

# Kinetic modelling of late stages of phase separation

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## 1 Introduction

We want to provide some tools for studying the behaviour of a fluid where two phases are present separated by a sharp layer which moves according to the dynamics of the system. We specialize to the situation of a mixture of two fluids 1 and 2, that, if quenched below the coexistence curve, start to segregate in domains, some of which are rich in fluid 1 and the others in fluid 2.

A classical approach to phase segregation distinguishes below the coexistence curve a region of unstable states from one of metastable states. If the system is cooled inside the metastable region, it begins to develop finite amplitude fluctuations like droplets. This process is known as nucleation. On the other hand, if we quench the system into the unstable region, infinitesimal fluctuations appear that yield macroscopic pattern. That is called spinodal decomposition. In late stages of phase segregation, the two processes tend to coincide.

There are several reasons to choice a kinetic model. First of all there is a clear physical intuition underlying the mathematical structure of the equations, because we can still think to interacting particles. Secondly those particles move in the continuous space and not on a lattice. Moreover there are convincing arguments relating Newtonian dynamics to the kinetic one and there are powerful tools to derive hydrodynamics from kinetic equations.

Phase segregation can occur in a single component fluid when the long range interaction between the particles is attractive. Then when the temperature is sufficiently low, different phases appear. But, of course, one of them can be characterized by high density. Often kinetic models have problems when densities are too high. Hence the idea of using a two component mixture. In this case particles of different type repel each other. The densities in all the phases can be now kept low. We will present two models corresponding to two different physical situations.

### 1.1 Vlasov-Fokker-Planck model

The physical situation we have in mind is the following: we have two different kinds of particles 1 and 2 in a torus  $\Omega_\epsilon = \epsilon^{-1}\Omega$ ,  $\Omega \subset \mathbb{R}^3$ , the torus of size 1. Particles of the same type do not interact at all. Particles 1 are repelled by particles 2 and vice-versa. The system is in contact with a thermal bath, that keeps the temperature constant. The thermalization mechanism is not characterized by collisions between particles of the fluid, but by the interaction with a somewhat idealized entity (the reservoir), whose internal structure is unknown and it is unchanged by the dynamics of the mixture. In this case we can also consider high densities and thus the model is suitable to describe systems as polymer blends. Indeed there is only one type of conserved quantity, namely the mass of each component of the mixture. Since energy and momentum are dissipated on a much shorter time scale, we expect that the late stages of the phase segregation are not influenced by hydrodynamical effects; on the contrary the motion will be quasi-static.

Each component of the mixture is described by the distribution function  $f_i$ ,  $i = 1, 2$ , in the one-particle phase space. The interaction is modelled through an auto-consistent Vlasov term. It means that the force  $F_i$  acting on each particle is the gradient of the average potential generated by all the others. In the underlying microscopic model, particles of different species interact through a two body Kac potential  $U_\gamma$ , which is repulsive, weak and long ranged. The action of the heat reservoir on the system is translated in terms of a Fokker-Planck operator  $L_\beta$ .

The equations are the following:

$$\partial_\tau f_i + v \cdot \nabla_x f_i + F_i \cdot \nabla_v f_i = L_\beta f_i \quad (1)$$

where

$$L_\beta f_i = \nabla_v \cdot \left( M_\beta \nabla_v \left( \frac{f_i}{M_\beta} \right) \right)$$

$M_\beta$  is a Maxwellian with mean zero and variance  $\beta^{-1}$ ,

$$M_\beta = \left( \frac{\beta}{2\pi} \right)^{\frac{3}{2}} e^{-\frac{\beta}{2} v^2}$$

$\beta^{-1}$  is the temperature of the reservoir. The auto-consistent Vlasov force is

$$F_i = -\nabla_x \int_{\Omega_\epsilon} dx' U_\gamma(x - x') \int_{\mathbb{R}^3} dv f_j(x', v, \tau)$$

and the Kac potential  $U_\gamma(x) = \gamma^3 U(|\gamma x|)$  has range and intensity modulated by the parameter  $\gamma > 0$ . The function  $U$  has compact support, it is smooth and its integral over the whole space is equal to one. We assume that the functions  $f_i$  are normalized in such a way that  $\int_{\Omega_\epsilon} dx \int_{\mathbb{R}^3} dv f_i(x, v)$  gives

the total mass in  $\Omega_\epsilon$  of the component  $i$ . Thus  $\rho_i(x) := \int_{\mathbb{R}^3} dv f_i(x, v)$  can be interpreted as mass density.

Equations (1) have stationary solutions of the form  $f_i = \rho_i M_\beta$ , where  $\rho_i$  are functions only of the position solving

$$\ln \rho_i(x) + \beta \int_{\Omega_\epsilon} dx' U_\gamma(x - x') \rho_j(x') = C_i, \quad x \in \Omega_\epsilon, \quad i, j = 1, 2, \quad i \neq j \quad (2)$$

and  $C_i$  are arbitrary constants, related to the masses of the components of the mixture and to their concentrations. It is proved in [CCELM], under the assumption of a monotone  $U_\gamma(x)$ , that at low temperature there are non homogeneous solutions to (2), thermodynamically stable in the sense that they minimize the free energy functional

$$\mathcal{F}(\rho_1, \rho_2) = \int_{\Omega_\epsilon} dx (\rho_1 \ln \rho_1 + \rho_2 \ln \rho_2) + \beta \int_{\Omega_\epsilon \times \Omega_\epsilon} dx dy U_\gamma(x - y) \rho_1(x) \rho_2(y) \quad (3)$$

which is obtained (apart unimportant constants) computing

$$\begin{aligned} \mathcal{G}(f_1, f_2) = & \int_{\Omega_\epsilon \times \mathbb{R}^3} dx dv (f_1 \ln f_1 + f_2 \ln f_2) + \frac{\beta}{2} \int_{\Omega_\epsilon \times \mathbb{R}^3} dx dv (f_1 + f_2) v^2 + \\ & \beta \int_{\Omega_\epsilon \times \Omega_\epsilon} dx dy U_\gamma(x - y) \int_{\mathbb{R}^3} dv f_1(x, v) \int_{\mathbb{R}^3} dv' f_2(y, v') \end{aligned}$$

on functions  $f_i = \rho_i M_\beta$ .  $\mathcal{G}$  is a Lyapunov functional for the evolution equations (1).

The structure of the minimizers is such that, when  $\gamma$  is much smaller than the typical size of the container, the volume  $\Omega_\epsilon$  is divided into two regions where the densities are those of the pure phases (the equilibrium values given by intersecting with an horizontal line the coexistence curve at the temperature of the mixture) with an interpolating region called the *interface* whose size is again of order  $\gamma$ . On the infinite line it is possible to characterize the equilibrium states in terms of the excess free energy functional: the non homogeneous minimizers  $w_i(z)$ ,  $z \in \mathbb{R}$  and  $i = 1, 2$ , of the the excess free energy arise by prescribing asymptotic values for the densities corresponding to the two different phases coexisting at equilibrium. They are known as *fronts*, have monotonicity properties and interpolate smoothly, over a region of size  $\gamma$  between the asymptotic constant values.

