

# Atomistic and Continuum Models for Phase Change Dynamics

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**Abstract.** The dynamics of dendritic growth of a crystal in an undercooled melt is determined by macroscopic diffusion-convection of heat and capillary forces acting on length scales compared to the nanometer width of the solid-liquid interface. Its modeling is useful for instance in processing techniques based on casting. The phase field method is widely used to study evolution of such microstructures of phase transformations on a continuum level; it couples the energy equation to a phenomenological Allen-Cahn/Ginzburg-Landau equation modeling the dynamics of an order parameter determining the solid and liquid phases, including also stochastic fluctuations to obtain the qualitative correct result of dendritic side branching. This lecture presents some ideas to derive stochastic phase field models from atomistic formulations by coarse-graining molecular dynamics and kinetic Monte Carlo methods.

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## 1. Introduction to Phase-field Models

The phase field model for modeling a liquid solid phase transformation is an Allen-Cahn/Ginzburg-Landau equation coupled to the energy equation

$$\begin{aligned} \partial_t \phi &= \operatorname{div}(k_1 \nabla \phi) - k_0 (f'(\phi) + g'(\phi) k_4 T) + \text{noise} \\ \partial_t (c_v T + k_2 g(\phi)) &= \operatorname{div}(k_3 \nabla T) \end{aligned} \quad (1.1)$$

with a double well potential  $f$  having local minima at  $\pm 1$ , smoothed step function  $g$ , temperature  $T$  and specific heat  $c_v$ , cf. [3]. The phase field variable  $\phi : \mathbb{R}^d \times [0, \infty) \rightarrow [-1, 1]$  interprets the solid and liquid phases as the domains  $\{x \in \mathbb{R}^d : \phi(x) > 0\}$  and  $\{x \in \mathbb{R}^d : \phi(x) < 0\}$  respectively. To have such an implicit definition of the phases, as in the level set method, is a computational advantage compared to a sharp interface model, where the necessary direct tracking of the interface introduce computational drawbacks. This phenomenological phase-field model, with free energy potentials motivated by thermodynamics, has therefore become a popular and effective computational method to solve problems with complicated microstructures of dendrite and eutectic growth, cf. [1],[3]. The phase-field model has mathematical wellposedness and convergence to sharp interface results [34].

Assuming that the reaction term in the Allen-Cahn equation takes a given form, e.g. a standard choice is

$$\begin{aligned} f(\phi) &:= (1 - \phi^2)^2 \\ g(\phi) &:= \frac{15}{16} \left( \frac{1}{5} \phi^5 - \frac{2}{3} \phi^3 + \phi \right) + \frac{1}{2}, \end{aligned}$$

then the parameters  $k_0, k_1, k_2, k_3, k_4$  in the phase-field model can be determined from atomistic molecular simulations [19]; an alternative in [1] uses a steeper step function  $g$  to easy derive consistency with sharp interface models. The evolution of the phase interface depends on the orientation of the solid crystal; this is modeled by an anisotropic matrix  $k_1$ . Added noise to system (1.1) is also important, e.g. to obtain sidebranching dendrites [22] explained in Section 5.4.

Phase changes can be modeled on an atomistic level by molecular dynamics or kinetic Monte Carlo methods. This lecture first presents some ideas and questions to derive a stochastic phase field model by coarse-graining molecular dynamics, to determine the reaction term (i.e.  $f$  and  $g$ ) and the noise. This is made in three steps in Sections 2 to 4: to give a precise quantitative atomistic definition of the phase-field variable, to introduce an atomistic molecular dynamics model based on Brownian dynamics, and to derive the dynamics for the coarse-grained phase-field. Section 5 derives stochastic hydrodynamical limits of solutions to an Ising model with long range interaction, i.e. coarse-graining a kinetic Monte Carlo method following [24]. Section 5.4 presents a simple kinetic Monte Carlo method for dendrite dynamics.

## 2. Quantitative Atomistic Definition of the Phase-field Variable

The aim is to give a unique definition of the phase-field variable, so that it can be determined precisely from atomistic simulations. The usual interpretation is to measure interatomic distances and use structure functions (or similar methods) to measure where the phase is solid and where it is liquid, which then implicitly defines the phase-field variable [3]. Here we instead use the energy equation for a quantitative and explicit definition of the phase-field variable. The macroscopic energy equation with a phase transformation and heat conduction is

$$\partial_t(c_v T + m) = \operatorname{div}(k \nabla T) \quad (2.1)$$

where  $m$  corresponds to the latent heat release. In (1.1) the latent heat determines the parameter  $k_2$ , since  $\phi$  is defined to jump from 1 to  $-1$  in the phase transformation. We will instead use this latent heat to directly define the phase field function, and not only the parameter  $k_2$ . The total energy,  $c_v T + m$ , can be defined from molecular dynamics of  $N$  particles with position  $X_i$ , velocity  $v_i$  and mass  $\mu$  in a potential  $V$ , see [20], [18],

$$c_v T + m = \sum_{i=1}^N \mu \frac{|v_i|^2}{2} + V(X_1, \dots, X_N). \quad (2.2)$$

Assume that the potential can be defined from pair interactions

$$V(X) = \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i} \Phi(X_i - X_j), \quad (2.3)$$

where  $\Phi : \mathbb{R}^3 \rightarrow \mathbb{R}$  is a molecular dynamics pair potential, e.g. a Lennard-Jones potential

$$\Phi(x) = z_1 \left( \frac{\sigma}{|x|} \right)^{12} - z_2 \left( \frac{\sigma}{|x|} \right)^6.$$

In the macroscopic setting the jump of  $m$  in a phase change is called the latent heat, which depends on the thermodynamic variables kept constant: with constant  $N, T$  and volume it is called the internal energy and with constant pressure instead of volume it is called enthalpy. The kinetic energy  $\sum_i \mu |v_i|^2/2$  is related to the temperature. It is therefore natural to let the phase field variable be determined by the potential energy  $V(X)$ . In a pointwise setting the potential energy can be represented by the distribution

$$\frac{1}{2} \sum_{i=1}^N \sum_{j \neq i} \Phi(X_i - X_j) \delta(x - X_i)$$

where  $\delta$  is the point mass at the origin [20]. We seek an averaged variant and we will study a microscopic phase change model where the interface is almost planar

in the microscopic scale with normal in the  $x_1$  direction. Therefore we take a smooth average and define the phase-field variable by

$$m(X, x) := \frac{1}{2} \sum_{i=1}^N \underbrace{\sum_{j \neq i} \Phi(X_i - X_j)}_{m_i(X)} \eta(x - X_i) \quad (2.4)$$

where  $\eta : \mathbb{R}^3 \rightarrow (0, \infty)$  is a smooth approximation of the point (delta) mass, with scale  $\epsilon_i > 0$  in the  $x_i$  direction,

$$\eta(x) := \prod_{i=1}^3 \frac{e^{-|x_i|^2/(2\epsilon_i^2)}}{(2\pi\epsilon_i^2)^{1/2}}. \quad (2.5)$$

Smooth averages have been used in molecular dynamics for fluid dynamics, cf. [18] and for the vortex blob method and the smoothed particle hydrodynamics approximation of moving particles in fluid dynamics, cf. [29] [2]. Sections 3-4 present a molecular dynamics model for the potential energy (2.4) and Section 5.4 formulates a kinetic Monte Carlo model.

