Active Phase Separation

- Phase Separation in Passive Systems
  - Thermodynamics of the Density Field
  - Diffusive Time Evolution: Model B
  - Phase Separation Kinetics

- Active Particles
  - Broken Time Reversal Symmetry
  - Macroscopic Consequences

- Adapting Model B for Active Matter
  - Phase Coexistence
  - Microphase Separation
  - Stead-State Entropy Production

Active Phase Separation

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And previously: J. Stenhammar, R. Wittkowski, D. Marenduzzo, A. Tiribocchi, B. Liebchen....

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THE ROYAL SOCIETY

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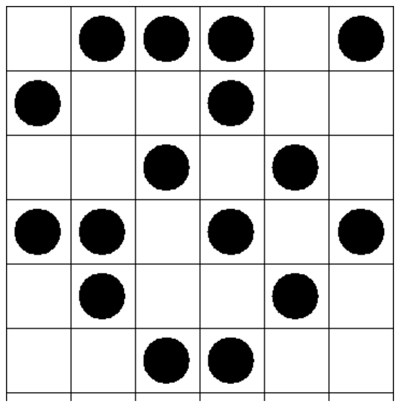
Thermodynamics of the Density Field

e.g. lattice gas with near-neighbor attraction u

N sites, coordination z, lattice constant = 1

particle concentration c, temperature T, k_B=1

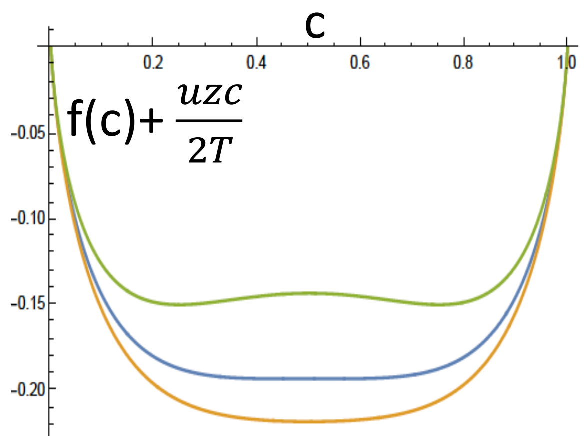


Mean field approximation:

entropy $-S/N = c \ln c + (1-c) \ln (1-c)$

energy $E/N = - u z c^2/2$

Free energy /site $f(c) = E/N - T S/N$



uz/2T = 1.9, 2, 2.2

$T > T_c$: f(c) is convex, stable
$T < T_c$: f(c) is concave, phase separation

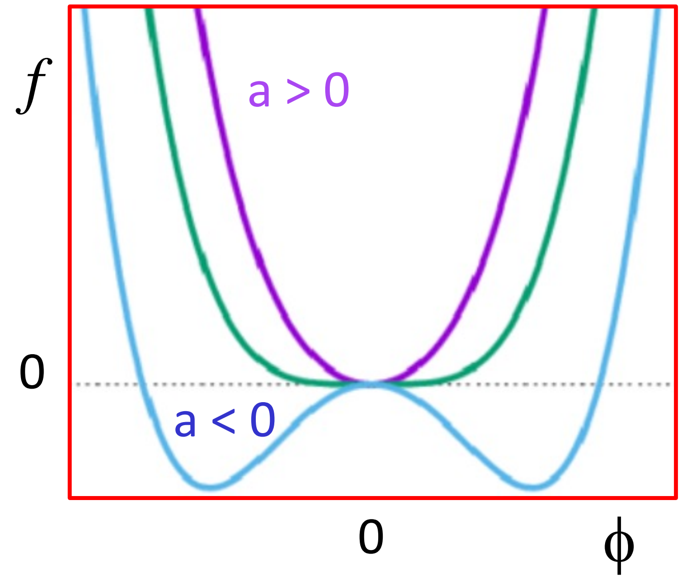
concavity first sets in at c = 1/2 (critical density) and $T = T_c = uz/4$

