Chapter 1

Nonlocal modelling of phase separation

In this chapter we introduce the different existing models, which describe phase separation.

1.1 Cahn-Hillard model

In this section we will describe the derivation procedure of the Cahn-Hillard model of isothermal phase separation. For isotropic heterogeneous binary systems with constant volume filling a domain Ω, the standard total free energy functional is postulated in the form

$$F_{CH}(u) = \int_{\Omega} F(u)dx, \tag{1.1}$$

with the energy density

$$F(u) = f(u) + \kappa u(1-u) + \frac{\lambda}{2}|\nabla u|^2, \tag{1.2}$$

which comprises the free energy density $f(u)+\kappa u(1-u)$ (for sufficiently large κ, and convex f) for the concentration u and the gradient term with a positive constant λ, representing an interfacial energy ("penalty term") between the phases. Qualitative speaking $f(u) + \kappa u(1-u)$ forms a so-called double well potential. If the system is isolated at the boundary (it means that there is no mass flux across the boundary) its isothermal equilibria are given by the stationary points of (1.1) subject to the additional constraint on the mean value of the concentration

$$\frac{1}{|\Omega|}\int_{\Omega} u(x)dx = \bar{u}. \tag{1.3}$$

with a given constant $\bar{u}$. This constraint means that the total mass of components A and B in the sample Ω is prescribed. Minimizing (1.1) under the constraint (1.3) one gets the corresponding Euler-Lagrange equation

$$f'(u) + \kappa(1-2u) - \lambda\Delta u = v \qquad \text{in } \Omega,$$

subject to the natural boundary condition

$$\nabla u \cdot n = 0 \qquad \text{on } \Gamma = \partial\Omega,$$

where n denotes the outward unit normal to Γ. Here v is the Lagrange multiplier corresponding to constraint (1.3), given by

$$v = \frac{\delta}{\delta u} F(u),$$

where $(\delta/\delta u)F_{CH}$ denotes the (formal) first variational derivative of the free energy functional F_{CH}, which may be interpreted as a generalized thermodynamic force, acting at each point $x \in \Omega$, that tends to decrease the value of the total free energy (see [6]). The first variational derivative of F_{CH} is defined by

$$\left\langle \varsigma, \frac{\delta}{\delta u} F(u) \right\rangle := \left.\frac{d}{d\epsilon}\right|_{\epsilon=0} F_{CH}(u + \epsilon\varsigma).$$

We remark that the gradient term in (1.2) has a smoothing effect on interfaces between different phases. In consequence, jumps of u (spatial inhomogenities) are not allowed, instead different phases are separated by walls, that are small subregions with rapid changes of u. The thickness of these walls is related to the value of λ. It is well-known that in the limit $\lambda \to 0$ the surface area of the interface is minimized locally in Ω. This corresponds to a free energy of the form

$$F(u) = \sigma \mathcal{H}^2(S(u)),$$

where σ is the *surface tension*, $S(u)$ is the discontinuity set of u and $\mathcal{H}^2$ denotes the 2-dimensional surface measure (see [25]). The dynamics of phase separation is described as follows. Let $u(t)$ be the concentration at time t, and v be the difference between the chemical potentials v_1, v_2 of the components A and B. It is defined as the first variation (see [32]) of the free energy functional

$$v = \frac{\delta}{\delta u} F(u), \tag{1.4}$$

that is

$$v = f'(u) + \kappa(1 - 2u) - \lambda \Delta u.$$

Let $j = j_1$ and j_2 denote the mass fluxes of A and B. Is is assumed that $j_1 + j_2 = 0$, and generalized Fick's law,

$$j = -\mu \nabla v, \tag{1.5}$$

is postulated, where $\mu \geq 0$ is a parameter (function) denoting a suitable diffusive mobility. Considering the mass balance law

$$\partial_t u + \nabla \cdot j = 0, \tag{1.6}$$

one ends up with the classical Cahn-Hillard equation

$$\partial_t u - \nabla \cdot [\,\mu \nabla (f'(u) + \kappa(1-2u) - \lambda \Delta u)] = 0, \tag{1.7}$$

where the boundary condition guarantees mass conservation

$$\int_\Omega u(t,x)dx = \int_\Omega u(0,x)dx.$$

A slightly more complicated model is the so called viscous Cahn-Hillard equation. This equation is derived by postulating the chemical potential in the following way