**Question 2.1.** How accurate is it to say that the (macroscopic) latent heat is equal to a jump in  $V$ ?

### 3. An Atomistic Brownian Dynamics Model

The standard method to simulate molecular dynamics is to write Newton's laws for the particles, cf. [10], [32]. We will instead use Brownian dynamics with the Ito differential equations

$$dX_i^t = -\partial_{X_i} V(X^t) dt + \sqrt{2\gamma} dW_i^t \quad (3.1)$$

where  $W_i$  are independent Brownian motions and the notation  $X_i^t := X_i(t)$  is the position of the  $i$ 'th particle at time  $t$ . This equation, called the Smoluchowski equation, is the zero relaxation time limit (i.e.  $\tau \rightarrow 0+$ ) of Langevin's equation (cf. [25], [30], [32], [21])

$$\begin{aligned} d\hat{X}_i^s &= p_i/\mu ds \\ dp_i^s &= -\partial_{X_i} V(\hat{X}^s) ds - \frac{p_i^s}{\tau} ds + \sqrt{\frac{2\gamma\mu}{\tau}} d\hat{W}_i^s, \end{aligned} \quad (3.2)$$

in the faster time scale  $s = \mu t/\tau$ , where  $\mu$  is the mass and  $\hat{W}_i$  are independent Brownian motions. The zero relaxation time limit is explained more in Remark 3.2. The simplified Brownian dynamics has the same invariant measure with density proportional to  $e^{-V(X)/\gamma}$  as in Monte-Carlo molecular dynamics simulations of equilibrium problems with  $\gamma = k_B T$ , where  $T$  is the absolute temperature and  $k_B$

is the Boltzmann constant. In this sense, the parameter  $\gamma/k_B$  in the Brownian dynamics is the local temperature  $T$ . In contrast to the standard Monte-Carlo method, the model (3.1) includes the time variable. Our microscopic model of a phase change is then the Brownian dynamics model (3.1) for the phase-field (latent heat) variable  $m$  in (2.4) coupled to the macroscopic energy equation (2.1). The Brownian dynamics uses  $\gamma := k_B T$ , where the temperature varies on the macroscopic scale, due to the energy equation, so that  $T$  is almost constant on the microscopic scale of a molecular dynamics simulation and makes its Gibbs equilibrium density proportional to  $e^{-V(X)/(k_B T(x))}$  reasonable.

We have two reasons to use Brownian dynamics instead of standard deterministic Newton dynamics ( $\tau = \infty$  in (3.2)): the most important reason is to have a formulation that separates the noise and the mean drift, which is a much harder issue in deterministic many particle dynamics, in fact so far the only derivation of the Euler equations of conservation laws from particle dynamics use a weak noise perturbation of a Hamiltonian system in [31]; and the second reason is to try to simulate molecular dynamics longer time.

**Question 3.1.** Is Brownian dynamics a reasonable alternative to standard molecular dynamics here?

**Remark 3.2** (Smoluchowski Limit of the Langevin Equation). The Smoluchowski high friction limit of the Langevin equation has been computed with different methods using strong [30] and weak convergence [25]. Strong convergence has the drawback to yield error estimates of order  $e^{Kt}\tau$ , due to a Gronwall estimate and Lipschitz bound  $K$  of the forces; in contrast, error estimates of probabilities using weak convergence can show good accuracy for long time. The proof that the Langevin solution  $\hat{X}_{\mu t/\tau}$  converges weakly (i.e. in law) to the Smoluchowski solution  $X_t$ , as  $\tau \rightarrow 0+$ , in [25, 28], uses a Chapman-Enskog expansion of the Kolmogorov backward equation, for the Langevin dynamics in the diffusion time scale  $t$ , combined with a general convergence result for such diffusion processes in [26]. Dissipative particle dynamics [15] has dissipation-fluctuation perturbations of a Hamiltonian system where the momentum is conserved, in contrast to the analogous Langevin dynamics. The work [25] also shows that a Smoluchowski type limit seems more subtly for dissipative particle dynamics.

## 4. Coarse-grained Phase-field Dynamics

We want to determine a mean drift function  $a(\bar{m})$  and a diffusion function  $b(\bar{m})$  so that the coarse-grained approximation  $\bar{m}^t$ , solving the coarse-grained equation

$$d\bar{m}^t = a(\bar{m}^t)dt + \sum_{k=1}^M b_k(\bar{m}^t)d\tilde{W}_k^t,$$

is an optimal approximation to the phase field  $m(X^t, \cdot)$  defined in (2.4), where  $X^t$  solves the Brownian dynamics (3.1). Here  $\tilde{W}_k$ ,  $k = 1, \dots, M$  are all independent Brownian motions, also independent of all  $W_i$ . For this purpose we seek to

minimize the error of the expected value at any time  $\mathcal{T}$

$$E[g(m(X^{\mathcal{T}}, \cdot))] - E[g(\bar{m}^{\mathcal{T}})]$$

for any given function  $g$  with the same initial value  $\bar{m}^0 = m(X^0, \cdot)$ . Here the expected value of a stochastic variable  $w$ , with set of outcomes  $\Omega$  and probability measure  $P$ , is defined by

$$E[w] := \int_{\Omega} w dP.$$

The first idea, in Section 4.1, is that Ito's formula and the Brownian dynamics (3.1) determine functions  $\alpha$  and  $\beta$ , depending on the microscopic state  $X$ , so that

$$dm(X^t, \cdot) = \alpha(X^t)dt + \sum_{j=1}^N \beta_j(X^t)dW_j^t. \quad (4.1)$$

The next step, in Section 4.2, is estimate the error, using the Kolmogorov equations for  $\bar{m}$  and (4.1), similar to [35, 24], which leads to

$$E[g(m(X^{\mathcal{T}}, \cdot)) - g(\bar{m}^{\mathcal{T}})] = E\left[\int_0^{\mathcal{T}} \langle \bar{u}', \alpha - a \rangle + \langle \bar{u}'', \sum_{j=1}^N \beta_j \otimes \beta_j - \sum_{k=1}^M b_k \otimes b_k \rangle dt\right],$$

where  $\langle \bar{u}', \cdot \rangle$  is the  $L^2(\mathbb{R})$  scalar product, corresponding to the variable  $x$  with  $\bar{u}'$ , which is the Gateaux derivative (i.e functional derivative) of the functional  $E[g(\bar{m}^{\mathcal{T}}) | \bar{m}^t = n]$  with respect to  $n$ ; and similarly  $\langle \bar{u}'', \cdot \rangle$  is the  $L^2(\mathbb{R} \times \mathbb{R})$  scalar product with the second Gateaux derivative  $\bar{u}''$  of the functional  $E[g(\bar{m}^{\mathcal{T}}) | \bar{m}^t = n]$  with respect to  $n$ . The notation  $b_k \otimes b_k(x, x') := b_k(x)b_k(x')$  is the tensor product.

The final step, in Section 4.3, is to use molecular dynamics simulations for a planar two phase problem and take averages in cross sections parallel to the interface, where  $\bar{u}'$ ,  $\bar{u}''$ ,  $a$ ,  $\sum_k b_k \otimes b_k$  are constant, to evaluate approximations to the functions  $a$  and  $\sum_k b_k \otimes b_k$  by

$$a = \frac{1}{\mathcal{T}} E\left[\int_0^{\mathcal{T}} \alpha dt\right],$$

$$\sum_k b_k \otimes b_k = \frac{1}{\mathcal{T}} E\left[\int_0^{\mathcal{T}} \sum_{j=1}^N \beta_j \otimes \beta_j dt\right].$$

**4.1. The Ito Formula for the Phase-field.** The Ito formula (cf. [13]) implies

$$dm(X^t, x) = \underbrace{\sum_{j=1}^N (-\partial_{X_j} m \partial_{X_j} V + \gamma \partial_{X_j X_j} m)}_{\alpha(X^t)} dt + \sum_{j=1}^N \underbrace{\sqrt{2\gamma} \partial_{X_j} m}_{\beta_j(X^t)} dW_j. \quad (4.2)$$