Thermodynamics of the Density Field

expand around critical point: Landau theory

$$f(\phi) = \frac{a}{2}\phi^2 + \frac{b}{4}\phi^4 + h\phi$$

$$a \propto T - T_c \ , \ \phi \propto c - 1/2$$

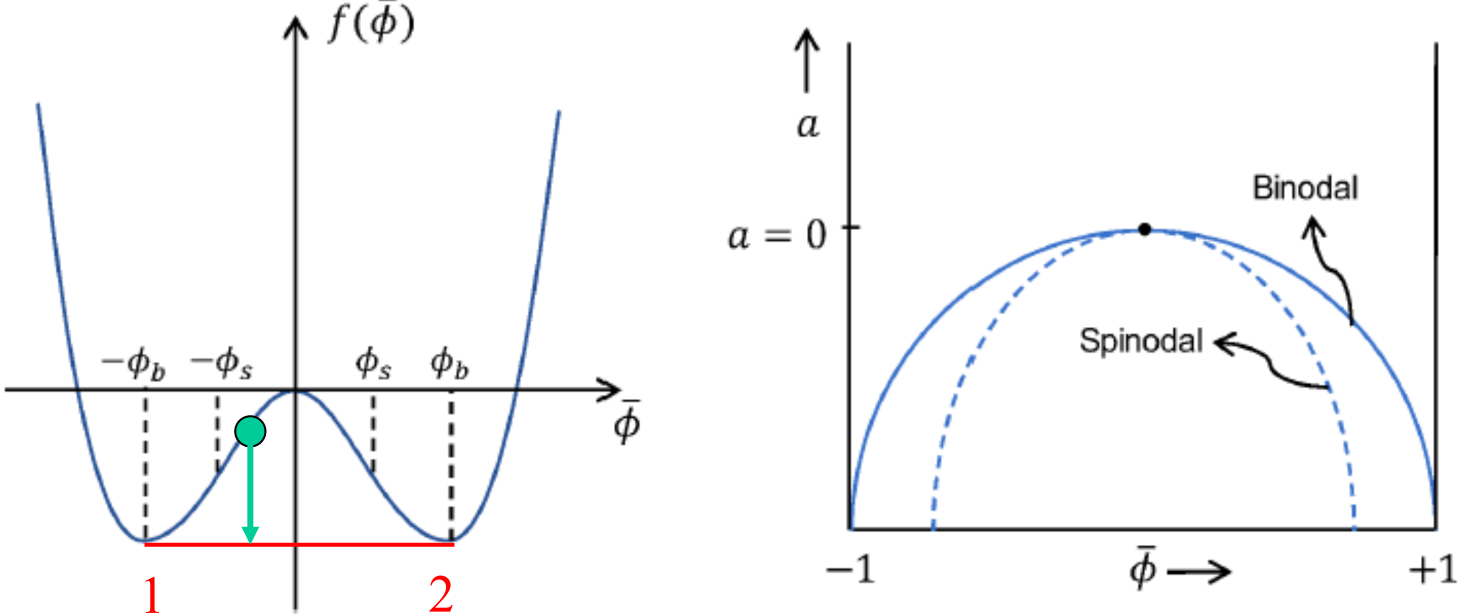


Notes:

- Linear term is ignorable (proved below) – set it to zero
- Cubic term vanishes if expanding around critical point

Thermodynamics of the Density Field

expand around critical point: Landau theory



For global density $\bar{\phi}$ obeying $-\phi_b < \bar{\phi} < +\phi_b$:

- phase separation reduces overall free energy $\mathcal{F}$
- resulting $\mathcal{F}/V$ lies on convex hull of $f(\phi)$ = common tangent
- Lever rule for phase volumes: $V_1+V_2 = V$, and $-\phi_b V_1 + \phi_b V_2 = V \bar{\phi}$