In late stages of phase segregation, when domains of different phases are well established and they are separated by sharp interfaces, the change in density across them is described by those stationary profiles. The dynamics of the system can be fully understood in terms of the following quasi-static problem:

$$\begin{cases} \Delta_r \psi(r, t) = 0 & r \in \Omega \setminus \Gamma_t \\ \psi(r, t) = c_1 SK(r, t) & r \in \Gamma_t \end{cases} \quad \begin{cases} \Delta_r \zeta(r, t) = 0 & r \in \Omega \setminus \Gamma_t \\ c_2 SK(r, t) = [\zeta]^\pm & r \in \Gamma_t \\ 0 = [\nu_t \cdot \nabla_r \zeta]^\pm & \end{cases}$$

$$V = c_3[\nu_t \cdot \nabla_r \psi]_{\pm}^{\pm} + c_4 \nu_t \cdot \nabla_r \zeta$$

where  $\Gamma_t$  is the interface at time  $t$  and  $\nu_t$  its outward normal. The quantities  $c_i$ ,  $i = 1, \dots, 4$ , depend on the initial data and on the temperature;  $S$  is the surface tension and  $K$  is the sum of the principal curvatures of  $\Gamma_t$ .  $V$  is the normal velocity of the interface. Finally with the symbol  $[\cdot]_{\pm}^{\pm}$  we mean the difference between the values of the argument on the two sides of the interface. We will comment later on the physical interpretation of  $\psi$  and  $\zeta$ , which are related to the chemical potentials.

The above dynamics conserve the volume of the inner domain, trying in the meanwhile to decrease the area of its surface. We will show how to derive that dynamics from our kinetic model, via a limiting procedure in which  $\epsilon$  plays the role of the vanishing parameter and  $\gamma$  has to be chosen properly.

## 1.2 Vlasov-Boltzmann model

We replace in the previous model the interaction of each species with the reservoir by elastic collisions between particles, independent of the species, that we model by a Boltzmann collision kernel. The evolution is then ruled by two coupled Vlasov-Boltzmann (VB) equations for the one-particle distributions  $f_i(x, v, \tau)$ ,  $i = 1, 2$ . These equations, which conserve the mass of each species, the total momentum and energy, have the form:

$$\partial_{\tau} f_i + v \cdot \nabla_x f_i + F_i \cdot \nabla_v f_i = J(f_i, f_1 + f_2), \quad i = 1, 2 \quad (4)$$

where  $J(f, g)$  is the non-symmetric Boltzmann collision operator for hard spheres [Ce],

$$J(f, g) = \int_{\mathbb{R}^3} dv_* \int_{S_2} d\omega B(|v - v_*|, \omega) [f(v')g(v'_*) - f(v)g(v_*)]$$

where  $S_2$  is the  $2-d$  sphere in  $\mathbb{R}^3$ ,  $d\omega$  is the surface measure on it, the vectors  $v$ ,  $v_*$  are the outgoing velocities of a binary elastic collision between two particles with incoming velocities  $v'$  and  $v'_*$  and  $B(|v - v_*|, \omega) = \frac{1}{2}|(v - v_*) \cdot \omega|$ .

The equilibrium states for this system can be characterized by looking to the (negative of the) entropy functional

$$\mathcal{H}(f_1, f_2) = \sum_{i=1}^2 \int_{\Omega_{\epsilon} \times \mathbb{R}^3} dx dv f_i \log f_i, \quad (5)$$

which is a Lyapunov functional for (4) in the sense that

$$\frac{d}{dt} \mathcal{H}(f_1, f_2) \leq 0 \quad (6)$$

The equilibrium states are then determined by imposing the equality in (6). They are local Maxwellian's with mean value  $u = 0$ , variance  $\beta^{-1}$ , and densities  $\rho_i = \int dv f_i(x, v, \tau)$  satisfying (2).

An alternative way to obtain equilibrium states is to minimize the entropy functional under the constraints on the total energy and total masses. The densities will be determined [CCELM] as the minimizers of the free energy functional  $\mathcal{F}(\rho_1, \rho_2)$  defined in (3).

Equations (2) are indeed the Euler-Lagrange equations for this minimization problem.  $\beta$  is determined by the constraint on the energy and  $C_i$  by the constraints on the masses.

Since this dynamics conserves masses, momentum and energy the hydrodynamics effects in the late stages of the coarsening process become relevant and when the fluid is well segregated with sharp interfaces between different phases the interface moves in its normal direction following the incompressible velocity field solution of the Navier-Stokes equation, while the pressure satisfy the Laplace's law relating it to the surface tension and curvature

This limiting evolution is ruled by the following free boundary problem. Let  $\Gamma^0$  be a regular surface in a  $3 - d$  torus  $\Omega$  (the interface at time zero) dividing the torus in two regions  $\Omega^+$  and  $\Omega^-$ . For each  $t$  one has to find a surface  $\Gamma_t$ , moving with velocity  $V$ , a continuous velocity field  $u(\cdot, t)$  and a pressure function  $p(\cdot, t)$  such that

$$\begin{cases} \partial_t u + (u \cdot \nabla)u + \nabla p = \eta \Delta u \\ V = -u \cdot \nu \\ [p]_{-}^{+} = K_{\Gamma_t} S & \text{on } \Gamma_t \\ \nabla \cdot u = 0 \\ \Gamma_0 = \Gamma^0, \quad u(\cdot, 0) = u_0(\cdot). \end{cases} \quad (7)$$

where  $\eta$  is the kinematic viscosity,  $S$  denotes surface tension,  $\nu(\cdot, t)$  is the normal to the surface pointing towards  $\Omega^+$ ,  $K_{\Gamma_t}$  stands for the curvature of  $\Gamma_t$  and  $[h]_{-}^{+} = h^+ - h^-$  stands for the jump of the observable  $h$  across  $\Gamma_t$ .

This free boundary problem was first formulated to describe the oscillations of an impermeable interface separating two viscous fluids in [H]. Chandrasekar [Cha] then studied the linear stability of this system. We mention that recently [CS] have obtained existence, uniqueness and regularity results for the one-side case, namely the flow of an incompressible Navier-Stokes fluid confined in a region with free boundary where suitable surface tension boundary conditions are specified. Such results can be extended to the present two-side case [Sh].

This flow diminishes the length of the boundary while conserving the volume and at the same time forces the velocity field to decay to zero. Hence, the stationary solution should be characterized by  $u = 0$  and a surface  $\Gamma$  determined by the isoperimetric problem on the torus, separating  $\Omega$  in two phase regions with different values of the pressure such that  $[p]_{-}^{+} = K_{\Gamma} S$ .

