EXACT MACROSCOPIC DESCRIPTION OF PHASE SEGREGATION IN MODEL ALLOYS WITH LONG RANGE INTERACTIONS

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Abstract. We derive an exact nonlinear non-local macroscopic equation for the time evolution of the conserved order parameter $\rho(\mathbf{r}, t)$ of a microscopic model binary alloy undergoing phase segregation: a d–dimensional lattice gas evolving via Kawasaki exchange dynamics, satisfying detailed balance for a Hamiltonian with a long range pair potential $\gamma^d J(\gamma|x|)$. The macroscopic evolution is on the spatial scale γ^{-1} and time scale γ^{-2}, in the limit $\gamma \to 0$. The domain coarsening, described by interface motion, is similar to that obtained from the Cahn-Hilliard equation.

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The process of phase segregation in alloys, following a quench (sudden cooling) from a high temperature into the miscibility gap, is a problem of great practical importance and theoretical interest. The time evolution of the local macroscopic order parameter, e.g. the concentration of A-atoms in a binary A-B alloy, is commonly described by the nonlinear Cahn-Hilliard equation (CHE)[1]. While the derivation of this equation is based on arguments embodying deep physical insight, there does not exist (to our knowledge) any microscopic model system, for which the CHE, or any modifications of it proposed so far [1], gives the exact macroscopic description.

In this note we rigorously derive a macroscopic equation, eq.(7), describing phase segregation in systems with long range interactions, the same models whose equilibrium properties are described by the van der Waals equation of state (with the

Maxwell construction) [2]. This equation, while structurally different from the CHE, yields similar behavior for the late stages of the coarsening process; this regime appears to be quite universal, see [1].

We begin by giving a simple heuristic derivation of a general CHE as an adaptation of the nonlinear diffusion equation

$$\frac{\partial \rho(\mathbf{r},t)}{\partial t} = \nabla \cdot [D(\rho)\nabla \rho] = \nabla \cdot [\sigma(\rho)\nabla \mu_{eq}(\rho)] = \nabla \cdot \left[\sigma(\rho)\nabla\left(\frac{\delta F_{eq}}{\delta \rho}\right)\right] \tag{1}$$

describing the evolution of a nonuniform macroscopic concentration profile $\rho(\mathbf{r},t)$ toward the uniform equilibrium state. In (1) $F_{eq} = \int f_{eq}(\rho)d\mathbf{r}$, D is the diffusion coefficient, $\mu_{eq}(\rho) = f'_{eq}(\rho)$ is the chemical potential, given by the derivative of the equilibrium Helmholtz free energy per unit volume $f_{eq}(\rho)$ in a system with uniform density ρ, and σ is the Onsager mobility, $\sigma = \chi D$, where $\chi = (\partial\mu_{eq}/\partial\rho)^{-1}$ is the compressibility (or susceptibility).

Eq. (1) can be derived rigorously for a variety of microscopic model systems when $\mathbf{r}$ and t are in units scaled by ϵ^{-1} and ϵ^{-2} respectively, compared to the microscopic units, in the limit $\epsilon \to 0$ [3]. The dynamics in these models are generally stochastic (although some deterministic examples are also available), conserve (only) particle number and have the equilibrium Gibbs distribution as the only stationary state. This includes the Ising model with Kawasaki dynamics for $T > T_c$ in $d = 2$, [4], and the continuous spin Ginzburg–Landau model with conservative Langevin dynamics, for all T and all dimensions [5]. In the coexistence region the mobility $\sigma(\rho)$, which is always given by a Green-Kubo formula , remains finite while $\mu_{eq}(\rho)$ is constant, so $\chi^{-1} = 0$ and $D(\rho) = \sigma(\rho)/\chi(\rho) = 0$ there [6]. Hence, when the range of densities in a nonuniform system lies within the miscibility gap, the right–hand side of (1) vanishes. This may seem at first paradoxical but one should remember that we are considering in (1) density variations on the macroscopic spatial scale ϵ^{-1} which is very large compared to the interaction range. This means that regions of size ϵ^{-1} can contain essentially equilibrated domains of both phases. Variations of the density on the spatial scale ϵ^{-1} can therefore be compensated for by changes in the volume fraction of the two phases. Of course the system will still try to aggregate further to reduce interfacial area but this evolution will occur on a time scale larger than ϵ^{-2}, so it is not seen in (1).

