B1}$$

APPENDIX C: SPH DISCRETIZATION OF SECOND DERIVATIVES

We first present some results about the moments of the function $F(r)$ defined in Eq. (48) that will be needed later. First, from the normalization to unity of the function $W(r)$ one obtains

$$\int d\mathbf{r} \, \mathbf{r} \cdot \boldsymbol{\nabla} W(r) = -\mathbf{1}, \tag{C1}$$

as can be seen by integration by parts. Using the definition of $F(r)$, it follows that the second moment of $F(r)$ is given by

$$\int d\mathbf{r} \, r^\mu r^\nu F(r) = \delta^{\mu\nu}, \tag{C2}$$

where $\delta^{\mu\nu}$ is the Kronecker delta. Odd moments of $F(r)$ are zero by symmetry. The fourth moment is given by the isotropic tensor

$$\int d\mathbf{r} \frac{r^\mu r^\nu r^{\mu'} r^{\nu'}}{r^2} F(r) = \frac{(\delta_{\mu\nu} \delta_{\mu'\nu'} + \delta_{\mu\nu'} \delta_{\mu'\nu} + \delta_{\mu\mu'} \delta_{\nu\nu'})}{D+2}, \tag{C3}$$

where D is the spatial dimension. Now, consider the following integral:

$$\int d\mathbf{q} [B(\mathbf{r}+\mathbf{q}) + B(\mathbf{r})][A(\mathbf{r}+\mathbf{q}) - A(\mathbf{r})] \frac{q^\mu q^\nu}{q^2} F(q). \tag{C4}$$

By expanding $B(\mathbf{r}+\mathbf{q}), A(\mathbf{r}+\mathbf{q})$ around $\mathbf{r}$, and neglecting spatial derivatives of order larger than the second, we arrive at the following approximate value for the integral (C4):

$$\approx \frac{1}{D+2} [\boldsymbol{\nabla} \cdot (B(\mathbf{r}) \boldsymbol{\nabla} A(\mathbf{r})) \delta^{\mu\nu} + \boldsymbol{\nabla}^\mu (B(\mathbf{r}) \boldsymbol{\nabla}^\nu A(\mathbf{r}))$$

$$+ \boldsymbol{\nabla}^\nu (B(\mathbf{r}) \boldsymbol{\nabla}^\mu A(\mathbf{r}))], \tag{C5}$$

where we have used Eq. (C3). The approximation of neglecting higher spatial derivatives will be a good one provided that the fields $A(\mathbf{r}), B(\mathbf{r})$ do not vary strongly in the range h of the weight function.

As a special case of Eq. (C5) we can set $B(\mathbf{r})=1$ and we have the result

$$\int d\mathbf{q}[A(\mathbf{r}+\mathbf{q}) - A(\mathbf{r})] \frac{q^\mu q^\nu}{q^2} F(q)$$

$$\approx \frac{1}{D+2} \left[\frac{1}{2} \nabla^2 A(\mathbf{r}) \delta^{\mu\nu} + \boldsymbol{\nabla}^\nu \boldsymbol{\nabla}^\mu A(\mathbf{r}) \right]. \tag{C6}$$

By setting $\mu = \nu$ in Eq. (C5) and summing over ν we arrive at the result

$$\int d\mathbf{q}[B(\mathbf{r}+\mathbf{q}) + B(\mathbf{r})][A(\mathbf{r}+\mathbf{q}) - A(\mathbf{r})]F(q)$$

$$\approx \boldsymbol{\nabla} (B(\mathbf{r}) \boldsymbol{\nabla} A(\mathbf{r})). \tag{C7}$$

In the case that $B(\mathbf{r})=1$ this equation (C7) becomes

$$\int d\mathbf{q}[A(\mathbf{r}+\mathbf{q}) - A(\mathbf{r})]F(q) \approx \tfrac{1}{2} \nabla^2 A(\mathbf{r}). \tag{C8}$$

We can combine Eqs. (C6) and (C8) in order to obtain an integral expression for the matrix of second derivatives of a function

$$\boldsymbol{\nabla}^\mu \boldsymbol{\nabla}^\nu A(\mathbf{r}) \approx \int d\mathbf{q}[A(\mathbf{r}+\mathbf{q}) - A(\mathbf{r})]F(q)$$

$$\times \left((D+2) \frac{q^\mu q^\nu}{q^2} - \delta^{\mu\nu} \right). \tag{C9}$$

