

Comparison of Continuum and Atomistic Models for Chemical Diffusion and Phase Separation

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Diffusion



Phase Separation

quantified by order parameter

Modeling Approaches

Continuum Model: Differential Equations

- Order parameter is a continuous quantity:

$$u: \Omega \times (0, \infty) \rightarrow [-1, 1], \quad u \in \mathcal{C}^2 \quad (1)$$

- Order parameter satisfies a single differential equation based on physical laws
- OUTPUT

Atomistic Model: Molecular Dynamics

- Collection of discrete classical particles
- Approximate interparticle forces are used to simulate Hamiltonian dynamics
- Generates trajectory of each particle

Model Type Comparison

Estimating the order parameter from molecular dynamics trajectory

Heat Equation

The heat (or diffusion) equation with initial condition $u_0(x)$ and periodic boundary conditions

$$\begin{cases} \frac{\partial u}{\partial t} = D \nabla^2 u & x \in \Omega, t > 0 \\ u|_{x_i=0} = u|_{x_i=1} & 1 \leq i \leq d \\ u_{x_i}|_{x_i=0} = u_{x_i}|_{x_i=1} & 1 \leq i \leq d \\ u(x, 0) = u_0(x) & x \in \Omega \end{cases} \quad (2)$$

Allen-Cahn Equation

The Allen-Cahn equation with initial condition $v_0(x)$ and periodic boundary conditions

$$\begin{cases} \frac{\partial v}{\partial t} = \gamma \nabla^2 v - \phi(v) & x \in \Omega, t > 0 \\ v|_{x_i=0} = v|_{x_i=1} & 1 \leq i \leq d \\ v_{x_i}|_{x_i=0} = v_{x_i}|_{x_i=1} & 1 \leq i \leq d \\ v(x, 0) = v_0(x) & x \in \Omega \end{cases} \quad (3)$$

Cahn-Hilliard Equation

The Cahn-Hilliard equation with initial condition $c_0(x)$ and periodic boundary conditions

Gradient Flow

Each equation we model can be viewed as the gradient flow of an energy functional F :

$$\frac{\partial u}{\partial t} = - \frac{\partial F}{\partial u} \quad (4)$$

where $F: L^2(\Omega) \rightarrow \mathbb{R}$ for (??) and (??). For (??), $F: H^{-1}(\Omega) \rightarrow \mathbb{R}$. The energy functionals are

$$F(u) = \int_{\Omega} \frac{1}{2} |\nabla u|^2 \, dx \quad (5)$$

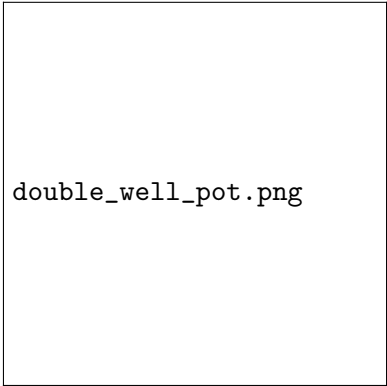
for diffusion and

$$F(v) = M \int_{\Omega} \psi(v) + \frac{\gamma}{2} |\nabla v|^2 \, dx \quad (6)$$

for phase separation.

The function ψ (??) is a double-well free energy function:

$$\psi(v) = \frac{1}{4}(v^2 - 1)^2 \quad (7)$$



double_well_pot.png

The minima of ψ reflects the stability of phase separation.

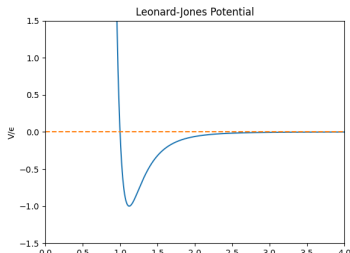
Ideal Gas

Leonard-Jones Potential

- Efficient and accurate model for pairwise London Dispersion interparticle forces
- Parameters describe equilibrium distance and well depth
- Generally implemented with range cutoff

6-12 Leonard-Jones potential:

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad r < r_c \quad (8)$$



Leonard-Jones Fluid

Difference Equations

Descretization of the domain:

- Divide

Stability

Stability conditions

Convergence

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