The CHE with some mobility $\sigma(\rho)$ can be obtained formally [1] by replacing F_{eq} (and thus $\mu_{eq}(\rho)$) in the right side of (1) by a free energy functional $\tilde{F}(\{\rho(\mathbf{r},t)\})$

$$\tilde{F} = \int d\mathbf{r} \left[\tilde{f}(\rho) + \frac{1}{2}\zeta(\nabla\rho)^2\right], \qquad \mu = \tilde{f}'(\rho) - \zeta\nabla^2\rho \tag{2}$$

where $\tilde{f}(\rho)$ is a *constrained equilibrium* free energy density which has a single minimum above T_c and a double well shape at $T < T_c$, and ζ is a constant related to the surface tension between the phases. This gives the general CHE

$$\frac{\partial\rho}{\partial t} = \nabla \cdot \left\{\tilde{\sigma}(\rho)\nabla\left[\tilde{f}'(\rho) - \zeta\nabla^2\rho\right]\right\}. \tag{3}$$

$\tilde{f}(\rho)$ is often taken to be a quadratic polynomial in ρ and $\tilde{\sigma}(\rho)$ set equal to a constant: one then obtains the *standard* CHE [1,7].

As noted, however, the model systems yielding (1) give $\partial\rho/\partial t = 0$ in the miscibility gap, where $f''_{eq}(\rho) = 0$, so (3) does not seem to have any microscopic derivation. To overcome this problem and find a macroscopic equation which describes exactly the phase segregation of some microscopic model, we consider the dynamics of a system in which the interaction responsible for phase segregation has a range, γ^{-1}, which is large compared to the interparticle spacings. The equilibrium properties of such a system are well known [2]: here we consider the evolution of the order parameter on the spatial scale γ^{-1} (or a hundred times as large).

The particles live in a cube Λ_γ of side $\ell\gamma^{-1}$, on the d-dimensional lattice $\mathbb{Z}^d$. The time evolution of the configuration η_t at time t, specified by $\eta_t(x) = 0$ or 1 for all $x \in \Lambda_\gamma$, proceeds via a Kawasaki type exchange dynamics, specified by giving the rate for the exchange of the occupancy of nearest neighbor sites x and y (using periodic boundary conditions) in the configurations η, i.e. for the transition $\eta \to \eta^{x,y}$. We take this rate to be

$$c_\gamma(x,y;\eta) = \exp\left\{-\frac{1}{2}\beta\left[H_\gamma(\eta^{x,y}) - H_\gamma(\eta)\right]\right\} \tag{4}$$

where $\beta \geq 0$ is the reciprocal temperature, and

$$H_\gamma(\eta) = -\frac{1}{2} \sum_{x,y \in \Lambda_\gamma} \gamma^d J(\gamma(x-y))\eta(x)\eta(y) \tag{5}$$

and $J(\mathbf{r}) \geq 0$ is a smooth function with $\int J(\mathbf{r})d\mathbf{r} = \alpha$. We choose ℓ to be much larger than the range of $J(\mathbf{r})$, so we don't have to worry about periodicity, and for simplicity let $J(\mathbf{r})$ depend only on $|\mathbf{r}|$; the anisotropic case can be treated too [8]. Assume furthermore that J is decreasing in $|\mathbf{r}|$. The dynamics (4) satisfies detailed balance w.r.t., the Gibbs measure $Z_N^{-1} \exp[-\beta H_\gamma(\eta)]$, with any fixed total number of particles $N = \sum_{x \in \Lambda_\gamma} \eta(\mathbf{x})$, which is the unique stationary measure (for N fixed).