The definition in (2.4),

$$m(X^t, x) = \sum_i m_i(X) \eta(x - X_i^t),$$

yields

$$\partial_{X_j} m = \sum_i \partial_{X_j} m_i \eta(x - X_i) + m_j \partial_{X_j} \eta(x - X_j).$$

In (4.2) we will use (2.5) to evaluate the last derivative as

$$\begin{aligned} \partial_{X_j} \eta(x - X_j) &= -\partial_x \eta(x - X_j) \quad \text{in } dt \text{ terms} \\ \partial_{X_j} \eta(x - X_j) &= -\eta(x - X_j) \left( \frac{(x - X_j)_1}{\epsilon_1^2}, \frac{(x - X_j)_2}{\epsilon_2^2}, \frac{(x - X_j)_3}{\epsilon_3^2} \right) \text{ in } dW_j \text{ terms,} \end{aligned}$$

in order to avoid spatial derivatives on the diffusion coefficient, while including them in the drift. Since

$$m_i = \frac{1}{2} \sum_{k \neq i} \Phi(X_i - X_k)$$

and

$$V(X) = \frac{1}{2} \sum_i \sum_{j \neq i} \Phi(X_i - X_j)$$

there holds

$$\begin{aligned} \partial_{X_j} m_i &= \frac{1}{2} \sum_{k \neq i} \Phi'(X_i - X_k) \delta_{ij} - \frac{1}{2} \Phi'(X_i - X_j) (1 - \delta_{ij}), \\ \partial_{X_j} V(X) &= \sum_{k \neq j} \Phi'(X_j - X_k), \end{aligned}$$

where

$$\delta_{ij} := \begin{cases} 1 & i = j, \\ 0 & i \neq j \end{cases}$$

is the Kronecker symbol. The second derivatives are

$$\partial_{X_j X_j} m = \sum_i \partial_{X_j X_j} m_i \eta(x - X_i) - 2 \partial_{X_j} m_j \partial_x \eta(x - X_j) + m_j \partial_{xx} \eta(x - X_j),$$

with

$$\partial_{X_j X_j} m_i = \frac{1}{2} \sum_{k \neq i} \Phi''(X_i - X_k) \delta_{ij} + \frac{1}{2} \Phi''(X_i - X_j) (1 - \delta_{ij})$$

and all terms in (4.2) are now expressed in terms of  $\Phi$ , its gradient  $\Phi'$  and Hessian  $\Phi''$ . We note that the drift,  $\alpha$ , has the form

$$\begin{aligned} \alpha &= \partial_{xx} A_2 + \partial_x A_1 + A_0 := \\ \gamma \partial_{xx} m(X^t, x) + \partial_x \left( \sum_{i=1}^N n_{1i}(X^t) \eta(x - X_i^t) \right) + \sum_{i=1}^N n_{0i}(X^t) \eta(x - X_i^t) \end{aligned} \quad (4.3)$$

of conservative and non conservative reaction terms. Similarly the diffusion,  $\beta_j$ , takes the form

$$\sum_{i=1}^N n_{3ji}(X^t)\eta(x - X_i^t) + n_{4j}(X^t)\eta(x - X_j^t)(x - X_j^t).$$

**Remark 4.1.** A similar derivation with Ito's formula shows that the density,  $\rho(x) := \sum_i \eta(x - X_i)$ , satisfies

$$d\rho = \gamma \partial_{xx} \rho dt - \sqrt{2\gamma} \partial_x \sum_{i=1}^N \eta(x - X_i) dX_i$$

which in the case of zero particle forces,  $V' = 0$ , reduces to the diffusion equation for the expected density,  $\bar{\rho} := E[\rho]$ ,

$$\partial_t \bar{\rho} = \gamma \partial_{xx} \bar{\rho}.$$

**4.2. The Error Representation.** The conditioned expected value

$$\bar{u}(n, t) := E[g(\bar{m}^T) \mid \bar{m}^t = n] \quad (4.4)$$

satisfies the Kolmogorov equation (cf. [35, 24])

$$\begin{aligned} \partial_t u + \langle \bar{u}', a \rangle + \langle \bar{u}'', \sum_{k=1}^M b_k \otimes b_k \rangle &= 0 \\ \bar{u}(\cdot, T) &= g \end{aligned} \quad (4.5)$$

Let  $m^t := m(X^t, \cdot)$ . The final condition in (4.5) and the definition (4.4) show that

$$E[g(m(X^T, \cdot)) - g(\bar{m}^T)] = E[\bar{u}(m^T, T)] - \bar{u}(m^0, 0) = E\left[\int_0^T d\bar{u}(m^t, t)\right].$$

Use the Ito formula and (4.2) to evaluate  $d\bar{u}(m^t, t)$  and Kolmogorov's equation (4.5) to replace  $\partial_t \bar{u}$  in this right hand side to obtain the error representation

$$\begin{aligned} &E[g(m(X^T, \cdot)) - g(\bar{m}^T)] \\ &= E\left[\int_0^T \langle \bar{u}', \alpha \rangle + \langle \bar{u}'', \sum_{j=1}^N \beta_j \otimes \beta_j \rangle + \partial_t \bar{u} dt\right] \\ &= E\left[\int_0^T \langle \bar{u}', \alpha - a \rangle + \langle \bar{u}'', \sum_{j=1}^N \beta_j \otimes \beta_j - \sum_{k=1}^M b_k \otimes b_k \rangle dt\right]. \end{aligned}$$

**4.3. Computation of Averages in Cross Sections.** The optimal choice of the function  $a$  is to minimize  $E[\int_0^T \langle \bar{u}', \alpha - a \rangle dt]$ , which seems hard to determine exactly, since  $\bar{u}'(m(X^t, \cdot), t)$  depends on  $X^t$ . However, the function



$\bar{u}'(m(X^t, \cdot), t)$  depends only mildly on the coarse-grained  $m(X^t, \cdot)$  and not directly on  $X^t$ . Therefore a reasonable approximation of this optimum is to think of an expansion of  $\bar{u}'$  in  $\alpha - a$  and determine  $a$  by the leading order condition  $E[\int_0^T \alpha - a dt] = 0$ , which means that the drift  $\bar{a}(x) := a(\bar{m}(\cdot, x))$  is

$$\bar{a}(x) = \frac{1}{T} E \left[ \int_0^T \alpha(x) dt \right],$$

and similarly for the diffusion matrix

$$\bar{d}(x, x') = \frac{1}{T} E \left[ \int_0^T \sum_{j=1}^N \beta_j(x) \otimes \beta_j(x') dt \right].$$

We expect the spatial averages of the microscopic variables to vary on a much smaller scale in the  $x_1$  direction normal to the phase front than in its orthogonal directions, consequently we use an average function  $\eta$  in (2.4) with higher resolution in the  $x_1$  direction, so that  $0 < \epsilon_1 \ll \epsilon_2 = \epsilon_3$ . In a microscopic simulation the molecular dynamics (3.1) has a small spatial volume, so that  $\epsilon_2$  is much larger than the size of the simulation box. Consequently we may first think of  $\alpha$  and  $\beta$  depending only on the  $x_1$  coordinate. Here the averages for the drift with its three terms  $A_i$  in (4.3) is made separately for each  $A_i$ , so that

$$\bar{a}(x) = \sum_{i=0}^2 \partial_x^i \frac{1}{T} E \left[ \int_0^T A_i(X^t, x) dt \right] =: \sum_{i=0}^2 \partial_x^i \bar{A}_i(x)$$

In practice, the drift terms  $\bar{A}_i$  and diffusion  $\bar{d}$  can only be determined for a discrete set of points

$$\{(x_1(1), x_2(1), x_3(1)), \dots, (x_1(M/3), x_2(M/3), x_3(M/3))\} =: \mathcal{X}_M$$

and  $\mathcal{X}_M \times \mathcal{X}_M$ , respectively, related to the scales  $\epsilon_i$ . The diffusion coefficient  $\bar{b}$ , as a function of  $x$ , can then be obtained from Choleski factorization of the  $M \times M$  matrix  $\bar{d}$

$$\sum_{k=1}^M \bar{b}_k(x) \bar{b}_k(x') = \bar{d}(x, x').$$

We expect that  $x_1 \mapsto \mathcal{T}^{-1} E[\int_0^T m^t dt]$  is monotone, for fixed  $(x_2, x_3)$ , so that its inverse function, denoted by  $m^{-1}$ , is well defined. Then the coarse-grained drift and the diffusion can be obtained as function of  $\bar{m}$  by

$$a(\bar{m}) := \sum_{i=0}^2 \partial_x^i \bar{A}_i(m^{-1}(\bar{m})),$$

and similarly for  $b_j$ .