By changing variables to $\mathbf{r}' = \mathbf{r} + \mathbf{q}$, we have the following results from (C7) and (C9),

$$
\boldsymbol{\nabla}^\mu \boldsymbol{\nabla}^\nu A(\mathbf{r}) \approx \int d\mathbf{r}'[A(\mathbf{r}') - A(\mathbf{r})]F(|\mathbf{r} - \mathbf{r}'|)
$$
$$
\times \left((D+2)\frac{(\mathbf{r}^\mu - \mathbf{r}'^\mu)(\mathbf{r}^\nu - \mathbf{r}'^\nu)}{(\mathbf{r} - \mathbf{r}')^2} - \delta^{\mu\nu} \right),
$$

$$
\boldsymbol{\nabla} \cdot (B(\mathbf{r})\,\boldsymbol{\nabla}\,A(\mathbf{r})) \approx \int d\mathbf{r}'[B(\mathbf{r}) + B(\mathbf{r}')][A(\mathbf{r}') - A(\mathbf{r})]
$$
$$
\times F(|\mathbf{r} - \mathbf{r}'|). \tag{C10}
$$

The next step consists on discretizing the integrals according to

$$
\int d\mathbf{r}' \rightarrow \sum_j \mathcal{V}_j = \sum_j \frac{1}{d_j}. \tag{C11}
$$

Again, this approximation will be valid if the scale of variation of the fields $A(\mathbf{r}), B(\mathbf{r})$ is large in front of h. In this way, we have the following approximations to the second derivatives (by letting $\mathbf{r} \rightarrow \mathbf{r}_i$ and $\mathbf{r}' \rightarrow \mathbf{r}_j$):

$$
\frac{1}{d_i}(\boldsymbol{\nabla}^\mu \boldsymbol{\nabla}^\nu A)_i \approx -\sum_j \frac{F_{ij}}{d_i d_j}A_{ij}[(D+2)\mathbf{e}_{ij}^\mu \mathbf{e}_{ij}^\nu - \delta^{\mu\nu}],
$$

$$
\frac{1}{d_i}(\boldsymbol{\nabla} \cdot B\,\boldsymbol{\nabla}\,A)_i \approx -\sum_j \frac{F_{ij}}{d_i d_j}(B_i + B_j)A_{ij}, \tag{C12}
$$

where we follow the convention (47) and we have defined the unit vectors $\mathbf{e}_{ij} = \mathbf{r}_{ij}/|\mathbf{r}_{ij}|$.

Using Eq. (C12), we can obtain a third useful approximation, by writing $\nabla B \nabla A$ as $\nabla(B\nabla A) - B\nabla\nabla A$, one arrives to

$$
\frac{1}{d_i}(\boldsymbol{\nabla} \cdot B\,\boldsymbol{\nabla}\,A)_i = \sum_j \frac{F_{ij}}{d_i d_j}A_{ij}B_{ij}. \tag{C13}
$$

Finally, one could reconsider Eq. (C4) in a more general way, and prove easily

$$
(\boldsymbol{\nabla} \cdot (BC\,\boldsymbol{\nabla}\,A))_i = -\sum_j \frac{F_{ij}}{d_i d_j}(B_i + B_j)\frac{C_i + C_j}{2}A_{ij}, \tag{C14}
$$

$$
(\boldsymbol{\nabla} \cdot (BCD\,\boldsymbol{\nabla}\,A))_i = -\sum_j \frac{F_{ij}}{d_i d_j}(B_i + B_j)\frac{C_i + C_j}{2}\frac{D_i + D_j}{2}A_{ij}. \tag{C15}
$$

When discretizing the surface tension terms in the continuum energy function we encounter the following integral:

$$
\int d\mathbf{r}\, n_\mathbf{r}\nabla^2 n_\mathbf{r}. \tag{C16}
$$

By using the integral representation of the Laplacian, Eq. (C8) we can write this term as

$$
\int d\mathbf{r}\, n_\mathbf{r}\nabla^2 n_\mathbf{r} = 2\int d\mathbf{r}\int d\mathbf{r}'\, n_\mathbf{r}(n_{\mathbf{r}'} - n_\mathbf{r})F(|\mathbf{r} - \mathbf{r}'|)
$$
$$
= -\int d\mathbf{r}\int d\mathbf{r}'(n_\mathbf{r} - n_{\mathbf{r}'})(n_\mathbf{r} - n_{\mathbf{r}'})F(|\mathbf{r} - \mathbf{r}'|). \tag{C17}
$$