We are interested in initial conditions described by a probability distribution (Prob_γ) on the configuration space (Prob_γ can be concentrated on one configuration) such that when $\gamma \to 0$, the typical microscopic configuration resembles more and more a smooth profile ρ_0 stretched by γ^{-1}, where ρ_0 is a smooth function from T^d, the d-dimensional torus of length ℓ, to [0,1]. More precisely, we shall require that for any continuous function $\phi(\mathbf{r})$ on T^d and every $\delta > 0$

$$\lim_{\gamma \to 0} \mathrm{Prob}_\gamma \left(\left| \gamma^d \sum_{x \in \Lambda_\gamma} \phi(\gamma x)\eta(x) - \int_{T^d} \phi(\mathbf{r})\rho_0(\mathbf{r})\mathrm{d}\mathbf{r} \right| > \delta \right) = 0. \tag{6}$$

Condition (6) is clearly satisfied if Prob_γ is such that $\langle \eta(x) \rangle = \rho_0(\gamma x)$ for all x in Λ_γ and the occupation number of the sites are independent but this is not required. We could, for example, also have initial conditions concentrated on single periodic configurations, etc. Our Theorem now says that (6) holds also in the limit $\gamma \to 0$ for $\eta_{t\gamma^{-2}}$, if we replace ρ_0 with $\rho(\mathbf{r},t)$, the solution of the integrodifferential equation.

$$\partial_t \rho(\mathbf{r},t) = \nabla \cdot \left[\nabla \rho(\mathbf{r},t) - \beta \rho(\mathbf{r},t)(1-\rho(\mathbf{r},t)) \int_{T^d} \nabla J(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}')\mathrm{d}\mathbf{r}' \right] \tag{7}$$

with initial value $\rho(\mathbf{r},0) = \rho_0(\mathbf{r})$. Eq.(7) is valid for all β and $t \in [0,\infty)$, including the miscibility gap. Existence and uniqueness of a suitable weak solution of (7) globally in time are part of the proof of this Theorem. Moreover it can be shown that $\rho(\mathbf{r},t)$ is bounded between 0 and 1 and that if $\rho_0(\mathbf{r})$ is smooth, then $\rho(\mathbf{r},t)$ is smooth. Further results on the behavior of this particle system on a macroscopic scale can be found in [9].

The result stated here is proven in [8] using the technique introduced in [10], see also [9]. It is essentially a consequence of the fact that, in a nearest neighbor exchange, due to the long range interactions, the energy difference is of order γ. Hence, the dynamics is a superposition of a Laplacian and a weak ($O(\gamma)$) asymmetric perturbation which generates, on the macroscopic scale, a *force* term given by the gradient of the (long range) energy density at $\mathbf{r}$, $\int J(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}')d\mathbf{r}'$. This force term is multiplied by a conductivity $\beta\rho(1-\rho)$: β measures the bias introduced in the exchange rates c_γ, given in (4), by energy differences, while $\rho(1-\rho)$ gives the rate at which exchanges actually take place when a particular site is picked at random and the system is *locally described* by a product measure with average density ρ. We note that the product measure is the correct equilibrium measure for our *reference* system, i.e. the system without the weak long range interaction J.

The analysis and (7) remain unchanged if we replace (4) with a general rate $c_\gamma(x,y;\eta) = \Phi\left(\beta\left[H_\gamma(\eta^{x,y}) - H_\gamma(\eta)\right]\right)$ which satisfies the detailed balance condition [3] $\Phi(E) = \Phi(-E)\exp(-E)$ as long as we rescale our time by $\Phi(0)$ and Φ is smooth.