**Question 4.2.** Will the computed  $a$  and  $b$  be reasonable?

**Question 4.3.** Can the phase-field method be coupled to the molecular dynamics method for improved localized resolution?

**Question 4.4.** Note that the approximation error  $E[g(m(X^T, \cdot)) - g(\bar{m}^T)]$  becomes proportional to the variances

$$E\left[\int_0^T \langle \alpha - a, \alpha - a \rangle dt\right],$$

$$E\left[\int_0^T \left\langle \sum_{j=1}^N \beta_j \otimes \beta_j - \sum_{k=1}^M b_k \otimes b_k, \sum_{j=1}^N \beta_j \otimes \beta_j - \sum_{k=1}^M b_k \otimes b_k \right\rangle dt\right].$$

The first variations  $\partial \bar{u}'(m(X^t, \cdot), t)/\partial \alpha$  and  $\partial \bar{u}''(m(X^t, \cdot), t)/\partial \beta_j$  determine the factors of proportionality. Can this be used to adaptively determine the resolution scale  $\epsilon$ ?

**Remark 4.5.** If we integrate the noise term over all  $x_1$ , i.e. take  $\epsilon_1$  very large, and let  $g(m) = m^2$ , then the error we are studying  $E[g(m(X^T, \cdot)) - g(\bar{m}^T)]$  is the usual fluctuation of energy  $E[V^2 - E[V]^2]$  (proportional to the specific heat [21]), provided we set  $\bar{m} = E[V]$ .

## 5. An Atomistic Kinetic Monte Carlo Method

Kinetic Monte Carlo methods can also be used to simulate solid-liquid phase changes on an atomistic level, cf. [14]. Here the reaction states and rates are given a priori, which makes it possible to simulate crystal growth on larger time scales than in molecular dynamics. The reaction rates and states can in principle be determined from a molecular dynamics simulations on smaller systems, cf. [37]; however often several reactions are involved making this a demanding modeling task. This section is a short version of [24] and derives stochastic hydrodynamical limits of the Ising model with long range interaction, which is the simplest model of this kind of an stochastic interacting particle system on a square lattice with two possible states in each lattice point, cf. [21].

Define a periodic lattice  $\mathcal{L} := \gamma Z^d / Z^d$ , with neighboring sites on distance  $\gamma$ , and consider spin configurations  $\sigma : \mathcal{L} \times [0, T] \rightarrow \{-1, 1\}$  defined on this lattice. Introduce a stochastic spin system where the spin  $\sigma_t(x)$ , at site  $x \in \mathcal{L}$  and time  $t$ , will flip to  $-\sigma_t(x)$  with the rate  $c(x, \sigma_t(\cdot))dt$ , in the time interval  $(t, t + dt)$ , independent of possible flips at other sites, cf. [27]. Let  $\sigma^x$  denote the configuration of spins after a flip at  $x$  of state  $\sigma$ , i.e.

$$\sigma^x(y) = \begin{cases} \sigma(y) & y \neq x \\ -\sigma(x) & y = x, \end{cases}$$

the probability density  $P(\sigma, t)$  of finding the spin system in configuration  $\sigma \in \{-1, 1\}^{\mathcal{L}}$  at time  $t$  then solves the master equation

$$\frac{dP(\sigma, t)}{dt} = \sum_{x \in \mathcal{L}} (c(x, \sigma^x)P(\sigma^x, t) - c(x, \sigma)P(\sigma, t)), \quad (5.1)$$

where the gain term  $\sum_x c(x, \sigma^x)P(\sigma^x, t)$  is the probability of jumping to state  $\sigma$  at time  $t$  and the loss term  $\sum_x c(x, \sigma)P(\sigma, t)$  is the probability to leave state  $\sigma$ . Similar master equations are used for microscopic models of chemical reactions and phase transformations, cf. [36, 14], where lattice sites are occupied by different species of particles. For instance with two species the state space could be  $\{0, 1\} \times \{0, 1\}$  instead of  $\{-1, 1\}$  for the classical spin model above.

We want a spin system that has statistical mechanics relevance, which can be achieved e.g. by choosing the rate function  $c$  as follows. Consider the Hamiltonian

$$H(\sigma) = -\frac{1}{2} \sum_{x \in \mathcal{L}} \sum_{y \neq x} J(x-y)\sigma(x)\sigma(y) - \sum_{x \in \mathcal{L}} h(x)\sigma(x)$$

$$J = \gamma^d J_0, \quad J_0(x) = 0 \quad \text{for } |x| \geq 1,$$

where the long range interaction potential,  $J_0 \in \mathcal{C}^2(\mathbb{R}^d)$ , is compactly supported and the function  $h \in \mathcal{C}^2(\mathbb{R}^d)$  is a given external field. Define the Glauber Markov process on  $\{-1, 1\}^{\mathcal{L}}$  with generator

$$\frac{d}{dt} E[f(\sigma_t) | \sigma] = Lf(\sigma) = \sum_{x \in \mathcal{L}} c(x, \sigma) (f(\sigma^x) - f(\sigma)) \quad (5.2)$$

for  $f : \{-1, 1\}^{\mathcal{L}} \rightarrow \mathbb{R}$  and the flip rate

$$c(x, \sigma) = \frac{e^{-\beta U(x)\sigma(x)}}{e^{-\beta U(x)} + e^{\beta U(x)}}$$

$$= \frac{1}{2} \left( 1 - \sigma(x) \tanh(\beta U(x)) \right), \quad (5.3)$$

$$U(x) = h(x) + \sum_{y \neq x} J(x-y)\sigma(y) =: h(x) + J * \sigma(x) - J(0)\sigma(x),$$

where  $\beta > 0$  is the inverse temperature. This flip rate has built in invariance of the Gibbs density,  $e^{-\beta H(\sigma)} / \sum_{\sigma} e^{-\beta H(\sigma)}$ , since it satisfies the detailed balance

$$c(x, \sigma) e^{-\beta H(\sigma)} = c(x, \sigma^x) e^{-\beta H(\sigma^x)},$$

which implies that this Gibbs density is a time independent (invariant) solution to (5.1). Having this invariant Gibbs measure implies that the model has statistical mechanics relevance, see [12], [4, 5, 6], [11]. For example in a neighborhood of  $x \in \mathcal{L}$ , where  $h$  and  $J * (1, \dots, 1)$  are positive, the construction of the flip rate  $c$  makes the system favor phases with spins mostly equal to 1 as compared to phases with spins mostly equal to  $-1$ .