## 2 Some words on the method

Aiming to describe a macroscopic system starting from a kinetic model, it is clear that at some point we will exploit the scale separation. The latter usually

provides a law of large numbers annihilating most of the strange fluctuations of the microscopic landscape. In other words we expect, at least, that if the system is initially close to a local equilibrium, it will evolve smoothly, with variations appreciable only on the macroscopic scale. Over a long span of space and time we will observe microscopically a lot of fluctuations, but none of these will be able to modify the macroscopic picture. If we want to get rid of all those meaningless informations, we can look at the solution of (1) only after macroscopic times and distances. This is why we define functions  $f_i^\epsilon(r, v, t) := f_i(\epsilon^{-1}r, v, \epsilon^{-a}t)$ , where  $\epsilon$  is the ratio between the kinetic and macroscopic scales and  $(r, t)$  are the macroscopic values of space and time. Choosing different  $a > 0$  we obtain different behaviours. For example if we chose  $a = 1$  we could not see any dissipation phenomena, because diffusion starts to be effective only after a time of order the square of the distance. Another important parameter in the theory is the range of the interaction  $\gamma^{-1}$ . Since the size of the interface is linearly related to the range of the interaction, by choosing  $\gamma = 1$ , the width of the interface on the macroscopic scale is of order  $\epsilon$ , so that in the limit  $\epsilon \rightarrow 0$  the interface becomes sharp. In the context of the Vlasov-Fokker-Plank (VFP) model, we will describe the dynamics in the case of a sharp interface at time  $\epsilon^{-3}t$ , when the system has almost completely relaxed to equilibrium, namely in each domain the values of the densities are those of the thermodynamic equilibrium; only the shape of the domains can still change. An other possible choice is  $a = 2$ : the limiting equation is a nonlinear diffusion equation with Dirichlet boundary conditions on the interface (Stefan problem).

From (1) we can derive an equation for  $f_i^\epsilon$  where the parameter  $\epsilon$  appears explicitly. The simple and powerful idea consists in seeking a solution as an asymptotic series of powers of  $\epsilon$ . Then we obtain a hierarchy of equations that can be solved step by step.

### 3 Sharp interface limit for the VFP model

Here we begin the analysis of the late stages dynamics provided by the VFP model.

#### 3.1 The initial data

We assume that the system at time zero is already characterized by macroscopic domains filled by different phases and that the layers dividing them are sharp. In other words their width is of order  $\epsilon$  in macroscopic units. The interface can so be approximated by a geometrical surface  $\Gamma_0$  in the sense that the transition between different phases takes place in a layer of width  $\epsilon$  around  $\Gamma_0$ . We will show that this picture is preserved by the evolution of the system, namely there is a well defined surface  $\Gamma_t^\epsilon$  able to give a description of the interface within errors of order  $\epsilon$ . We are definitely interested in such a  $\Gamma_t^\epsilon$ .

As explained above, we introduce functions  $f_i^\epsilon(r, v, t) = f_i(\epsilon^{-1}r, v, \epsilon^{-3}t)$ ,  $r \in \Omega$ , a 3-d torus of size 1,  $t > 0$ .  $f_i^\epsilon$  describes the large scale variations of the system, when observed after very long time intervals. We recall that the fronts are the non-homogeneous stationary solutions of the one dimensional version of the problem (1). They are unique, given the initial physical conditions of the systems, modulo translations, then we define  $w_i$  to be the fronts centered on the origin, that is  $w_1(0) = w_2(0)$ . The asymptotic values are  $w_i(\pm\infty) = \rho_i^\pm$  with the additional symmetry  $\rho_1^\pm = \rho_2^\mp$ .

The initial data are given by  $\bar{f}_i^\epsilon = \rho_i^\epsilon M_\beta$ , where

$$\rho_i^\epsilon(r) = w_i(\epsilon^{-1}d(r, \Gamma_0)) + O(\epsilon) \quad (8)$$

and  $d$  is the signed distance from the interface.

### 3.2 The rescaled equation

The functions  $f_i^\epsilon$  solve

$$\partial_t f_i^\epsilon + \epsilon^{-2}v \cdot \nabla_r f_i^\epsilon + \epsilon^{-2}F_i^\epsilon \cdot \nabla_v f_i^\epsilon = \epsilon^{-3}L_\beta f_i^\epsilon. \quad (9)$$

$$F_i^\epsilon(r, t) = -\nabla_r \int_\Omega dr' \epsilon^{-3}U(\epsilon^{-1}|r - r'|) \int dv' f_j^\epsilon(r', v', t) =: -\nabla_r g_i^\epsilon.$$

The function  $g_i^\epsilon$  is the Vlasov mean potential experienced by particles of type  $i$ .

Equations (9) complemented with the initial condition  $f_i^\epsilon(r, v, 0) = \bar{f}_i^\epsilon(r, v)$  are the mathematical object of our study.

### 3.3 Notation and definitions

We assume that during its evolution the interface does not develop singularities within a time interval  $[0, T]$ , where  $T > 0$  can be eventually very small. More precisely we define the interface as the set

$$\Gamma_t^\epsilon = \{r \in \Omega : \rho_1^\epsilon(r, t) = \rho_2^\epsilon(r, t)\}$$

Then we suppose that in any point  $x \in \Gamma_t^\epsilon$  it is possible to compute the principal curvatures. Then let  $k(x)$  be the maximum between those principal curvatures in  $x$ . We can introduce now  $k(\Gamma_t^\epsilon)$  as the supremum of  $\{k(x) : x \in \Gamma_t^\epsilon\}$ .

Our main assumption is the existence of  $\epsilon_0$  and of a time  $T > 0$  such that the quantity  $\delta$ , defined by  $\delta^{-1} = \sup_{0 \leq t \leq T, 0 \leq \epsilon \leq \epsilon_0} k(\Gamma_t^\epsilon)$ , is strictly greater than zero. Under that hypothesis let  $d^\epsilon(r, t)$  be the signed distance of  $r$  from  $\Gamma_t^\epsilon$ ; then, if

$$\mathcal{N}(\delta, t) = \{r \in \Omega : |d^\epsilon(r, t)| < \delta\}$$

and  $r \in \mathcal{N}$ , there exists a unique point  $s(r)$  on  $\Gamma_t^\epsilon$  such that

$$\nu^\epsilon(s(r))d^\epsilon(r, t) + s(r) = r \quad (10)$$

where  $\nu^\epsilon(s(r)) = \nabla_r d^\epsilon(r, t)$  is the unit normal vector to  $\Gamma_t^\epsilon$ . We will use  $s(r)$  to build a local system of reference moving with the interface.

In terms of  $d^\epsilon$  we can also define the normal velocity  $V^\epsilon$  of the interface and its curvature  $K^\epsilon$  (actually the sum of the principal curvatures):

$$V^\epsilon(s(r)) = \partial_t d^\epsilon(r, t), \quad K^\epsilon = \Delta_r d^\epsilon(r, t), \quad r \in \Gamma_t^\epsilon$$

The interface  $\Gamma_t^\epsilon$  divides the domain  $\Omega_\epsilon$  in two sub-domains  $\Omega_{\epsilon, t}^\pm$  such that  $d^\epsilon > (<) 0$  in  $\Omega_{\epsilon, t}^{+(-)}$ . Clearly  $\Omega_\epsilon = \Gamma_t^\epsilon \cup \Omega_{\epsilon, t}^+ \cup \Omega_{\epsilon, t}^-$ . From now on we will drop the apex  $\epsilon$ .