Thermodynamics of the Density Field

Landau-Ginzburg theory

Phase separated states have nonuniform density field $\phi(\mathbf{r})$

Free energy functional $\mathcal{F}$ comprises local part + gradient corrections

$$\mathcal{F} = \int dV [f(\phi) + \frac{\kappa}{2}(\nabla\phi)^2]$$

Notes:

- linear terms in $f(\phi)$ are ignorable:

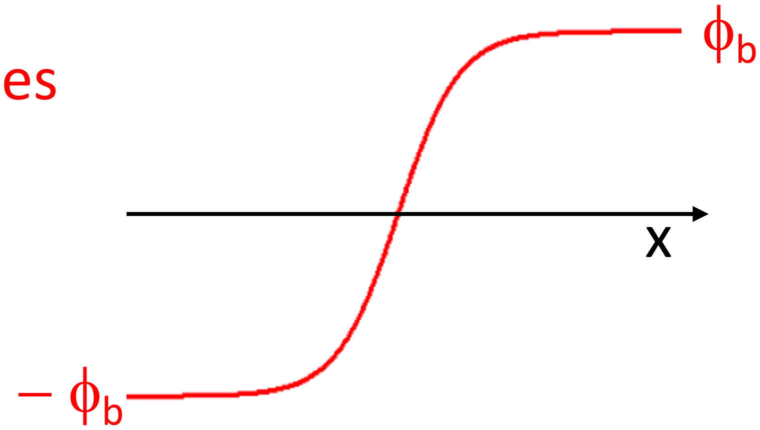
$$\int \phi(\mathbf{r}) dV = N + \text{const.} \quad \Rightarrow \text{additive constants in } \mathcal{F}$$

- $\kappa \sim ud^2$ stems from finite range d of attractions

  this resists sharp changes in density

Thermodynamics of the Density Field

Interfacial profile between bulk phases



$\phi = \phi(x)$, flat in y,z

Procedure:

Minimize $\mathcal{F}$ at fixed contents: $\dfrac{\delta}{\delta\phi}\left[\mathcal{F}[\phi] - \lambda \int \phi \, dV\right] = 0$

$\Rightarrow$ General equilibrium condition:

Chemical potential $\mu \equiv \dfrac{\delta \mathcal{F}}{\delta \phi} = a\phi + b\phi^3 - \kappa \nabla^2 \phi$ $= \lambda$ is uniform

Functional Derivatives

Start with: $$\mathcal{F} = \int_0^{L=\mathcal{N}\Delta x} \left[f(\phi) + \frac{\kappa}{2} (\nabla\phi)^2 \right] dx$$

Discretize: $$\mathcal{F} = \Delta x \sum_{i=0}^{\mathcal{N}} f(\phi_i) + \frac{\kappa}{2} \left(\frac{\phi_{i+1} - \phi_i}{\Delta x} \right)^2$$

Change ϕ at site j: $$\frac{\partial \mathcal{F}}{\partial \phi_j} = \Delta x \left[f'(\phi_j) - \kappa \frac{\phi_{j+1} + \phi_{j-1} - 2\phi_j}{\Delta x^2} \right]$$

discrete Laplacian

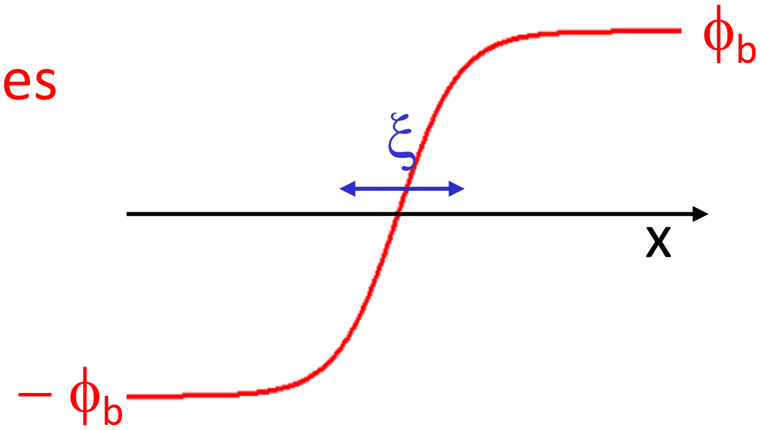
Sum over all such changes:

$$\delta\mathcal{F} = \sum_j \frac{\partial \mathcal{F}}{\partial \phi_j} \delta\phi_j \xrightarrow[\text{limit}]{\text{continuum}} \int \frac{\delta \mathcal{F}}{\delta \phi(x)} dx$$

where: $$\frac{\delta \mathcal{F}}{\delta \phi(x)} = f'(\phi(x)) - \kappa \nabla^2 \phi(x)$$

Thermodynamics of the Density Field

Interfacial profile between bulk phases



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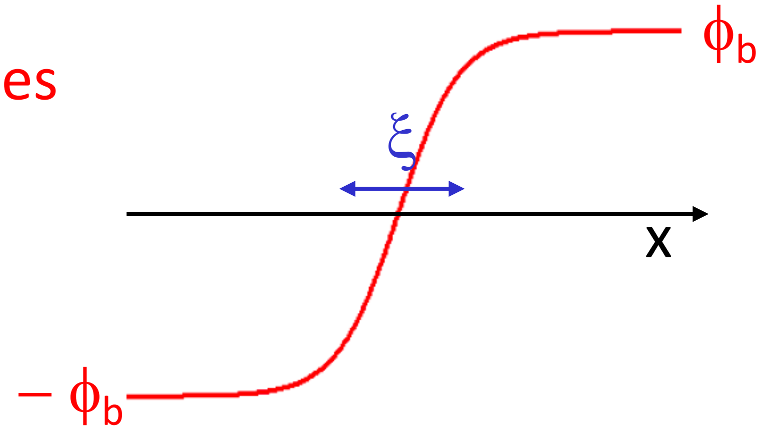
Here: ODE for $\phi(x)$

Solution $\phi(x) = \pm\phi_b \tanh\left(\dfrac{x - x_0}{\xi}\right)$ where $\xi = \sqrt{\dfrac{\kappa}{-2a}}$

Thermodynamics of the Density Field

Interfacial profile between bulk phases

$\phi = \phi(x)$, flat in y,z



Interfacial tension γ:

Substitute $\phi(x) = \pm\phi_b \tanh\left(\frac{x - x_0}{\xi}\right)$

into $\mathcal{F} = \int dV \left[f(\phi) + \frac{\kappa}{2}(\nabla\phi)^2\right]$

to get: $\mathcal{F} = V_1 f(-\phi_b) + V_2 f(+\phi_b) + A_{12}\,\gamma$

with $\gamma = \left(\frac{-8\kappa a^3}{9b^2}\right)^{1/2}$

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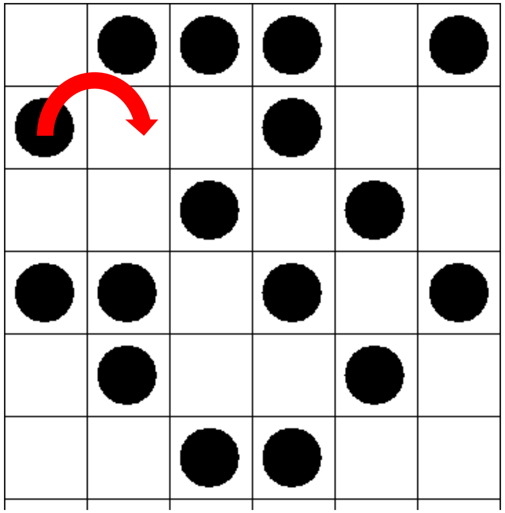
Diffusive Time Evolution

e.g. lattice gas with hopping into vacant sites



detailed balance = microscopic reversibility:

$$\frac{\mathbb{P}(\text{forward})}{\mathbb{P}(\text{backward})} = \exp[-\beta \Delta E]$$

