

A multiscale approach to cluster growth problems

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Mesosopic modeling and cluster/island growth in a broad class of chemical processes with multiple length and time scales.

- Catalytic Reactors
- Deposition processes
- Epitaxial growth

Related Problems:

- Kinetics of phase separation in alloys, polymer mixtures.
- Particle suspensions in fluids.
- Pattern formation in biological systems and materials.

Main Issues:

- Attractive particle/particle interactions lead to cluster/island formation and propagation. Multiple surface mechanisms are present. How do the micromechanisms influence the macroscopic picture?
- Interaction of the surface processes with the gas phase. Need to couple the continuum model in the gas phase with the microscopic one(s) on the surface; widely separated scales.

Mesoscopic theories of surface processes may provide a framework where such questions can be addressed. Mesoscopic models (PDE, SPDE), describe “intermediate” scales, which are not just *phenomenological* but also include microscopic, molecular information.

MICROSCOPIC MODELS

- A. Molecular dynamics, brownian particles.
- B. Lattice models, Ising-type systems.

Ising Systems: random spin systems on \mathbf{Z}^N . At each lattice site x an order parameter – “spin” – is allowed to take the values ± 1 .

- *Spin:* $\sigma(x) \in \{-1, 1\}$ at the lattice site $x \in \mathbf{Z}^N$
- *Spin configuration:* $\sigma = \{\sigma(x) \mid x \in \mathbf{Z}^N\}$.

- **Hamiltonian:**

$$H(\sigma) = \sum_{x \neq y} J(x, y) \sigma(x) \sigma(y) + h \sum_x \sigma(x),$$

- h : external magnetization field
- J : interaction potential, $J \geq 0$.
- Equilibrium states at a given temperature: Gibbs measure(s). Non-uniqueness, phase transitions.

A. Spin Flip Dynamics–Desorption: Sequence of spin flips at each lattice site x .

- Spin flip rate:

$$c(x, \sigma) = \Psi(-\beta(H(\sigma^x) - H(\sigma))),$$

i.e. a spin flip occurs at x , during $[t, t + \Delta t]$ with probability

$$c(x, \sigma)\Delta t + O(\Delta t^2).$$

$\beta > 0$: inverse temperature.

σ^x : configuration after a spin flip at the site x .

$\Psi \geq 0$ satisfies the **detailed balance law**:

$$\Psi(r) = \Psi(-r)e^{-r}$$

- Typical choices of Ψ 's are:

$$\Psi(r) = (1 + e^r)^{-1} \text{ (Glauber dynamics).}$$

$$\Psi(r) = e^{-r^+} \text{ (Metropolis dynamics).}$$

B. Spin Exchange Dynamics—Surface diffusion.

- **Hamiltonian:** $H(\sigma) = \sum_{x \neq y} J(x, y) \sigma(x) \sigma(y)$
 J : interaction potential, $J \geq 0$.

- **Dynamics:** Sequence of spin exchanges with nearest neighbors.

- Spin exchange rate:

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

$\sigma^{(x,y)}$: configuration after a spin exchange between sites x and y .

- Detailed balance.

- Typical choices of Ψ 's are:

$$\Psi(r) = 2(1 + e^r)^{-1} \text{ (Kawasaki dynamics).}$$

$$\Psi(r) = e^{-r^+} \text{ (Metropolis dynamics).}$$

MESOSCOPIC THEORIES

Key condition: Long range interaction potential J on the underlying lattice $\gamma\mathbf{Z}^N$, $\gamma \ll 1$.

- *Average magnetization:*

$$m_\gamma(x, t) = \frac{1}{|B_x|} \sum_{y \in B_x} \sigma_t(y)$$

B_x : ball with radius \mathbf{R} centered at x ,

$\gamma =$ lattice size $\ll \mathbf{R} \ll$ effective interaction range.

- $\gamma\mathbf{Z}^N \rightarrow \mathbf{R}^N$ as $\gamma \rightarrow 0$. Asymptotic limit of $m_\gamma(x, t)$.