Since the transition layer between different phases has width of order  $\epsilon$  and we expect that the density profile will approach exponentially fast the equilibrium values in the bulk, in  $\mathcal{N}$  there is plenty of space to perform the transition if  $\epsilon$  is sufficiently small (i.e.  $\epsilon \ll \delta$ ). Because of the boundedness assumption on the curvature of the interface, locally it will appear flat; it means, on a first approximation, that only in the normal direction something interesting can happen. The macroscopic units are not able to reveal these fine structures of the interface; then it is quite natural to introduce for any point  $r \in \mathcal{N}$  a fast varying variable  $z = \epsilon^{-1}d(r, t)$  and for any function  $h(r, t)$  a new function  $\tilde{h}(z, r, t)$  such that  $\tilde{h}(z, r, t) = h(\epsilon z \nu(s(r)) + s(r), t)$  and  $\tilde{h}(z, r + \ell \nu(s(r)), t) = \tilde{h}(z, r, t)$ ,  $\forall \ell$  such that  $r + \ell \nu(s(r)) \in \mathcal{N}$ . In other words, if  $h$  has a fast varying behaviour, then it! is more convenient to replace it with  $\tilde{h}$  which is able to zoom around the interface; so, with respect to  $z$  the transition will appear smooth. In  $\tilde{h}(z, r, t)$  the second argument contains all the informations on the dependence on  $r$  except that on the distance from the interface which is encoded in the first argument. Of course we can add velocity as an additional argument. From  $h(r, t) = \tilde{h}(\epsilon^{-1}d(r, t), r, t)$  we can derive the following relations:

$$\begin{aligned} \nabla_r h &= \frac{1}{\epsilon} \nu \partial_z \tilde{h} + \bar{\nabla}_r \tilde{h}; & \partial_t h &= \frac{1}{\epsilon} V \partial_z \tilde{h} + \partial_t \tilde{h}; \\ \Delta_r h &= \frac{1}{\epsilon^2} \partial_z^2 \tilde{h} + \frac{1}{\epsilon} (\nabla_r \cdot \nu) \partial_z \tilde{h} + \bar{\Delta}_r \tilde{h} \end{aligned} \quad (11)$$

where the bar on the derivative operators means derivatives with respect to the second argument  $r$ , keeping fixed the other variables. Note that  $\nu \cdot \bar{\nabla}_r h(z, r, t) = 0$ .

### 3.4 Hilbert expansion

We follow the approach based on the truncated Hilbert expansion introduced by Caffish [C]: we try to find a solution of (9) as a power series in  $\epsilon$

$$f_i^\epsilon = \sum_{n=0}^{\infty} \epsilon^n f_i^{(n)}. \quad (12)$$

Of course we need to expand also any other quantity depending on  $\epsilon$ . We start writing  $U^\epsilon \star \sum_{n=0}^{\infty} \epsilon^n \rho_j^{(n)} = \sum_{n=0}^{\infty} \epsilon^n g_i^{(n)}$  and  $F_i^{(n)} = -\nabla_r g_i^{(n)}$ . Then

$$d(r, t) = \sum_{n=0}^{\infty} \epsilon^n d^{(n)}(r, t) \quad (13)$$

and  $\nu^{(n)}$  is the gradient  $\nabla_r d^{(n)}$ ,  $\bar{\nu} := \nu^{(0)}$ . The condition  $|\nabla_r d| = 1$  implies that  $|\nabla_r d^{(0)}| = 1$  as well; so  $d^{(0)}$  can be interpreted as a signed distance from an interface that we denote by  $\bar{\Gamma}_t = \{r \in \Omega : |d^{(0)}(r, t)| = 0\}$ . Similarly

$$\mathcal{N}^{(0)}(\delta') = \{r \in \Omega : |d^{(0)}(r, t)| < \delta'\}, \quad \Omega^{+(-)} = \{r \in \Omega : d^{(0)}(r, t) > (<) 0\}$$

For any  $\epsilon$  sufficiently small the assumptions made on the smoothness of the full interface still hold for  $\bar{\Gamma}_t$ .

As pointed out at the end of the previous section, near the interface it is convenient to use as coefficients in the series (12) functions  $\tilde{f}_i^{(n)} = \tilde{f}_i^{(n)}(z, r, v, t)$ . In the bulk it is sufficient to use only macroscopic coordinates. However, in order to avoid misunderstandings, we call  $\hat{f}_i^{(n)} = \hat{f}_i^{(n)}(r, v, t)$  the coefficients of the series in the bulk. In other words we write in  $\Omega \setminus \mathcal{N}^{(0)}(\delta')$

$$f_i^\epsilon = \sum_{n=0}^{\infty} \epsilon^n \hat{f}_i^{(n)}. \quad (14)$$

and in  $\mathcal{N}^0(\delta')$

$$f_i^\epsilon = \sum_{n=0}^{\infty} \epsilon^n \tilde{f}_i^{(n)}. \quad (15)$$

On the border of  $\mathcal{N}^{(0)}$ , the two expansions, from now on denoted by inner and outer expansion, have to be matched. Then we choose  $\delta' = \epsilon^c$ ,  $c \in (0, 1)$  and we require that as  $\epsilon \rightarrow 0$  ([CF])

$$\begin{aligned} \tilde{f}_i^{(0)} &= (\hat{f}_i^{(0)})^\pm + O(e^{-\alpha|z|}) \\ \tilde{f}_i^{(1)} &= (\hat{f}_i^{(1)})^\pm + \nu^{(0)} \cdot (\nabla_r \hat{f}_i^{(0)})^\pm (z - d^{(1)}) + O(e^{-\alpha|z|}) \\ \tilde{f}_i^{(2)} &= (\hat{f}_i^{(2)})^\pm + \nu^{(0)} \cdot (\nabla_r \hat{f}_i^{(1)})^\pm (z - d^{(1)}) \\ &\quad + (\nabla_r \hat{f}_i^{(0)})^\pm \cdot (-\nu^{(0)} d^{(2)} + \nu^{(1)}(z - d^{(1)})) \\ &\quad + \frac{1}{2} (\partial_{r_n} \partial_{r_k} \hat{f}_i^{(0)})^\pm \nu_h^{(0)} (z - d^{(1)}) \nu_k^{(0)} (z - d^{(1)}) + O(e^{-\alpha|z|}) \\ &\quad \dots \end{aligned}$$

where the symbol  $(\hat{h})^\pm$  stands for  $\lim_{\ell \rightarrow 0^\pm} \hat{h}(r + \bar{\nu}\ell)$ ,  $r \in \bar{\Gamma}_t$ . We will refer to the above relations as *matching conditions*.

We replace (14) and (15) in the equations and equate terms of the same order in  $\epsilon$  separately in  $\Omega^\pm \setminus \mathcal{N}^0(\delta')$  and  $\mathcal{N}^0(\delta')$ . We will use the notation  $\rho_i^{(n)} = \int dv f_i^{(n)}$ , and we denote by  $\hat{h}, \tilde{h}$  a function  $h(f_i^{(n)})$  whenever it is evaluated on  $\hat{f}_i^{(n)}, \tilde{f}_i^{(n)}$ .