It is now an observation, which at first sight appears surprising, that (7) can be rewritten in the form

$$\frac{\partial\rho(\mathbf{r},t)}{\partial t} = \nabla\cdot\left[\sigma^0(\rho)\nabla\left(\frac{\delta\mathcal{F}^0}{\delta\rho}\right)\right] \tag{8}$$

where $\sigma^0(\rho) = \beta\rho(1-\rho)$ and

$$\mathcal{F}^0(\{\rho\}) = \int f_c^0(\rho(\mathbf{r}))d\mathbf{r} + \frac{1}{4}\int\int J(\mathbf{r}-\mathbf{r}')\left[\rho(\mathbf{r})-\rho(\mathbf{r}')\right]^2 d\mathbf{r}d\mathbf{r}' \tag{9}$$

with $f_c^0(\rho) = f_{eq}^0(\rho) - \frac{1}{2}\alpha\rho^2$ and $f_{eq}^0(\rho) = -\beta^{-1}s(\rho)$; $s(\rho) = -\rho\log\rho - (1-\rho)\log(1-\rho)$. $f_{eq}^0(\rho)$ is clearly just the free energy density of the reference system while $\mathcal{F}^0(\{\rho\})$, which is a non-local functional of the density, is just the total constrained free energy of this system in the limit $\gamma\to 0$, see [2, 11]. For ρ constant the second term in (9) vanishes, and $f_c^0(\rho)$ is in fact the correct equilibrium free energy density as long as $\beta \le \beta_c = 1/T_c = 4\alpha^{-1}$. If $\beta > \beta_c$, $f_c^0(\rho)$ has a double minimum at $\rho = \rho_\beta^\pm$, the two nontrivial solutions of $\log(\rho/(1-\rho)) = \beta\alpha(\rho - 1/2)$, and the correct free energy is then obtained by the double tangent construction [2, 11].

The mobility $\sigma^0(\rho)$, as in (1), is just χD, with $\chi = \chi^0 = \beta\rho(1-\rho)$ and $D = D^0 = 1$ for the reference system [3]. It is this, at first sight fortuitous, coincidence of χ^0 with the *conductivity* appearing in front of the long range force term on the right site of (7) which makes it possible to transform (7) into the physically more revealing form (8). Further thought shows however that the form (8) is really forced by the requirement that the Gibbs measure $\exp\{-\beta H_\gamma\}/Z_N$ be stationary for the dynamics. This is most easily seen by adding to the reference system not H_γ but a one body external potential, $U_\gamma(\eta) = \sum_x U(\gamma x)\eta(x)$, in which case the integral in (7) is replaced by $\nabla U(\mathbf{r})$. The coincidence is now simply the Einstein relation (or linear response theory) between the conductivity for the current induced by the weak perturbation U_γ and the diffusion coefficient D^0 of the reference system, c.f. ref. [2, p. 233–234] and [12].

The superscript ^{0} in (8) and (9) is to remind us that our reference system is one in which there are no short range interactions (except for the hard core exclusion preventing multiple occupancy at a site). We consider now the macroscopic dynamics of a system in which there is also a short range interaction $H_s(\eta)$, making the total energy $H = H_s + H_\gamma$. The system evolves microscopically according to a Kawasaki exchange rate $c_\gamma(x,y;\eta)$ which satisfies detailed balance with respect to the Gibbs measure, $\exp\{-\beta[H_s + H_\gamma]\}/Z_N$ (Z_N is the corresponding canonical partition function). The dynamics of this system, at a temperature β^{-1} above the critical temperature of the reference system, will again be a superposition of diffusive dynamics for the reference system and a current linear in the force coming from the weak long-range interaction. Using the same reasoning as before, the conductivity coefficient in front of this force, given by the integral in (7), must, by the stationarity of equilibrium measure (Einstein relation), be equal to the mobility σ of the reference system. It is known [2, 11] that the constrained free energy of such a system are obtained from those with $H_s = 0$ by replacing in the integrand of (9) $f^0_{eq}(\rho)$ by $f_{eq}(\rho)$, the equilibrium free energy density of the reference system with short range Hamiltonian $H_s(\eta)$. Hence we expect that the macroscopic evolution of such a system will again be given by an equation of the form (8) and (9) without the superscript ^{0}, i.e. $f_c^0 \to f_{eq} - (1/2)\alpha\rho^2$ (which may have two minima, so that there will be phase segregation) and $\sigma^0 \to \sigma = \chi D$, where D is the diffusion coefficient (generally ρ dependent) and χ the susceptibility of the reference system. This has already been proven explicitly in some cases [13] and it is surely quite general.