$$v := \frac{\delta}{\delta u} F(u) + u_t. \tag{1.8}$$

Here v contains an additional rate term u_t, which describes viscosity. For example (see [26]) in viscous systems, such as polymer-polymer systems, the viscosity can be important. Another justification for (1.8) was made by Gurtin [21] and is based on a new balance law for *microforces* and which takes into account the working of internal microforces (we can note that microforces describe forces which are associated with microscopic configurations of atoms, whereas standard forces are associated with macroscopic lengthscales, hence a reason to consider separate balance laws for microforces and standard forces). For an isotropic material, (1.8) leads to the following generalization of equation (1.7):

$$\partial_t u - \nabla \cdot [\,\mu \nabla (f'(u) + \kappa(1-2u) - \lambda \Delta u + u_t)] = 0,$$

where the term u_t in (1.8) describes the influence of the internal microforces. These equations (1.7) and (1.8) have been studied intensively; see e.g. the review articles [12] and [27].

1.2 Nonlocal Cahn-Hillard equation

Inspecting Cahn-Hillards arguments (see [7], *"... would expect that the local free energy per molecule, F(u), in region of nonuniform composition will depend both on the local composition and on the composition of the immidiate environment..."*) establishing (1.1) as the free energy of binary systems it seems to be reasonable and even more adequate [15] to choose an alternative expression for the energy density like

$$F(u) = f(u) + \frac{1}{2} u w,$$

where

$$w(x) := \int_\Omega \mathcal{K}(|x-y|)(1-2u(y))dy. \tag{1.9}$$

The kernel $\mathcal{K}$ of the integral term (1.9) describes *nonlocal interactions* [8]. The nonlocal total free energy reads

$$F_{NL}(u) = \int_{\Omega} F(u) dx. \tag{1.10}$$

In equilibrium Statistical Mechanics functionals of the form (1.10) arise as free energies of continuum limits of Ising spin systems on lattices; in that setting u represents a macroscopic magnetization density and $\mathcal{K}$ is a ferromagnetic Kac potential (cf. [16] and references therein). By using (1.4) and the symmetry of w we get

$$v = f'(u) + w. \tag{1.11}$$

Together with (1.5)-(1.6) this yields the nonlocal Cahn-Hillard equation

$$u_t - \nabla \cdot (\mu \nabla (f'(u) + w)) = 0.$$

Assuming that f is strictly convex, the strictly monotone function f' has an inverse function f'^{-1}. Thus, as a consequence of (1.11) we automatically get the a priori estimate

$$u(x) \in \operatorname{Im}(f'^{-1}).$$

In standard cases one usually chooses for f the convex (Information) entropy function

$$f(u) = u \log(u) + (1-u) \log(1-u).$$

Consequently we have

$$f'(u) = \log\left(\frac{u}{1-u}\right) \quad \text{and} \quad u = f'^{-1}(v-w) = \frac{1}{1+\exp(v-w)}.$$

Here the function f'^{-1} is the Fermi function, whose image is the interval $[0,1]$. Thus, the nonlocal model naturally satisfies the physical requirement

$$0 \leq u(x) \leq 1, \quad \forall t \geq 0.$$

and the maximum principle is available, which is not true for fourth order equations like in the case of the local Cahn-Hillard equations.

Nonlocal viscous model: We aim to formulate a general nonlocal model, which also takes into accout viscosity effects. In the local theory this was done by adding a rate term to the chemical potential (1.8). Now we are going to formulate this additional term in the nonlocal philosophy, so we not only want to get nonlocality in space (1.11) but also nonlocality in time. The chemical potential in our case is given by

$$v := \frac{\delta}{\delta u} F(u) + \psi, \qquad -\gamma \Delta \psi_t + \psi = u_t, \quad \gamma > 0. \tag{1.12}$$

Here γ is a modell parameter, which is positive and guarantees the nonlocal structure of the additional term ψ in v. This means in Gurtin's language that the influence of microforces is nonlocal. At this moment we are not able to formulate a new nonlocal balance law for nonlocal microforces similar to the balance law in Gurtin [21]. We think that we recover the previous local viscous model (1.8) by choosing $\gamma = 0$. Thus our model is a real expansion to previous existing models. From mathematical point of view the term $-\gamma\Delta\psi_t$ in our model has a regularizing effect. Taking into account (1.12) we get the *nonlocal viscous Cahn-Hillard equation*:

$$\begin{aligned} u_t - \nabla \cdot \mu \nabla v = 0, \quad & v = f'(u) + w + \psi, \\ w(x) = \int\limits_{\Omega} & \mathcal{K}(|x-y|)(1-2u(y))dy, \\ -\gamma\Delta\psi_t + \psi = u_t, \quad & \gamma > 0. \end{aligned} \tag{1.13}$$

Here we have to complement (1.13) with suitable initial and boundary conditions. This will be done in the next chapter.