We will study localized projection averages of  $\sigma$  on scale  $\epsilon$ . In particular we will find approximations to expected values of such averages. The error analysis uses consistency with the backward equation

$$\partial_t \tilde{u} + L\tilde{u} = 0 \quad t < \mathcal{T}, \quad \tilde{u}(\cdot, \mathcal{T}) = g.$$

corresponding to the master equation (5.1) for expected values

$$\tilde{u}(\xi, t) := E[g(\sigma_{\mathcal{T}}) | \sigma_t = \xi].$$

**5.1. A Coarse-grained Kinetic Monte Carlo Method.** Define the coarse periodic lattice  $\bar{\mathcal{L}} := q\gamma Z^d / Z^d$  with neighboring sites on distance  $q\gamma =: \epsilon$ , where  $q$  is an even positive integer and  $q^d$  is the number of fine sites projected to a coarse site: the lattice points  $y \in \bar{\mathcal{L}}$  define the coarse cells

$$C_y = \{x \in \mathcal{L} : -q\gamma/2 \leq x_i - y_i < q\gamma/2\},$$

of  $q^d$  neighboring points in the fine lattice and the averaging operator

$$A_\epsilon(z, x) = \begin{cases} 1/q^d & \text{if } x \text{ and } z \text{ are in the same coarse cell } C_y \\ 0 & \text{if } x \text{ and } z \text{ are in different coarse cells.} \end{cases}$$

We will study the behavior of the localized projection averages

$$\bar{X}(z) := \sum_{x \in \mathcal{L}} A_\epsilon(z, x) \sigma(x), \quad (5.4)$$

for  $z \in \bar{\mathcal{L}}$ . The coarse-grained average  $\bar{X}$  can be interpreted as a function on the coarse lattice since the restriction of  $\bar{X}$  to each coarse cell  $C_z$  is constant, i.e.  $\bar{X} = \sum_{x \in C_z} \sigma(x) / q^d$ .

The work [23] derives a coarse-grained kinetic Monte Carlo equation approximating the average  $\bar{X}$ . The next section shows as in [24] that the average spin,  $\bar{X}$ , can be approximated by the solution,  $X : \bar{\mathcal{L}} \times [0, T] \times \Omega \rightarrow \mathbb{R}$ , to the Ito stochastic differential equation

$$dX_t(x) = a(X_t)(x)dt + b(X_t)(x)dW^x, \quad X_0 = \bar{X}_0, \quad (5.5)$$

with the drift,  $a : \mathbb{R}^{\bar{\mathcal{L}}} \rightarrow \mathbb{R}^{\bar{\mathcal{L}}}$ , and diffusion,  $b : \mathbb{R}^{\bar{\mathcal{L}}} \rightarrow \mathbb{R}^{\bar{\mathcal{L}}}$ , coefficients given by

$$\begin{aligned} a(X) &= -X + \tanh(\beta(J * X + h - J(0)X)), \\ b(X)(x) &= \left(\frac{\gamma}{\epsilon}\right)^{d/2} \sqrt{|1 - X \tanh(\beta(J * X + h - J(0)X))(x)|} \eta(X(x)), \\ \eta(r) &= \begin{cases} 1 & \text{for } x \in [-1, 1], \\ 0 & \text{for } x \in (-\infty, -\hat{r}) \cup (\hat{r}, \infty), \end{cases} \\ \hat{r} &:= \min(1 + e^{-2\beta(2|J|_{\ell^1} + \|h\|_{L^\infty})}, 3/2) \end{aligned} \quad (5.6)$$

and a Wiener process  $W : \bar{\mathcal{L}} \times [0, T] \times \Omega \rightarrow \mathbb{R}$  on a probability space  $(\Omega, P, \{\mathcal{F}_t\}_{t=0}^T)$ , with the set of outcomes  $\Omega$ , probability measure  $P$  and sigma algebra  $\mathcal{F}_t$  of events up to time  $t$ . Here  $W^x$  are independent one dimensional standard Brownian motions for  $x \in \bar{\mathcal{L}}$ , so that formally

$$\begin{aligned} E[dW_t^x] &= 0, \\ E[dW_s^x dW_t^y] &= 0 \text{ for } s \neq t, \\ E[dW_t^x dW_t^y] &= 0 \text{ for } x \neq y, \text{ and} \\ E[dW_t^x dW_t^x] &= dt. \end{aligned}$$

The  $C^\infty$  cut-off function  $\eta : \mathbb{R} \rightarrow [0, 1]$ , with compact support, is introduced to handle the complication that  $|X(x)|$  may be larger than 1, although  $|\bar{X}(x)|$  is not,

so that  $1 - X \tanh(\beta(J * X + h - J(0)X))(x)$  may be close to zero causing large values on derivatives of

$$\sqrt{|1 - X \tanh(\beta(J * X + h - J(0)X))(x)|},$$

note that we have  $|\bar{X}(x)| \leq 1$  and consequently the cut-off  $\eta$  improves the approximation by switching off the noise before  $1 - X \tanh(\beta(J * X + h - J(0)X))(x)$  becomes zero making  $b$  a  $\mathcal{C}^\infty$  function.

The approximation uses that the high dimensional value function  $u : \mathbb{R}^{\bar{\mathcal{L}}} \times [0, T] \rightarrow \mathbb{R}$  defined by

$$u(\xi, t) = E[g(X_{\mathcal{T}}) | X_t = \xi]$$

solves a corresponding Kolmogorov backward equation, where the drift and diffusion coefficients in (5.6) are chosen to minimize the error  $E[g(\bar{X}_{\mathcal{T}})] - E[g(X_{\mathcal{T}})]$ . To define the Kolmogorov backward equation introduce the scalar products

$$\begin{aligned} w \cdot v &:= \sum_{y \in \bar{\mathcal{L}}} w_y v_y && \text{for } w, v \in \mathbb{R}^{\bar{\mathcal{L}}}, \\ w \cdot v &:= \sum_{x, y \in \bar{\mathcal{L}}} w_{xy} v_{xy} && \text{for } w, v \in \mathbb{R}^{\bar{\mathcal{L}}^2}, \\ w \cdot v &:= \sum_{x, y, z \in \bar{\mathcal{L}}} w_{xyz} v_{xyz} && \text{for } w, v \in \mathbb{R}^{\bar{\mathcal{L}}^3}. \end{aligned}$$

Then  $u$  satisfies the Kolmogorov backward equation

$$\begin{aligned} \partial_t u + a \cdot u' + D \cdot u'' &= 0, \text{ for } t < T, \\ u(\cdot, T) &= g, \end{aligned}$$

with the diagonal diffusion matrix

$$D_{xy} = \begin{cases} (1 - X \tanh(\beta(J * X + h))(x)) \eta^2(X(x)) & y = x, \\ 0 & y \neq x, \end{cases}$$

and the first and second order derivatives  $u'(\xi, t) = \partial_\xi u(\xi, t) = (u'_1, u'_2, \dots, u'_{|\bar{\mathcal{L}}|})$  and  $u''(\xi, t) = (\partial_{xy} u)$ . We write  $\partial g(\xi) / \partial \xi_x = \partial_x g = g'_x$  and similarly for higher order derivatives.

We consider expected values of three times differentiable functions  $g$  satisfying the bounds

$$\begin{aligned} \sup_{\xi \in \mathbb{R}^{\bar{\mathcal{L}}}} |g'_i(\xi)| &= \mathcal{O}(\epsilon^d) \\ \sup_{\xi} |g''_{ii}(\xi)| &= \mathcal{O}(\epsilon^d), \quad \sup_{\xi} |g''_{ij}(\xi)| = \mathcal{O}(\epsilon^{2d}) \quad j \neq i \\ \sup_{\xi} |g'''_{iii}(\xi)| &= \mathcal{O}(\epsilon^d), \quad \sup_{\xi} |g'''_{ijj}(\xi)| = \mathcal{O}(\epsilon^{2d}) \quad j \neq i \\ \sup_{\xi} |g'''_{ijk}(\xi)| &= \mathcal{O}(\epsilon^{3d}) \quad j \neq i, k \neq i. \end{aligned} \tag{5.7}$$

This means that  $g$  measures global properties, related to thermodynamic observables. For instance, the potential energies  $\sum_{x, y \in \bar{\mathcal{L}}} \bar{J}(x-y) X(x) X(y) \epsilon^d$ ,  $\sum_{x \in \bar{\mathcal{L}}} h(x) X(x)$  and  $\sum_{x \in \bar{\mathcal{L}}} h(x) f(X(x))$  satisfy (5.7), for  $h(x) = \epsilon^d h_0(x)$  with  $h_0$  a continuous function on the periodic unit cube and  $f \in \mathcal{C}^3(\mathbb{R})$ .