We shall now compare solutions of the evolution (7) with those of the CHE ((2) and (3)) in the late stage of the domain coarsening process [1]: at this stage there are well defined interfaces between domains of linear sizes L, large compared to that of the interface width, in which the densities are close to those of the pure phases, $\rho_\beta^\pm$. In this *sharp* interface limit, the CHE has been studied analytically, mostly by means of formal matched asymptotic expansions [7,14,15] and this type of analysis is extended in [8] to eq.(7). Since in this regime the mean curvature of the boundary of the domains is $O(1/L)$, the local structure of the interface is given in first approximation by the one dimensional *instantonic* solutions of (7). These are stationary solutions $U_\beta(z)$ of (7) which depend only on one coordinate of $\mathbf{r}$ (in this case $\mathbf{r}$ is in $\mathbb{R}^d$), say $z = r_1$, which connect in a monotone increasing way the low (ρ_β^-) and high (ρ_β^+) density phases, i.e. $U_\beta(z) \to \rho_\beta^\pm$ as $z \to \pm\infty$. Once we fix $U_\beta(0) = 1/2$, there is only one (smooth) *instantonic* profile [16], given by the solution of

$$m_\beta(z) = \tanh\left\{\frac{\beta}{2}\int \tilde{J}(z-z')m_\beta(z')dz'\right\} \tag{10}$$

where $m_\beta(z) = 2U_\beta(z) - 1$ and $\tilde{J}(r_1) = \int_{\mathbb{R}^{d-1}} J(\mathbf{r})\mathrm{d}r_2 \ldots \mathrm{d}r_d$.

Let us now consider the evolution eq.(7) on a torus $L\Omega$, where Ω is a fixed $d-$dimensional torus. Setting $\mathbf{x} = L^{-1}\mathbf{r}$ and $\tau_q = L^{-q}t$, $\rho^L(\mathbf{x}, \tau_q) = \rho(L\mathbf{x}, L^q\tau_q)$, the equation becomes

$$L^{2-q}\partial_{\tau_q}\rho^L(\mathbf{x}, \tau_q) = \nabla\left[\sigma(\rho^L(\mathbf{x}, \tau_q))\nabla\mu^L(\mathbf{x}, \tau_q)\right] \tag{11}$$

in which $\mu^L(\rho^L)(\mathbf{x}, \tau) = -s'(\rho^L(\mathbf{x}, \tau)) - \beta\int J_L(\mathbf{x}-\mathbf{x}')\rho^L(\mathbf{x}', \tau)d\mathbf{x}'$ and $J_L(\mathbf{x}) = L^dJ(L\mathbf{x})$.

We are interested in cases in which $\rho^L(\mathbf{x}, 0) = \rho_\beta^\pm + O(1/L)$ unless $\mathbf{x}$ is at a distance $O(1/L)$ from a (hyper)surface $\Gamma_0 \subset \Omega$, which is the interface. In the thin ($O(1/L)$) layer around the interface, ρ^L will be approximated by a stationary instanton. The relevant time scale for such an initial condition is given by $q = 3$, as for the CHE [7,14]. A formal asymptotic expansion, based mainly on the assumption that the interface is stable, can be used (as in [7] for the CHE) to study the evolution of the interface Γ_{τ_3} for τ_3 positive. One obtains [8] that the normal velocity of a point x on Γ_{τ_3} is given by