### 3.5 Outer expansion

At the lowest order ( $\epsilon^{-3}$ ):

$$L_\beta \hat{f}_i^{(0)} = 0$$

which implies that  $\hat{f}_i^{(0)}$  has to be Maxwellian in velocity with variance  $\beta^{-1}$  times a function  $\hat{\rho}_i^{(0)}(r, t)$  which will be determined through the  $\epsilon^{-1}$  order equation. At order  $\epsilon^{-2}$ :

$$v \cdot \nabla_r \hat{f}_i^{(0)} + \hat{F}_i^{(0)} \cdot \nabla_v \hat{f}_i^{(0)} = L_\beta \hat{f}_i^{(1)}. \quad (16)$$

The solution can be found explicitly simply trying with a Maxwellian multiplied by a polynomial of degree one in  $v$ . Of course the solution is not unique because the kernel of  $L_\beta$  is not void. So  $\hat{f}_i^{(1)}$  can be written as

$$\hat{f}_i^{(1)} = \hat{\rho}_i^{(1)} M_\beta - M_\beta \hat{\rho}_i^{(0)} v \cdot \nabla_r \hat{\mu}_i^{(0)} \quad (17)$$

where  $\mu_i^\epsilon(\rho^\epsilon) = \frac{1}{\beta} \ln \rho_i^\epsilon + U^\epsilon \star \rho_j^\epsilon$  and  $\mu_i^\epsilon = \sum_{n=0}^{\infty} \epsilon^n \mu_i^{(n)}$  and the function  $\hat{\rho}_i^{(1)}$  will be determined by imposing the solvability of the  $\epsilon^0$  order equation.

The order  $\epsilon^{-1}$  equation is

$$v \cdot \nabla_r \hat{f}_i^{(1)} + \hat{F}_i^{(0)} \cdot \nabla_v \hat{f}_i^{(1)} + \hat{F}_i^{(1)} \cdot \nabla_v \hat{f}_i^{(0)} = L_\beta \hat{f}_i^{(2)}. \quad (18)$$

The solvability condition for this equation says that the integral on the velocity of the l.h.s. has to be zero. By integrating over the velocity and using the explicit expression for  $\hat{f}_i^{(1)}$  we get

$$-\frac{1}{\beta} \nabla_r \cdot (\hat{\rho}_i^{(0)} \nabla_r \hat{\mu}_i^{(0)}) = 0.$$

The choice of the initial data implies that the only solution of that equation is the piecewise constant function equal to  $\rho_i^\pm$  in  $\Omega^\pm \setminus \mathcal{N}(\delta')$ .

$\hat{f}_i^{(2)}$  is determined by replacing (17) in equation (18). The result is

$$\hat{f}_i^{(2)} = -M_\beta \hat{\rho}_i^{(0)} v \cdot \nabla_r \hat{\mu}_i^{(1)} + \hat{\rho}_i^{(2)} M_\beta. \quad (19)$$

where  $\hat{\mu}_i^{(1)} = \hat{\rho}_i^{(1)} / (\beta \hat{\rho}_i^{(0)}) + \hat{g}_i^{(1)}$ .

As above, by integrating over  $v$  the  $\epsilon^0$  order equation and taking into account that  $\hat{f}_i^{(0)}$  is Maxwellian in velocity, we get the following condition on  $\hat{u}^{(2)}$ , where  $u_i^{(n)} = \int dv v f_i^{(n)}$ ,

$$\nabla_r \cdot \hat{u}_i^{(2)} = 0. \quad (20)$$

Now we use  $\hat{f}_i^{(2)}$  as given by (19) to get  $\hat{u}_i^{(2)} = -\frac{1}{\beta} \hat{\rho}_i^{(0)} \nabla_r \hat{\mu}_i^{(1)}$  and plug it in (20) to get the equation for  $\hat{\mu}_i^{(1)}$ :

$$\Delta_r \hat{\mu}_i^{(1)} = 0.$$

### 3.6 Inner expansion

At the lowest order ( $\epsilon^{-3}$ )

$$v \cdot \bar{\nu} \partial_z \tilde{f}_i^{(0)} - \bar{\nu} \cdot \nabla_v \tilde{f}_i^{(0)} \partial_z \tilde{g}_i^{(0)} = L_\beta \tilde{f}_i^{(0)}.$$

It can be proved that any solution of this equation has the form  $M_\beta(v) \tilde{\rho}_i^{(0)}$ , with  $\tilde{\rho}_i^{(0)}$  a function of  $z$ . Plugging back in the equation we have

$$\partial_z \tilde{\rho}_i^{(0)} + \beta \tilde{\rho}_i^{(0)} \partial_z (\tilde{U} \star \tilde{\rho}_j^{(0)}) = 0 \iff \partial_z \tilde{\mu}_i^{(0)} = 0, \quad (21)$$

where  $\tilde{U}$  is the potential  $U$  integrated over all the coordinates but one. We solve this equation and the following ones as  $z$  was defined on the whole line; the asymptotic values  $\rho_i^\pm$  are provided by the matching conditions. The solution is given exactly by the fronts  $w_i$ . It is clear that for finite  $\epsilon$  this solution cannot be matched with the outer expansion, but it should be possible to prove the exponential convergence of  $w_i$  through standard methods (see for example [DOPT]). In that case we would only commit an exponentially small error.

We now find  $\tilde{f}_i^{(1)}$  by examining the  $\epsilon^{-2}$  order:

$$v \cdot \bar{\nu} \partial_z \tilde{f}_i^{(1)} - \bar{\nu} \cdot \nabla_v \tilde{f}_i^{(0)} \partial_z \tilde{g}_i^{(1)} - \bar{\nu} \cdot \nabla_v \tilde{f}_i^{(1)} \partial_z \tilde{g}_i^{(0)} = L_\beta \tilde{f}_i^{(1)}. \quad (22)$$

Note that  $\nu^{(1)} \cdot (v \partial_z \tilde{f}_i^{(0)} - \nabla_v \tilde{f}_i^{(0)} \partial_z \tilde{g}_i^{(0)}) = \beta v \cdot \nu^{(1)} M_\beta \tilde{\rho}_i^{(0)} \partial_z \tilde{\mu}_i^{(0)} = 0$ , because  $\tilde{f}_i^{(0)}$  is solution of the lowest order equation and the bar operators vanish because  $\tilde{\rho}_i^{(0)}$  is function of  $z$  only. Again the solution has to be necessarily Maxwellian in velocity, so that we can write  $\tilde{f}_i^{(1)} = \tilde{\rho}_i^{(1)} M_\beta$  with  $\tilde{\rho}_i^{(1)}$  to be determined by the following equation

$$\partial_z \tilde{\rho}_i^{(1)} + \beta \tilde{\rho}_i^{(0)} \partial_z \tilde{g}_i^{(1)} + \beta \tilde{\rho}_i^{(1)} \tilde{U} \star \partial_z \tilde{\rho}_j^{(0)} = 0. \quad (23)$$

Taking into account that  $-\beta \tilde{U} \star \partial_z \tilde{\rho}_j^{(0)} = \partial_z \ln w_i$ , from the equation for the front, we get

$$\partial_z \left( \frac{1}{\beta} \tilde{\rho}_i^{(1)} (w_i)^{-1} + \tilde{g}_i^{(1)} \right) = 0 \iff \partial_z \tilde{\mu}_i^{(1)} = 0. \quad (24)$$