## 5.2. Stochastic Hydrodynamical Limit of the Particle System.

The main result in [24] is

**Theorem 5.1.** *Assume  $g : \mathbb{R}^{\bar{\mathcal{L}}} \rightarrow \mathbb{R}$  satisfies (5.7). At a fixed time  $\mathcal{T}$ , the average spin,  $\bar{X}_{\mathcal{T}}$ , can be approximated by the solution,  $X_{\mathcal{T}}$ , to the Ito stochastic differential equation (5.5) with error*

$$E[g(\bar{X}_{\mathcal{T}})] - E[g(X_{\mathcal{T}})] = \mathcal{O}(\epsilon + (\gamma/\epsilon)^{2d}), \quad \text{as } \epsilon \text{ and } \gamma \text{ tend to zero.} \quad (5.8)$$

Note that  $a = 0$  gives  $\mathcal{O}(1)$  error, while  $b = 0$  gives  $\mathcal{O}((\gamma/\epsilon)^d)$  error so that  $b$  defined by (5.6) is justified for  $\gamma \ll \epsilon \ll \gamma^{2d/(2d+1)}$ , with  $\mathcal{T}$  fixed.

The stochastic differential equation (5.5) has  $\mathcal{C}^\infty$  coefficients, where perturbations of solutions may grow exponentially in time. The proof is in three steps: first to derive an error representation based on  $u(\xi, t) = E[g(X_{\mathcal{T}}) \mid X_t = \xi]$  along  $\xi = \bar{X}_t$ , then to estimate the error using the long range interaction and finally to bound derivatives of  $u(\xi, t)$ .

*Proof of the theorem. Step 1.* The definitions of  $u$ , the generator (5.2) and the average (5.4) imply

$$\begin{aligned} E[g(\bar{X}_{\mathcal{T}})] - E[g(X_{\mathcal{T}})] &= E[u(\bar{X}_{\mathcal{T}}, \mathcal{T})] - E[u(X_0, 0)] \\ &= E\left[\int_0^{\mathcal{T}} du(\bar{X}_t, t)\right] = \int_0^{\mathcal{T}} E[Lu + \partial_t u] dt = \int_0^{\mathcal{T}} E[E[Lu - a \cdot u' - D \cdot u'' \mid \bar{X}_t]] dt \\ &= \int_0^{\mathcal{T}} E\left[E\left[\sum_{x \in \mathcal{L}} c(x, \sigma_t) \left(u(\bar{X}(\sigma_t^x), t) - u(\bar{X}(\sigma_t), t)\right) \right. \right. \\ &\quad \left. \left. - a \cdot u'(\bar{X}(\sigma_t), t) - D \cdot u''(\bar{X}(\sigma_t), t) \mid \bar{X}_t\right]\right] dt \\ &= \int_0^{\mathcal{T}} E\left[E\left[\sum_{x \in \mathcal{L}} c(x, \sigma_t) \left(u(\bar{X}_t - 2A_\epsilon(x, \cdot)\sigma_t(x), t) - u(\bar{X}_t, t)\right) \right. \right. \\ &\quad \left. \left. - a \cdot u'(\bar{X}_t, t) - D \cdot u''(\bar{X}_t, t) \mid \bar{X}_t\right]\right] dt. \end{aligned} \quad (5.9)$$

The first step to estimate this error is to write the difference of  $u$  in terms of its derivatives by Taylor expansion, for some  $s \in [0, 1]$ ,

$$\begin{aligned} &u(\bar{X}(\sigma) - 2A_\epsilon(x, \cdot)\sigma(x), t) - u(\bar{X}(\sigma), t) \\ &= -2u'(\bar{X}, t) \cdot A_\epsilon(x, \cdot)\sigma(x) \\ &\quad + 2u''(\bar{X}, t) \cdot A_\epsilon(x, \cdot)A_\epsilon(x, \cdot)\sigma^2(x) \\ &\quad - \frac{4}{3}u'''(\bar{X} - 2sA_\epsilon(x, \cdot)\sigma(x), t) \cdot A_\epsilon(x, \cdot)A_\epsilon(x, \cdot)A_\epsilon(x, \cdot)\sigma^3(x), \end{aligned} \quad (5.10)$$

so that the error representation (5.9) becomes

$$\begin{aligned}
& E[g(\bar{X}_T)] - E[g(X_T)] \\
&= \int_0^T E \left[ E[u'(\bar{X}_t, t) \cdot (-2 \sum_{x \in \mathcal{L}} c(x, \sigma_t) A_\epsilon(x, \cdot) \sigma_t(x) - a) \right. \\
&\quad \left. + u''(\bar{X}_t, t) \cdot (\sum_{x \in \mathcal{L}} 2c(x, \sigma_t) A_\epsilon(x, \cdot) A_\epsilon(x, \cdot) \sigma_t^2(x) - D) \right. \\
&\quad \left. - \frac{4}{3} \sum_{x \in \mathcal{L}} u'''(\bar{X}_t - 2sA_\epsilon(x, \cdot) \sigma_t(x), t) \cdot c(x, \sigma_t) A_\epsilon(x, \cdot) A_\epsilon(x, \cdot) A_\epsilon(x, \cdot) \sigma_t^3(x) \mid \bar{X}_t] \right] dt.
\end{aligned}$$

We note that the matrix  $F_{yz} := -2 \sum_{x \in \mathcal{L}} c(x, \sigma) A_\epsilon(x, y) A_\epsilon(x, z) - D_{yz}$  is diagonal (i.e.  $F_{yz} = 0$  for  $y \neq z$ ) and the tensor  $R_{yzv} := c(x, \sigma) A_\epsilon(x, y) A_\epsilon(x, z) A_\epsilon(x, v) \sigma^3(x)$  is also diagonal (i.e.  $R_{yzv} = 0$  if not  $y = z = v$ ). Therefore the error representation reduces to

$$\begin{aligned}
& E[g(\bar{X}_T)] - E[g(X_T)] \\
&= \int_0^T E \left[ E \left[ \sum_{y \in \bar{\mathcal{L}}} u'_y(\bar{X}_t, t) (-2 \sum_{x \in \mathcal{L}} c(x, \sigma_t) A_\epsilon(x, y) \sigma_t(x) - a(y)) \right. \right. \\
&\quad \left. \left. + \sum_{y \in \bar{\mathcal{L}}} u''_{yy}(\bar{X}_t, t) F_{yy} - \frac{4}{3} \sum_{x \in \mathcal{L}} \sum_{y \in \bar{\mathcal{L}}} u'''_{yyy}(\bar{X}_t - 2sA_\epsilon(x, y) \sigma_t(x), t) R_{yyy}(x) \mid \bar{X}_t \right] \right] dt.
\end{aligned} \tag{5.11}$$