A. Spin flip dynamics [De Masi, Orlandi, Presutti and Triolo], [K., Souganidis]

$m_\gamma(x, t) \approx m(\gamma x, t)$, $x \in \mathbf{Z}^N$, where $m = m(r, t)$, solves the **Local Mean Field** equation:

$$m_t + \Phi(\beta(J * m))[m - \tanh \beta(J * m)] = 0,$$

$$\Phi(r) = \Psi(-2r)(1 + e^{-2r}).$$

B. Spin exchange dynamics [Giacomin, Lebowitz]

$m_\gamma(x, \gamma^{-2}t) \approx m(\gamma x, t)$, where m solves:

$$m_t - D\nabla \cdot [\nabla m - \beta(1 - m^2)\nabla(J * m)] = 0.$$

- Non-conservative dynamics, Allen-Cahn theory. Large space/time asymptotics: curvature-driven interfaces [K., Souganidis].
- Conservative dynamics, Cahn-Hilliard theory. Mullins-Sekerka flow, formal derivations [Giacomin, Lebowitz].

SURFACE PROCESSES

K., D. Vlachos (Chem. Eng. UMass)

1. Mesoscopic Theory for Arrhenius Diffusion Dynamics

Microscopic order parameter: $\sigma(x) = 1$ or 0 .

- Site activation energy at x : U_0 .
- Interaction energy at x :

$$U(x) = \sum_{z \neq x} J(x-z)\sigma(z).$$

- Arrhenius diffusion rate, detailed balance:

$$c(x, y, \sigma) = \exp[-\beta(U_0 + U(x))].$$

- Other Arrhenius-type dynamics: Parabolic jump models, ...

Mesoscopic Equation:

$$m_t - \nabla \cdot \{D \exp(-\beta J * m) [\nabla m - \beta m(1-m) \nabla J * m]\} = 0.$$

$$D = \exp(-\beta U_0).$$

Variational formulation

Free Energy:

$$E[m] = -\frac{1}{2} \int \int J(r - r') m(r) m(r') dr dr' + \int \frac{1}{\beta} [m \ln m + (1 - m) \ln(1 - m)] dr ,$$

$$m_t - \nabla \cdot \left\{ \mu[m] \nabla \left(\frac{\delta E[m]}{\delta c} \right) \right\} + \gamma^{d/2} N_t = 0$$

N_t : microscopic space/time conservative noise.

Nonlocal mobility:

$$\mu[m] = D\beta m(1 - m) \exp(-\beta J * m)$$

Spinodal Decomposition: When $J_0 = \int J(r) dr$ and $m = m_0 + \epsilon \exp(\omega t + i\xi \cdot x)$,

$$\omega = -|\xi|^2 \exp(-\beta(U_0 + J_0)) [1 - \beta u_0(1 - u_0) \hat{J}(\xi)] .$$

Dispersion relation for Metropolis/Kawasaki:

$$\omega = -|\xi|^2 [1 - \beta u_0(1 - u_0) \hat{J}(\xi)] .$$

2. Cluster formation and propagation in surface processes

- Adsorption/desorption → Ising spin flip model.

Interaction potential J_d

- Surface diffusion → Ising spin exchange model.

Interaction potential J_{diff}

The microprocesses take place simultaneously.

- $J_d \neq J_{diff}$ in general, substrate mediated interactions.
- Why long range interactions?

Monte Carlo molecular simulations (microscopic):
[Vlachos, Schmidt, Aris], ...

Global mean field model (ODEs), reaction diffusion models: [Kevrekidis, Schmidt, Aris], ...

Mesoscopic LMF theory

Average occupation number m solves:

$$m_t - D \nabla \cdot [\nabla m - \beta m(1 - m) \nabla J_{diff} * m] + \\ + k_a p(1 - m) - k_d m \exp[-\beta J_d * m] + \\ + \gamma^{d/2} N_t^{diff} + \gamma^{d/2} N_t^{des} + \gamma^{d/2} N_t^{ads} = 0$$

$N_t^{1,2,3}$: independent microscopic space/time noises, nucleation mechanism(s).

D : diffusion constant, k_d , k_a : desorption, adsorption constants, p : partial pressure obtained from a gas-phase model (for the analysis below we assume p is constant).

- Steady states: 1 or 3 depending on the relative values of p , k_d , k_a .
- Monolayer model.
- "Reaction diffusion" equation that includes microscopics and detailed stochastic effects.
- [Mikhailov, Ertl], [Hildebrandt, Mikhailov]: Catalytic surfaces.