Hence, the value of  $\tilde{\mu}_1^{(1)} - \tilde{\mu}_2^{(1)}$  in  $z = 0$  is enough to find  $\tilde{\mu}_1^{(1)} - \tilde{\mu}_2^{(1)}$  for any  $z$ . It can be shown (see for details [MM]) that

$$(\tilde{\mu}_1^{(1)} - \tilde{\mu}_2^{(1)})(0, r, t)[w_1]_{-\infty}^{+\infty} = \bar{K}(r, t) S. \quad (25)$$

where  $\bar{K}(r, t)$  is the sum of the principal curvature of  $\bar{\Gamma}_t$  at point  $r$  and time  $t$  and  $S$  is the surface tension for this model:

$$S = \sum_{(i,j) \in \{(1,2), (2,1)\}} \int dz dz' w'_i(z) (z - z') \tilde{U}(z - z') w_j(z') \quad (26)$$

Now we integrate in  $v$  the order  $\epsilon^{-2}$  equation to obtain, after several cancellations due to the fact that  $\tilde{f}_i^{(0)}$  and  $\tilde{f}_i^{(1)}$  are Maxwellian in velocity,

$$w_i' \bar{V} + \partial_z(\bar{v} \cdot \tilde{u}_i^{(2)}) = 0, \quad (27)$$

As  $\epsilon \rightarrow 0$  we can define the hat functions until the interface. Then to determine their values exactly on  $\bar{\Gamma}$  we use the matching conditions imposing that  $\tilde{\mu}_1^{(1)} - \tilde{\mu}_2^{(1)} \rightarrow (\hat{\mu}_1^{(1)})^\pm - (\hat{\mu}_2^{(1)})^\pm$  for  $z \rightarrow \pm\infty$ , so that for  $r \in \bar{\Gamma}_t$

$$[(\hat{\mu}_1^{(1)})^\pm - (\hat{\mu}_2^{(1)})^\pm][w_1]_{-\infty}^{+\infty} = \bar{K}(r, t)S. \quad (28)$$

Moreover  $\tilde{u}_i^{(2)} \rightarrow (\hat{u}_i^{(2)})^\pm$  when  $z \rightarrow \pm\infty$ , so that

$$-\bar{V}[w_i]_{-\infty}^{+\infty} = [\bar{v} \cdot \hat{u}_i^{(2)}]_{-}^{+}, \quad r \in \bar{\Gamma}_t. \quad (29)$$

### 3.7 Limiting equations

We can now collect the results of the previous two subsections, considering  $\epsilon = 0$  because all quantities involved are independent of  $\epsilon$ . Then the system is fully described by the hat functions, because the layer  $\mathcal{N}$  has shrunk to the surface  $\bar{\Gamma}_t$ . We have

$$\begin{cases} \Delta \hat{\mu}_i^{(1)} = 0 & r \in \Omega \setminus \bar{\Gamma}_t \\ (\hat{\mu}_1^{(1)} - \hat{\mu}_2^{(1)})[\bar{\rho}_1^+ - \bar{\rho}_1^-] = \bar{K}(r, t)S & r \in \Omega \setminus \bar{\Gamma}_t \\ \bar{V}(\bar{\rho}_i^+ - \bar{\rho}_i^-) = \left[ \frac{1}{\beta} \bar{\rho}_i \bar{v} \cdot \nabla_r \hat{\mu}_i^{(1)} \right]_{-}^{+} & r \in \bar{\Gamma}_t \end{cases} \quad (30)$$

where  $\bar{\rho}_i = \hat{\rho}_i^{(0)} = \hat{\rho}^+ \chi_{\Omega^+} + \hat{\rho}^- \chi_{\Omega^-}$ ,  $\chi_A$  being the characteristic function of the set  $A$ .

Those equations can be put in a more physically meaningful format, but we need some additional notations. First of all we introduce

$$\bar{\rho}(r) = \frac{\bar{\rho}_1(r) + \bar{\rho}_2(r)}{2} \quad \text{and} \quad \bar{\varphi}(r) = \frac{\bar{\rho}_1(r) - \bar{\rho}_2(r)}{2}.$$

Then let

$$\psi = \hat{\mu}_1^{(1)} - \hat{\mu}_2^{(1)} \quad \text{and} \quad \zeta = \bar{\rho}_1 \hat{\mu}_1^{(1)} + \bar{\rho}_2 \hat{\mu}_2^{(1)}$$

After some algebra we can recast equations (30) in the following way

$$\begin{cases} \Delta_r \psi(r, t) = 0 & r \in \Omega \setminus \bar{\Gamma}_t \\ \psi(r, t) = \frac{S\bar{K}(r, t)}{\bar{\rho}_1^+ - \bar{\rho}_1^-} & r \in \bar{\Gamma}_t \\ \bar{V} = \frac{1}{2\beta[\bar{\rho}_1^+ - \bar{\rho}_1^-]} \left[ \frac{1}{\bar{\rho}} (\bar{\rho}^2 - |\bar{\varphi}|^2) [\bar{v} \cdot \nabla_r \psi]_{-}^{+} + \frac{1}{\bar{\rho}} [\bar{\varphi} \bar{v} \cdot \nabla_r \zeta]_{-}^{+} \right] & r \in \bar{\Gamma}_t. \end{cases} \quad (31)$$

and

$$\begin{cases} \Delta_r \zeta(r, t) = 0 & r \in \Omega \setminus \bar{\Gamma}_t \\ [\zeta]_{-}^{+} = 2|\bar{\varphi}|S\bar{K}(r, t)/(\bar{\rho}_1^{+} - \bar{\rho}_1^{-}) & r \in \bar{\Gamma}_t \\ 0 = [\bar{v} \cdot \nabla_r \zeta]_{-}^{+} & r \in \bar{\Gamma}_t. \end{cases} \quad (32)$$

The limiting motion is a superposition of a Mullins-Sekerka type flow, described by the first set of equations, and of an Hele-Shaw problem, ruled by the second set of equations. We note that the velocity is composed by two terms: one depending on  $\psi$ , the other on  $\zeta$ . Let us call  $V_{MS}$  the former and  $V_{HS}$  the latter.  $V_{MS}$  is the velocity of an interface in the Mullins-Sekerka motion and  $V_{HS}$  is the velocity of an interface in the Hele-Shaw problem.

We remark that the Hele-Shaw motion has more conserved quantities than the Mullins-Sekerka motion. In fact, the former conserves the volume of each connected component of both phases, while the latter conserves only the total volume.

The relative importance of the two contributions  $V_{HS}$  and  $V_{MS}$  is ruled by the coefficients: if  $(\bar{\rho}^{-})^{-1} - (\bar{\rho}^{+})^{-1} \ll 1$  (near the critical point of the coexistence curve) the  $V_{MS}$  term dominates, while for deep quenches the  $V_{HS}$  term prevails.

Equations (31) and (32) are identical to the equations in [OE], describing the sharp interface arising in a polymer blend. In that paper the hydrodynamical equation is a modification of the Cahn-Hilliard equation for a mixture of two fluids, where a Lagrangian multiplier  $p$  (“pressure”) appears to take into account the constraint of constant total density:

$$\begin{aligned} \partial_t \rho_i &= \nabla \cdot (\rho_i \nabla (\mu_i + p)) \quad i = 1, 2 \\ \rho_1 + \rho_2 &= 1. \end{aligned}$$

It is exactly  $p$  which gives rise to the Hele-Shaw contribution to the velocity in the sharp interface limit. If we perform a parabolic scaling on the VFP equations in order to derive the hydrodynamics, we can argue that  $\zeta$  has the same role as  $p$ . Then we conclude that  $\zeta$  describes the pressure in the VFP model.