Therefore, by discretizing the integrals according to Eq. (C11), the integral admits the natural discretization

$$
\int d\mathbf{r}\, n_\mathbf{r}\nabla^2 n_\mathbf{r} \approx -\sum_{ij}(N_i - N_j)(N_i - N_j)F_{ij}, \tag{C18}
$$

where $N_i = \mathcal{V}_i n_i$ is the number of molecules in the volume element $\mathcal{V}_i$ that has a number density n_i.

[1] H. T. Davis, *Statistical Mechanics of Phases, Interfaces and Thin Films* (Wiley-VCH, New York, 1996).

[2] J. M. Yeomans, Annu. Rev. Comput. Phys. **7**, 61 (1999).

[3] S. R. de Groot and P. Mazur, *Non-equilibrium Thermodynamics* (North-Holland, Amsterdam, 1964).

[4] A. Beris and B. Edwards, *Thermodynamics of Flowing Systems with Internal Microstructure* (Oxford University Press, New York, 1994).

[5] D. M. Anderson, G. B. McFadden, and A. A. Wheeler, Annu. Rev. Fluid Mech. **30**, 139 (1998).

[6] J. Lowengrub and L. Truskinovsky, Proc. R. Soc. London, Ser. A **454**, 2617 (1998).

[7] L. K. Antanovskii, Phys. Rev. E **54**, 6285 (1996).

[8] S. Bastea, R. Esposito, J. L. Lebowitz, and R. Marra, J. Stat. Phys. **101**, 1087 (2000).

[9] P. Español and C. Thieulot, J. Chem. Phys. **118**, 9109 (2003).

[10] J. J. Monaghan, Annu. Rev. Astron. Astrophys. **30**, 543 (1992).

[11] J. P. Morris, Int. J. Numer. Methods Fluids **33**, 333 (2000).

[12] S. Nugent and H. A. Posch, Phys. Rev. E **62**, 4968 (2000).

[13] H. C. Öttinger and M. Grmela, Phys. Rev. E **56**, 6633 (1997).

[14] P. Español, M. Serrano, and H. C. Öttinger, Phys. Rev. Lett. **83**, 4542 (1999).

[15] M. Serrano and P. Español, Phys. Rev. E **64**, 046115 (2001).

[16] P. Español and M. Revenga, Phys. Rev. E **67**, 026705 (2003).

[17] I. Pagonabarraga and D. Frenkel, J. Chem. Phys. **115**, 5015 (2001).

[18] P. B. Warren, Phys. Rev. Lett. **87**, 225702 (2001).

[19] S. Y. Trofimov, E. L. F. Nies, and M. A. J. Michels, J. Chem. Phys. **117**, 9383 (2002).

[20] P. B. Warren, Phys. Rev. E **68**, 066702 (2003).

[21] P. J. Hoogerbrugge and J. M. V. A. Koelman, Europhys. Lett. **19**, 155 (1992).

[22] P. Español and P. B. Warren, Europhys. Lett. **30**, 191 (1995).

[23] H. B. Callen, *Thermodynamics* (Wiley, New York, 1960).

[24] H. C. Öttinger, Phys. Rev. E **57**, 1416 (1998).

[25] P. Español, in *Trends in Nanoscale Mechanics: Analysis of Nanostructured Materials and Multi-Scale Modeling*, edited by V. M. Harik and M. D. Salas (Kluwer, Berlin, 2003).

[26] J. L. Lebowitz and E. M. Waisman, Phys. Today **4**, 24 (1980).

[27] R. D. Groot and P. B. Warren, J. Chem. Phys. **107**, 4423 (1997).

[28] A. Malevanets and R. Kapral, J. Chem. Phys. **110**, 8605 (1999).

[29] T. Ihle and D. M. Kroll, Phys. Rev. E **67**, 066705 (2003).