*Step 2.* The next step is to determine the optimal  $a$  and  $b$  which minimize the error (5.11). For this purpose we shall in the flipping rate approximate the coupling  $J * \sigma$  by  $\bar{J} * \bar{X}$ , using the long range  $\mathcal{O}(1)$  interaction distance of  $J$ . We have

$$\begin{aligned}
& \sum_x A_\epsilon(x, y) = 1, \\
& \sum_x A_\epsilon(x, y) A_\epsilon(x, y) = (\gamma/\epsilon)^d, \\
& \sum_x A_\epsilon(x, y) A_\epsilon(x, y) A_\epsilon(x, y) = (\gamma/\epsilon)^{2d}.
\end{aligned} \tag{5.12}$$

The definition of the average (5.4) implies

$$J * \bar{X} = \sum_{z, y \in \mathcal{L}} J(\cdot - y) A_\epsilon(y, z) \sigma(z)$$

and consequently the coupling has the uniform error estimate

$$\begin{aligned}
J * \sigma(x) - J * \bar{X}(x) &= \sum_{z \in \mathcal{L}} (J(x - z) - \sum_{y \in \mathcal{L}} J(x - y) A_\epsilon(y, z)) \sigma(z) \\
&= \sum_{y, z \in \mathcal{L}} (J(x - z) - J(x - y)) A_\epsilon(y, z) \sigma(z) = \mathcal{O}(\epsilon),
\end{aligned} \tag{5.13}$$

since, for any of the  $\gamma^{-d}$  points  $z$ , either  $A_\epsilon(y, z) = 0$  or  $A_\epsilon(y, z) = (\gamma/\epsilon)^d$  and

$$|J(x-z) - J(x-y)| = \mathcal{O}(\epsilon)\gamma^d$$

for  $(\epsilon/\gamma)^d$  points  $y \in C_z$ . The definition of  $\bar{J}$  shows

$$J * \bar{X}(x) = \sum_{y \in \bar{\mathcal{L}}} \sum_{z \in C_y} \gamma^d J_0(x-z) \bar{X}(y) = \bar{J} * \bar{X}(x)$$

and consequently

$$\sup_{x \in \bar{\mathcal{L}}} |J * \sigma(x) - \bar{J} * \bar{X}(x)| = \mathcal{O}(\epsilon). \quad (5.14)$$

This error estimate and the flip rate (5.3) imply

$$\begin{aligned} - \sum_{x \in \bar{\mathcal{L}}} 2c(x, \sigma) A_\epsilon(x, \cdot) \sigma(x) &= -\bar{X} + A_\epsilon \cdot \tanh(\beta(J * \sigma + h)) \\ &= -\bar{X} + \tanh(\beta(\bar{J} * \bar{X} + h)) + \mathcal{O}(\epsilon), \end{aligned} \quad (5.15)$$

and

$$\begin{aligned} \sum_{x \in \bar{\mathcal{L}}} 2c(x, \sigma) A_\epsilon(x, \cdot) A_\epsilon(x, \cdot) \sigma^2(x) &= \left(\frac{\gamma}{\epsilon}\right)^d \left[1 - \bar{X} \tanh(\beta(\bar{J} * \bar{X} + h))\right] \\ &\quad + \mathcal{O}((\gamma/\epsilon)^{2d} + \epsilon^2). \end{aligned} \quad (5.16)$$

We have  $\bar{X}_t \in [-1, 1]^{\bar{\mathcal{L}}}$ , therefore we need estimates of the derivatives of  $u$  in this set. Lemma 3.2 in [24] proves that

$$\sup_{\xi \in [-1, 1]^{\bar{\mathcal{L}}}} \sum_{x \in \bar{\mathcal{L}}} |u'_x(\xi, t)| + \sup_{\xi \in [-1, 1]^{\bar{\mathcal{L}}}} \sum_{x \in \bar{\mathcal{L}}} |u''_{xx}(\xi, t)| + \sup_{\xi \in [-1, 1]^{\bar{\mathcal{L}}}} \sum_{x \in \bar{\mathcal{L}}} |u'''_{xxx}(\xi, t)| = \mathcal{O}(1), \quad (5.17)$$

as  $\epsilon, \gamma \rightarrow 0+$ , which together with the expansions (5.11), (5.12), (5.15) and (5.16) proves the theorem.  $\square$

We also have

**Lemma 5.2.** *Assume  $g : \mathbb{R}^{\bar{\mathcal{L}}} \rightarrow \mathbb{R}$  satisfies (5.7) and that the initial spin  $\sigma_0$  has expected value  $m$ , where  $\sigma_0(x) - m_x$  are i.i.d. with bounded variance and second order difference quotients  $|d^2m/dx^2| = \mathcal{O}(1)$ . Then the deterministic mean field solution,  $\hat{X} : \mathbb{R}^{\bar{\mathcal{L}}} \times [0, T] \rightarrow \mathbb{R}$ ,*

$$d\hat{X}/dt = -\hat{X} + \tanh(\beta(\bar{J} * \hat{X} + h - J(0)\hat{X})), \quad \hat{X}_0 = E[\bar{X}_0],$$

*depends on  $\epsilon$  only through the initial data and satisfies*

$$E[g(\bar{X}_T)] - E[g(\hat{X}_T)] = \mathcal{O}(\epsilon + (\gamma/\epsilon)^d)$$

*provided the drift  $a$  is defined by (5.6).*

*Proof of Lemma 5.2.* Think of  $\hat{X}$  as an  $X$  with  $b = 0$  and apply the corresponding expansion (5.9), (5.10) and (5.12). Then it remains to verify that the initial data satisfy

$$E[u(\bar{X}_0, 0) - u(\hat{X}_0, 0)] = \mathcal{O}((\gamma/\epsilon)^d),$$

but this is a direct consequence of the central limit theorem and the initial  $\sigma_0 - E[\sigma_0]$  being i.i.d. with bounded variance.  $\square$



### 5.3. Alternative Invariant Measure Diffusion for Mean Exit

**Times.** Not all expected values  $E[g(\bar{X}_\tau)]$  can be approximated using the stochastic differential equation (5.5) with Einstein diffusion, due to the required bounds on the derivatives of  $u$ ; such an example is to determine the expected first exit time  $\tau(Y) = \inf\{t : Y_t \notin A\}$  from a neighborhood  $A$  of an equilibrium point  $y' \in A$ , where  $a(y') = 0$  and  $Y_0 \in A$ . Then the expected exit time is exponentially large, i.e.

$$\lim_{\gamma/\epsilon \rightarrow 0+} (\frac{2}{\epsilon})^d \log E[\tau(\bar{X})] \text{ and } \lim_{\gamma/\epsilon \rightarrow 0+} (\frac{2}{\epsilon})^d \log E[\tau(X)] \quad (5.18)$$

are both strictly positive.

These expected values are related to transition rates  $k$  and  $E[\tau] = 1/k$  in simple cases, see [17], [9]. Hanggi et. al. [16] have proposed a remedy by approximating the master equation by a different stochastic differential equation with the same asymptotic drift but a modified diffusion, to leading order, chosen so that the SDE invariant density  $Z^{-1}e^{-U/(\gamma/\epsilon)^d}$  is asymptotically the same as for the master equation. One perspective on the two different SDEs with Einstein diffusion or invariant measure diffusion is that the two limits, coarse-graining and time tending to infinity, do not commute. Because of (5.18) the theory of large deviations for rare events is relevant for exit times, cf. [9].