Routes to equation of motion for density $\phi(\mathbf{r},t)$:

1. Bottom-up: choose microscopic rules and coarse-grain
2. Top-down: construct phenomenologically and check for DB

we take route 2

Diffusive Time Evolution: Model B

Ingredients:

ϕ is a conserved density $\Rightarrow$ $\dot{\phi} = -\nabla.\mathbf{J}$ (no birth /death)

Mean current: $\bar{\mathbf{J}} = -M\nabla\mu$ (stuff flows from high to low μ)

M does not depend on ϕ (for simplicity)

Example: noninteracting particles

$$\mathcal{F} = \int \frac{1}{2} f''(0)\phi^2(\mathbf{r})\, dV \qquad \mu = f''(0)\phi$$

$$\Rightarrow \quad \dot{\phi} = M f''(0)\nabla^2\phi = \tilde{D}\nabla^2\phi$$

Diffusion equation

Diffusive Time Evolution: Model B

Ingredients:

ϕ is a conserved density $\Rightarrow$ $\dot{\phi} = -\nabla.\mathbf{J}$ (no birth /death)

Mean current: $\bar{\mathbf{J}} = -M\nabla\mu$ (stuff flows from high to low μ)

M does not depend on ϕ (for simplicity)

So far, the stationary solution minimizes $\mathcal{F}$ (gradient flow)

We want instead the Boltzmann distribution $P[\phi] \propto \exp[-\beta\mathcal{F}]$

Adding a gaussian white noise, $\mathbf{J} = \bar{\mathbf{J}} + \sqrt{2k_BT\,M}\boldsymbol{\Lambda}$, achieves this

$\boldsymbol{\Lambda}$ = unit white: $\langle \Lambda_i(\mathbf{r},t)\Lambda_j(\mathbf{r}',t')\rangle = \delta_{ij}\delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$

Diffusive Time Evolution: Model B

$$\dot{\phi} = -\nabla.\mathbf{J}$$
$$\mathbf{J} = -\nabla\mu + \sqrt{2D}\boldsymbol{\Lambda}$$
$$\mu = a\phi + b\phi^3 - \kappa\nabla^2\phi$$

Λ = unit white noise
D = k_BT M
M = 1 mobility

This defines Model B

Role of Noise:

- without noise, gradient flow, $\mathcal{F}$ monotone decreasing
- with chosen noise: Boltzmann distribution + detailed balance
- final free energy from path integral over $\phi(\mathbf{r})$:

$$F = -k_B T \ln Z = -k_B T \ln \int e^{-\beta\mathcal{F}}\,\mathcal{D}\phi$$

Reversibility of Model B

Proof of detailed balance

Gaussian white noise $$\mathbb{P}[\mathbf{\Lambda}(\mathbf{r},t)] \propto \exp\left[-\frac{1}{2}\int |\mathbf{\Lambda}(\mathbf{r},t)|^2\, d\mathbf{r}\, dt\right]$$

$$\mathbf{J} + \nabla\mu = \sqrt{2D}\mathbf{\Lambda} \;\Rightarrow\; \mathbb{P}_{F,B} \propto \exp\left[-\frac{1}{4D}\int |\pm\mathbf{J} + \nabla\mu|^2\, d\mathbf{r}\, dt\right]$$

Signs: $\mathbf{J}$ is odd on time reversal, while $\mu = \delta\mathcal{F}/\delta\phi$ is even $\Rightarrow$

$$k_B T \ln\frac{\mathbb{P}_F}{\mathbb{P}_B} = -\int_{t_1}^{t_2} \mathbf{J}\cdot\nabla\frac{\delta\mathcal{F}}{\delta\phi}\, d\mathbf{r}\, dt = +\int_{t_1}^{t_2} \dot{\phi}\frac{\delta\mathcal{F}}{\delta\phi}\, d\mathbf{r}\, dt = \mathcal{F}_2 - \mathcal{F}_1$$

i.e. $$\mathbb{P}_F/\mathbb{P}_B = e^{-\beta(\mathcal{F}_2-\mathcal{F}_1)}$$ (detailed balance)