## 4 Sharp interface limit for the VB model

We introduce again the macroscopic coordinate  $r = \epsilon x$ ,  $x \in \epsilon^{-1}\Omega$ ,  $r \in \Omega$ , the torus of size 1. We wish to study the small  $\epsilon$  behavior of a solution of the VB equations (4). In order to observe diffusive effects one has to consider very long times of order  $\epsilon^{-2}t$ , with  $t$  the macroscopic time. We also choose  $\gamma = \epsilon$  for reasons that will be explained later on. Setting  $f_i^\epsilon(r, v, t) = f_i(\epsilon^{-1}r, v, \epsilon^{-2}t)$ ,  $\rho_i^\epsilon(r, t) = \int dv f_i^\epsilon(r, v, t)$ , the Vlasov-Boltzmann equation, in this space-time scaling, becomes

$$\partial_t f_i^\epsilon + \epsilon^{-1}v \cdot \nabla_r f_i^\epsilon + \epsilon^{-1}F_i^\epsilon \cdot \nabla_v f_i^\epsilon = \epsilon^{-2}J(f_i^\epsilon, f_1^\epsilon + f_2^\epsilon) \quad (33)$$

$$\begin{aligned}
F_i^\epsilon(r, t) &= -\nabla_x \int_{T_1} dr' \epsilon^{-6} U(\epsilon^{-2}|r - r'|) \int_{T_1} dv' f_j^\epsilon(r', v', t). \quad (34) \\
&=: -\nabla_r U^\epsilon * \rho_j^\epsilon
\end{aligned}$$

Consider now a situation in which there is, at the initial time, an interface separating the system in two regions with densities corresponding to the equilibrium values at temperature  $T$  (i.e. with coexistence of two phases, one richer in species 1 and the other richer in species 2). For  $\epsilon$  finite, we approximate the density profiles by one-dimensional fronts in the direction orthogonal to the interface in each point. The fronts interpolate between the two phases on a scale  $\epsilon^2$ . If the interface were flat, this would be a stationary solution of the VB equations. Since the interface is not flat the fluid starts to move because of the unbalance of the pressure on the two sides of the interface (surface tension). This pushes the interface to move with the component of the fluid velocity in the direction of the normal at each point of the surface. Since the initial density in the bulk is the equilibrium and the space-time scaling is diffusive, we expect that the fluid in the bulk will evolve as an incompressible Navier-Stokes (INS) fluid. We recall that the INS equations can be obtained from an equation of the type (33) when the average velocity is small (low Mach numbers). Therefore, the effect of the surface tension has to be suitably small in order not to get too big velocities. The surface tension effect is proportional to the size of the interface and this is the reason why we choose in this case  $\gamma = \epsilon$ .

We construct an expansion in the bulk (outer) and a different expansion close to the interface (inner) and impose matching conditions on an intermediate region. At the first order we find the following free boundary problem for the velocity field  $u$ :

$$\partial_t u + (u \cdot \nabla) u + \nabla p = \eta \Delta u$$

The kinematic viscosity  $\eta$  is obtained from the Boltzmann equation as in [Ce],  $u$  is continuous across the interface  $\Gamma_t$  whose normal velocity is given by

$$v_{\Gamma_t}(r) = -u(r, t) \cdot \nu(r, t)$$

while the pressure is discontinuous at the surface and satisfies Laplace's law

$$(p_+ - p_-) = SK,$$

Here  $(p_+)$   $p_-$  is the pressure on the side of  $\Gamma_t$  (not) containing the normal  $\nu$ ;  $K$  is the mean curvature of  $\Gamma_t$ ,  $S$  is the surface tension given in terms of the fronts  $w_i$  by (26).

Moreover, we get equations for the first correction to the temperature  $T^{(1)}$  (which at order zero is the constant  $\bar{T}$ ) and concentration  $\phi^{(1)}$

$$\begin{aligned}
D_t \phi^{(1)} &= DA_1 \Delta \phi^{(1)} + DA_2 \Delta T^{(1)} \\
D_t T^{(1)} &= k \Delta T^{(1)} + A_3 D_t \phi^{(1)}
\end{aligned} \quad (35)$$

where the diffusion coefficient  $D$ , the heat conductivity  $k$  and the constants  $A_i$  are explicit functions of  $\bar{\rho}, \bar{T}$ . These equations are similar to the ones in the phase field models [CF], but for the facts that in the (35) the non linear term in the concentration is missing and the term proportional to the temperature is replaced by the Laplacian of the temperature times a possibly negative coefficient.

## 5 Open problems

### 5.1 Stability

Consider the excess free energy functional in one dimension on the infinite line defined as

$$\mathcal{G}(\rho_1, \rho_2) - \mathcal{G}(M\rho^+, M\rho^-) \quad (36)$$

Here  $\rho^\pm$  are the values of the densities at infinity,  $\lim_{x \rightarrow \pm\infty} \rho_1 = \rho^\pm = \lim_{x \rightarrow \mp\infty} \rho_2$ . These values are functions of the parameters  $\beta$  and  $C$  (the latter related to the chemical potential) through

$$\ln \rho^+ + \beta \rho^- = C, \quad \ln \rho^- + \beta \rho^+ = C$$

We choose  $\beta$  and  $C$  so that  $\rho^+ - \rho^- > 0$ , namely in the phase transition region of the phase diagram. It is not difficult to extend the arguments in [CCELM] to prove that there exist non homogeneous minimizers of the excess free energy such that  $\lim_{x \rightarrow \pm\infty} f_1(x) = M\rho^\pm, \lim_{x \rightarrow \pm\infty} f_2(x) = M\rho^\mp$ . They are monotone, regular and are solutions of the Euler-Lagrange equations for the functional, namely equations (1). We have called them fronts and their stability properties play an important role in the motion of the interfaces. Since this functional is invariant by translations we construct a one parameter family of fronts by translating a given solution. The same is true for the stationary solutions of (1).

Here we show that all the stationary solutions which are monotone and regular (with first derivative) are thermodynamically stable in the following sense. Consider a small perturbation  $(\alpha_1(r), \alpha_2(r)), r \in \mathbb{R}^d$  of a given stationary solution  $Mw_i$ :

$$f_1 = Mw_1 + \epsilon\alpha_1 \quad \text{and} \quad f_2 = Mw_2 + \epsilon\alpha_2,$$

such that  $\int dx dv \alpha_i = 0$ . We have that

$$\begin{aligned} & \mathcal{G}(Mw_1 + \epsilon\alpha_1, Mw_2 + \epsilon\alpha_2) - \mathcal{G}(Mw_1, Mw_2) \\ &= S(f/M) + \mathcal{F}(w_1 + \epsilon\eta_1, w_2 + \epsilon\eta_2) - \mathcal{F}(w_1, w_2) \end{aligned} \quad (37)$$

where  $\eta_i = \int dv \alpha_i$ ,  $\mathcal{F}$  is defined in (3) and  $S(f/M)$  is the relative entropy between the state  $(f_1, f_2)$  and the Maxwellian state  $(M \int dv f_1, M \int dv f_2)$  defined as

$$S(f/M) = \sum_{i=1,2} \int dx dv f_i (\log f_i - \log(M \int dv f_i)).$$

We easily compute that

$$= \epsilon^2 \left[ \frac{1}{2\beta} \left[ \int_{\mathbb{R}} \frac{\eta_1^2(r)}{\bar{\rho}_1(z)} dr + \int_{\mathbb{R}} \frac{\eta_2^2(r)}{\bar{\rho}_2(z)} dr \right] + \int_{\mathbb{R}} \int_{\mathbb{R}} U(|r-r'|) \eta_1(r) \eta_2(r') dr dr' \right] + \mathcal{O}(\epsilon^3)$$