Case 1: $J_{diff} = J_d$

- Existence, uniqueness of standing waves in the bistable regime. **Non-monotone** traveling waves. Invariant measures for $J_d = J_{diff}$. When D is small enough: perturbation of the desorption mechanism, IFT.

- Lyapunov functional:

$$E[m] = -\frac{1}{2} \int \int J(r-r') m(r) m(r') dr dr' + \int \frac{1}{\beta} F(m) dr ,$$

$$F(u) = [u \ln u + (1 - u) \ln(1 - u)].$$

- No comparison principle.
- **Cluster formation and propagation.** Velocity of the moving boundary (close to the line of stationary coexistence):

$$V = -\mu\sigma\kappa + \mu\Lambda.$$

κ = mean curvature of the cluster boundary.
Level set methods.

Green-Kubo formulae:

- **Mobility:**

$$\mu = \beta \left[\int_{-\infty}^{\infty} \frac{\dot{q}(\xi)\chi(\xi)}{k_a p(1-q)} d\xi \right]^{-1},$$

- **Surface tension:**

$$\sigma = \frac{1}{2} \int_{-\infty}^{\infty} \int J(r') \dot{q}(\xi + r' \cdot e) \chi(\xi) (\hat{e} \cdot r')^2 dr' d\xi,$$

$$\Lambda = \frac{h}{p\beta} (m_+ - m_-).$$

Furthermore q is the **standing wave** and χ solves:

$$-\left\{ q(1-q) \left(\frac{D}{k_a p(1-q)} \chi \right) \right\} + \chi = \dot{q}, \quad \chi(\pm\infty) = 0.$$

- The **macroscopic** quantities μ, σ are explicitly related to the microscopic ones, as well as the partial pressure p .
- Other local laws: $V = -\epsilon\mu\sigma\kappa + c(\alpha, \lambda)$, where $c(\alpha, \lambda)$ is the speed of the corresponding traveling wave.
- Nucleation radius, Anisotropy.

Case 2: $J_{diff} = 0$

$$m_t - D\Delta m + k_a p(1 - m) - k_d m \exp[-\beta J_d * m] = 0$$

Typically $J_{diff} < J_d$, or $J_{diff} \ll J_d$.

- Comparison principle, for $J_d \geq 0$.
- Existence, uniqueness of **monotone** traveling waves in the bistable regime: perturbation of the desorption mechanism, IFT, comparison principle. See also: [Bates, Fife, Ren, Wang], [Chen].
- Large space/time asymptotics, cluster evolution, Green-Kubo formulae.

$$V = -\mu\sigma\kappa + \mu\Lambda.$$

- General spin flip dynamics: K., Souganidis.
- The adsorption/desorption mechanism *dominates* the surface diffusion at macroscopic length scales but still affects the transport properties of the clusters.

New mathematical difficulties:

- Multiple surface mechanisms; the linearized operator around the traveling waves of LMF is not self-adjoint.
- Non-monotone approximations of the curvature evolutions, when $J_{diff} \neq 0$. Simplified Ginzburg-Landau models. Cluster evolution past singularities, Varifold formulation.

Other related work:

- Kinetics of phase separation in polymer mixtures. Multiple species. Diffusion mechanism only. Mesoscopic modeling. Group of H. Fraaije, [Univ. of Leiden, Netherlands]. MesoDyn project.
- Mesoscopic theories for molecular suspensions. [Keller, Rubinstein], [Butta, Lebowitz]. Relaxation models for equilibrium turbulence in the 2-D Euler system [Robert, Sommeria].
- Rigorous results for general potentials [R. Jordan (WPI), K.]. Formulation as a time-step minimization problem, Wasserstein metric.
- Spectral methods for mesoscopic equations. Incorporate random fluctuations, [Horntrop, K., Vlachos]

Conclusion

- We derive mesoscopic theories for surface processes which include detailed/microscopic information.
- We employ the mesoscopic equations to relate macroscopic theories, (such as cluster evolution) and their respective constitutive laws to the underlying micromechanisms.
- We validate the mesoscopic theories using MC simulations
- Current work, open problems.

Preprints: <http://www.gang.umass.edu/>