Let  $\gamma_1 := \gamma/\epsilon$ . Consider an SDE

$$dX_t(x) = (a(X_t) + \gamma_1^d c(X_t))(x)dt + \gamma_1^{d/2} \tilde{b}(X_t)(x) dW_t^x,$$

with the generator

$$Lf = (a + \gamma_1^d c) \cdot f' + \gamma_1^d \tilde{D} \cdot f'', \quad D_{ij} = \tilde{b}_i \tilde{b}_j \delta_{ij};$$

the idea in [16] is to find  $c$  and  $D$  so that the corresponding SDE asymptotically has the same invariant density  $e^{-U/\gamma_1^d}/Z$  as the master equation. Hanggi et.al. [16] determines the diagonal diffusion matrix  $\tilde{D}$  and the small contribution to the drift,  $\gamma_1^d c$ , by

$$\begin{aligned} \tilde{D}_{ii} &= -a_i/U'_i \\ c_i &= -\partial_{x_i} \tilde{D}_{ii}; \end{aligned} \quad (5.19)$$

note that since  $a$  and  $U$  have the same zeros, the constructed function  $\tilde{D}_{ii}$  is positive in general. The equation (5.19) can be obtained by the WKB expansion

$$\begin{aligned} 0 \simeq L^* e^{-U/\gamma_1^d} &= \left( \gamma_1^{-d} (a_i U'_i + \tilde{D}_{ii} U'_i U'_i) \right. \\ &\quad + \gamma_1^0 (\partial_i a_i + 2U'_i \partial_i \tilde{D}_{ii} + U''_{ii} \tilde{D}_{ii} + c_i U'_i) \\ &\quad \left. + \gamma_1^d (\partial_i c - \partial_{ii} \tilde{D}_{ii}) \right) e^{-U/\gamma_1^d} \end{aligned}$$

together with the two leading order conditions that the terms of order  $\gamma_1^{-d}$  and  $\gamma_1^0$  vanish; here  $L^*$  is the Fokker-Planck operator adjoint to  $L$ . Consequently the

choice (5.19) will in general generate an SDE with an invariant density  $e^{-\tilde{U}/\gamma_1^d}/Z$ , where  $|\tilde{U} - U| = \mathcal{O}(\gamma_1^{2d})$ .

Let us indicate why good approximation of the invariant measure implies that also the expected values,  $E[\tau]$ , for exit problems related to rare events with large deviations, are accurately computed: the work [9] shows that

$$\lim_{\gamma_1 \rightarrow 0+} \gamma_1^d \log E[\tau(X)] = \inf_{y \in \partial A} U(y) - U(y'), \quad (5.20)$$

for one stable attracting equilibrium point  $y' \in A$ . The work [24] shows that the exit time (5.20) with SDE's and invariant measure diffusion is asymptotically the same as for the master equation for the 1D Curie-Weiss model:

$$\lim_{\gamma_1 \rightarrow 0+} \gamma_1^d \left( \log E[\tau(X)] - \log E[\bar{\tau}(\bar{X})] \right) = 0, \quad (5.21)$$

where  $E[\tau(X)]$  and  $E[\bar{\tau}(\bar{X})]$  denote the mean exit time for the Hanggi SDE and the Curie-Weiss master equation, respectively. The Curie-Weiss model is a simple adsorption/desorption Ising model with constant interaction potential, cf. Section 5.4. The technique to establish this asymptotic agreement is to use logarithmic (Hopf-Cole) transformations of the two mean exit times, as functions of the initial location, which transforms the corresponding two linear Kolmogorov backward equations to two nonlinear Hamilton-Jacobi equations, cf. [8]. The two processes give rise to two different asymptotic Hamilton-Jacobi equations, however the key observation is that they have the same viscosity solution since they are both convex and have the same set of zeros.

**5.4. Dendrites with Einstein Diffusion.** We see by Theorem 5.1 and Lemma 5.2 that the mean field differential equation solution is also an accurate approximation to the spin dynamics, provided the derivatives of the value function are bounded; this indicates that the stochastic differential equation (5.5) then only offers a small quantitative improvement. However, if the derivatives of the value function are large the mean field solution may give a qualitatively wrong answer, with  $\mathcal{O}(1)$  error as  $\gamma/\epsilon \rightarrow 0+$ , while the stochastic differential equation still yields an asymptotically correct limit; such an example is dendrite formation in phase transformations, cf. [22, 19, 3], [14].

Let us try to motivate why the noise in Theorem 5.1 seems applicable to dendrite formation. Dendrite dynamics can be formulated by the phase field method with an Allen-Cahn/Ginzburg-Landau equation coupled to a diffusion equation for the energy, as in (1.1), and by master equations coupled to the energy equation, cf. [14]. Mean field equations related to such a phase field system have been derived from a spin system coupled to a diffusion equation, see [7].

A master equation variant of the molecular dynamics model in Sections 2-4 is to let the coarse-grained potential energy be defined by

$$m(\sigma, z) := \sum_x \left( \sum_{y \neq x} \frac{1}{2} J(x-y) \sigma(y) - h \right) \sigma(x) A_\epsilon(x, z),$$

where  $A$  is the average in (5.4), and replace the Glauber dynamics with Arrhenius dynamics. That is, the microscopic dynamics is given by independent spins  $\sigma(x) \in \{0, 1\}$ , for each lattice point  $x \in \mathcal{L}$ , flipping with adsorption rate

$$c_a(x) = d_0(1 - \sigma(x)),$$

from states 0 to 1, and with desorption rate

$$c_d(x) = d_0\sigma(x) \exp\left(-\frac{1}{k_B T} \left(\sum_{y \neq x} J(x-y)\sigma(y) - h\right)\right),$$

from states 1 to 0, where  $h$  is a surface binding energy or an external field and  $d_0$  is a given rate, cf. [23]. Arrhenius dynamics also satisfies detailed balance with the same Gibbs density

$$e^{(\sum_x \sum_{y \neq x} J(x-y)\sigma(x)\sigma(y) / 2 - \sum_x h\sigma(x)) / (k_B T)}$$

as for Glauber dynamics. The dynamics for the potential energy variable can then be coupled to the energy equation (2.1)

$$\partial_t(c_v T + m) = \text{div}(k \nabla T)$$

by letting the temperature  $T$  vary on the coarse-grained scale.

The dendrite grows with a positive non vanishing speed. Without noise in the model there is no side branching, while the side branching is present with added noise to the phase field model, cf. [3], or to the mean field model derived in [14]. This noise induced side branching is explained by the high sensitivity with respect to small perturbations at the dendrite tip, cf. [22]. Therefore the derivatives of an appropriate value function are large. Here the value function,  $u$ , could for instance measure the total dendrite surface at a fixed time. The inconsistent approximation of the mean field solution could by Lemma 5.2 be explained by having

$$(\gamma/\epsilon)^d \|u''\|_{\ell^1} = \mathcal{O}(1). \tag{5.22}$$

The smallest scale in the problem is the dendrite tip radius  $\rho$ ; with a bounded value function its derivatives could then be

$$\begin{aligned} \|u'\|_{\ell^1} &= \mathcal{O}(1/\rho), \\ \|u''\|_{\ell^1} &= \mathcal{O}(1/\rho^2), \\ \|u'''\|_{\ell^1} &= \mathcal{O}(1/\rho^3). \end{aligned}$$

Consequently (5.22) yields  $(\gamma/\epsilon)^{d/2} = \rho$ , so that the noise error for the stochastic differential equation with the Einstein diffusion of Theorem 5.1 would be bounded by  $(\gamma/\epsilon)^{2d} \|u'''\|_{\ell^1} = \mathcal{O}((\gamma/\epsilon)^{d/2})$ , which tends to zero as  $\gamma/\epsilon \rightarrow 0+$ . Therefore, this adsorption/desorption kinetic Monte Carlo model with long range interaction generates an approximating stochastic differential equation, which could be applicable also to coupling with the energy equation if the derivation remains valid with slowly varying temperature. An essential and maybe more difficult question is to find accurate kinetic Monte Carlo methods for real systems with dendrite dynamics, e.g. using ideas from the molecular dynamics coarse-graining in Sections 2-4.

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