$$V_3(\mathbf{x}) = \frac{\sigma_\beta}{2\rho_\beta^+ - 1}[\nu \cdot \nabla \mu_1]_-^+(\mathbf{x}) \tag{12}$$

where $\nu(\mathbf{x})$ is the unit normal at the point $\mathbf{x}$ of the interface, pointing in the direction of the denser phase; $\sigma_\beta = \beta\rho_\beta^+(1-\rho_\beta^+) = \beta\rho_\beta^-(1-\rho_\beta^-)$ is the mobility on the homogeneous phase. The expression between square brackets is the jump of the normal derivative of the first order correction to the chemical potential ($\mu^L = \mu_0 + L^{-1}\mu_1 + O(L^{-2})$) across the interface, in the direction ν. Such a correction can be computed by solving the following static problem

$$\begin{cases} \Delta\mu_1(\mathbf{x}) = 0 & \text{for } \mathbf{x} \in \Omega_{\tau_3}^+ \cup \Omega_{\tau_3}^- \\ \mu_1(\mathbf{x}) = -S_\beta K(\mathbf{x})/(2\rho_\beta^+ - 1) & \text{for } \mathbf{x} \in \Gamma_{\tau_3} \end{cases} \tag{13}$$

in which we have used the natural decomposition of Ω into an interface and the domains $\Omega_{\tau_3}^\pm$ of the opposite phases ($\Omega = \Omega_{\tau_3}^+ \cup \Omega_{\tau_3}^- \cup \Gamma_{\tau_3}$). Moreover in (13) μ_1 is a continuous function on Ω which is at least twice differentiable in $\Omega_{\tau_3}^+ \cup \Omega_{\tau_3}^-$, $K(\mathbf{x})$ is $(d-1)$ times the mean curvature of the interface at $\mathbf{x}$ and S_β is the surface tension for the model (i.e. the free energy density associated with the instantonic solution U_β, see [17]) which can be written as

$$S_\beta = \frac{1}{2}\int_{\mathbb{R}\times\mathbb{R}} \partial_z U_\beta(z) U_\beta(z')(z'-z)\tilde{J}(z-z')\mathrm{d}z\mathrm{d}z' \tag{14}$$

The geometric motion generated by $V_3(\mathbf{x})\nu(\mathbf{x})$ is known as the *symmetric solidification model* or *Mullins–Sekerka* motion [18]. A trivial extension of [7], to include a mobility term, shows that in the same scaling the CHE gives rise to the same interface evolution (12) and (13). The only change is in the surface tension, which in the CHE case is given by, $S_\beta = \zeta \int (\partial_z U_\beta^{CH}(z))^2 \mathrm{d}z$, where $U_\beta^{\mathrm{CH}}(z)$ is the instantonic solution for the CHE with β dependence. A way of introducing the temperature in the CHE is given in [15] and, for β finite, U_β and U_β^{CH} are qualitatively similar. However (see [8]) U_β approaches a step function as β approaches infinity, which is not the case for U_β^{CH}, for fixed ζ.

In [8] we argue that also on the diffusive time scale ($q = 2$ in (11)), that is the case in which the density in the bulk is not yet relaxed to the equilibrium one, the CHE equation and (7) show a very similar behavior. And the same is true in the limit $\beta \to \infty$, in which V_3 (given in (12)) vanishes and the motion (surface diffusion) has to be observed on the time scale $q = 4$: the analogous result for CHE is shown in [15].

We conclude by noting that we have derived rigorously a macroscopic equation describing phase segregation in alloys with long range interactions $\gamma^d J(\gamma x)$, whose only inputs are the equilibrium free energy density and diffusion constant of the reference system. The late stage coarsening described by this equation, in which the details of J enter only in determining the surface tension, is in the same universality class as the CHE [1].

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