We now define the operator  $\mathcal{A}$  through the quadratic form

$$\begin{aligned} \langle (\eta_1, \eta_2), \mathcal{A}(\eta_1, \eta_2) \rangle &= \frac{1}{2\beta} \left[ \int_{\mathbb{R}} \frac{\eta_1^2(r)}{w(z)} dr + \int_{\mathbb{R}} \frac{\eta_2^2(r)}{w_2(z')} dr' \right] \\ &+ \int_{\mathbb{R}} \int_{\mathbb{R}} U(|r-r'|) \eta_1(r) \eta_2(r') dr dr' . \end{aligned}$$

We have that [wip]

**Proposition** *The operator  $\mathcal{A}$  is positive with*

$$\mathcal{A}(\eta_1, \eta_2) = (0, 0)$$

*if and only if  $(\eta_1, \eta_2)$  is a scalar multiple of  $(w'_1, w'_2)$ .*

The main ingredients in the proof are the Euler-Lagrange equations and the monotonicity properties. Moreover, it is well known that the relative entropy is non negative and is zero if and only if  $f_i$  is Maxwellian. The conclusion is that the difference

$$\mathcal{G}(Mw_1 + \epsilon\alpha_1, Mw_2 + \epsilon\alpha_2) - \mathcal{G}(Mw_1, Mw_2)$$

is nonnegative for  $\epsilon$  small and is zero if and only if  $f_i = Mw'_i$ .

A natural and relevant question is if the stationary solutions are also dynamically stable versus the evolution (1). The fact that the excess free energy decreases should force a small perturbation to tend to the family of fronts and the conservation law should select one of the family. The invariance by translation of the theory is one of the main difficulty in establishing the result. A similar difficulty has been faced in [CCO2] for a conservative dynamics describing the evolution on a mesoscopic scale of the magnetization for a Kac-Ising model. Relaxation to the stationary state and rate of convergence have been established in this case. On the other hand, a new approach based on a suitable micro-macro decomposition of the distribution function has been successful in providing many stability results for kinetic models [LY], [G], [SG]. We think that a suitable merging of these methods could provide stability results for the Vlasov-Fokker-Plank and also for the Vlasov-Boltzmann dynamics.

## 5.2 Surface tension

In more than one dimension the geometric structure of the nonuniform minimizers is not clear. We can consider an approximation for large volume of the

free energy, computed on the non uniform minimizers: the first term is given by the bulk free energy, obtained in the infinite volume limit, the next term is a correction proportional to the surface area separating the two phases (divided by the volume) which corresponds to the surface tension:

$$\inf_{\rho_i: \int dx \rho_i = n_i} \mathcal{F}_\Omega(\{\rho_1, \rho_2\}) = f(n_1, n_2)|\Omega| + b(n_1, n_2)|\Omega|^{1-1/d} + \text{lower order terms}$$

where  $b(n_1, n_2) = S|\Gamma|$ , with  $|\Gamma| = da(d)r_0^{d-1}$  the surface of the sphere with equimolar radius  $r_0$  (depending on  $n_1, n_2$ ),  $a(d)$  being the volume of the unit sphere in  $\mathbb{R}^d$ , and  $S$  is the surface tension (26). Moreover,

$$f(n_1, n_2) = CE \left[ \sum_i n_i \log n_i + \alpha n_1 n_2 \right].$$

where  $\alpha = \int_{\mathbb{R}^d} U(x) dx$ , and  $CEf(n_1, n_2)$  denotes the maximal convex function lying below  $f$ .

Then, the phase boundaries will be arranged so to have the minimum surface area, and their shape will be determined by the solution of the isoperimetric problem on the torus. The surface tension correction has been computed for the case of the Cahn-Hilliard functional in literature and in [CCELM2] the analysis has been extended to include also the possibility that in some case the minimizing profile of the density  $\rho$  might correspond to the “dissolution” of a droplet of the minority phase, as proved for the 2d Ising model in [BCK]. In [CCELM1], [CCELM2] the critical density for droplet formation for the Cahn-Hilliard functional has been exactly determined. The Cahn-Hilliard functional is defined as

$$\mathcal{F}_\Omega(\{m\}) = \int_\Omega \left( \frac{\theta^2}{2} |\nabla m|^2 + F(m(x)) \right) dx, \quad (38)$$

where  $F(t) = (t^2 - 1)^2/4$  is a symmetric double well potential which has minima at  $t = \pm 1$ .

One of the ingredient is a Hilbert expansion for the minimizers in the parameter  $\frac{1}{L}$  ( $L$  the linear dimension of the box). This approach could be useful to study also the case of functionals involving non local interactions, like  $\mathcal{F}$ , because there is a close formal connection between the Cahn-Hilliard free energy functional and the non-local free energy functionals. To see that, let us write the functional (3) as

$$\begin{aligned} \mathcal{F}(\rho_1, \rho_2) = & \int_\Omega dx [(\rho_1 \ln \rho_1)(x) + (\rho_2 \ln \rho_2)(x) + \beta \alpha \rho_1(x) \rho_2(y)] \\ & - \frac{1}{2} \int_{\Omega \times \Omega} dx dy \gamma^3 U(\gamma(x-y)) [\rho_1(x) - \rho_1(y)] [\rho_2(x) - \rho_2(y)] \end{aligned}$$

Making the approximation that the densities vary sufficiently slowly on the range of the potential we replace in  $\mathcal{F}(\rho_1, \rho_2)$  the first-order Taylor approximation

$$\rho_i(y) \approx \rho_i(x) + \nabla \rho_i(x) \cdot (y - x)$$

getting

$$\mathcal{F}(\rho_1, \rho_2) \approx \int_{\Omega} \left[ f(\rho_1, \rho_2) - \frac{\theta^2}{2} \nabla \rho_1(x) \nabla \rho_2(x) \right] dx ,$$

with  $\theta^2 = \int_{\mathbb{R}^d} x^2 U(x) dx$ . In terms of the variables  $\phi$  and  $\rho$

$$\mathcal{F}(\rho, \phi) \approx \int_{\Omega} \left[ f(\rho, \phi) + \frac{\theta^2}{2} [(\nabla \phi(x))^2 - (\nabla \rho(x))^2] \right] dx ,$$

$$f(\rho, \phi) = \frac{\rho + \phi}{2} \log \frac{\rho + \phi}{2} + \frac{\rho - \phi}{2} \log \frac{\rho - \phi}{2} + \frac{1}{4} \alpha (\rho^2 - \phi^2)$$

This functional reduces to a Cahn-Hilliard functional type (38) for  $\rho$  constant with  $f(\rho, \phi)$  for  $\alpha$  low enough a double-well potential whose essential features are represented by  $F(m) = (m^2 - 1)^2/4$ .

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