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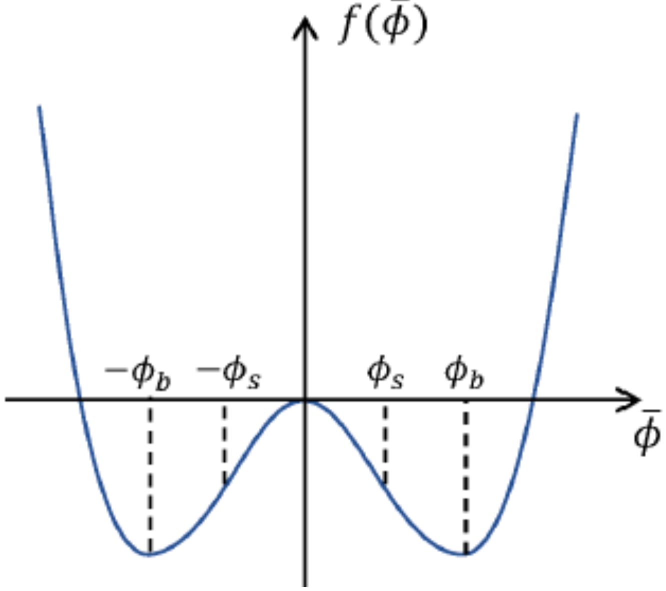
Phase Separation Kinetics

(a) Spinodal decomposition



$-\phi_s < \bar{\phi} < +\phi_s : f''(\bar{\phi}) = \alpha < 0$

$$\mu = \alpha(\phi - \bar{\phi}) - \kappa\nabla^2\phi$$

$$\dot{\phi} = \nabla^2\mu \quad + \text{ noise}$$

expand as $\phi(\mathbf{r},t) = \bar{\phi} + \sum_{\mathbf{q}} \phi_{\mathbf{q}} e^{i\mathbf{q}.\mathbf{r}}$

$$\Rightarrow \quad \dot{\phi}_{\mathbf{q}} = -q^2(\alpha + \kappa q^2)\phi_{\mathbf{q}} = r(q)\phi_{\mathbf{q}} \quad + \text{noise}$$

Phase Separation Kinetics

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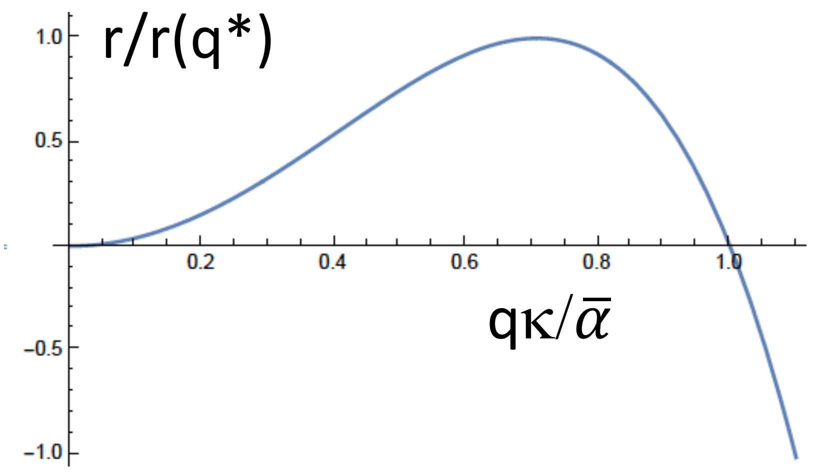

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- exponential growth of fluctuations for $0 < q < \bar{\alpha}/\kappa$ $(\bar{\alpha} \equiv -\alpha)$
- fastest mode: $q^* = (\bar{\alpha}/2\kappa)^{1/2} \Rightarrow$ characteristic length scale π/q^*

Phase Separation Kinetics

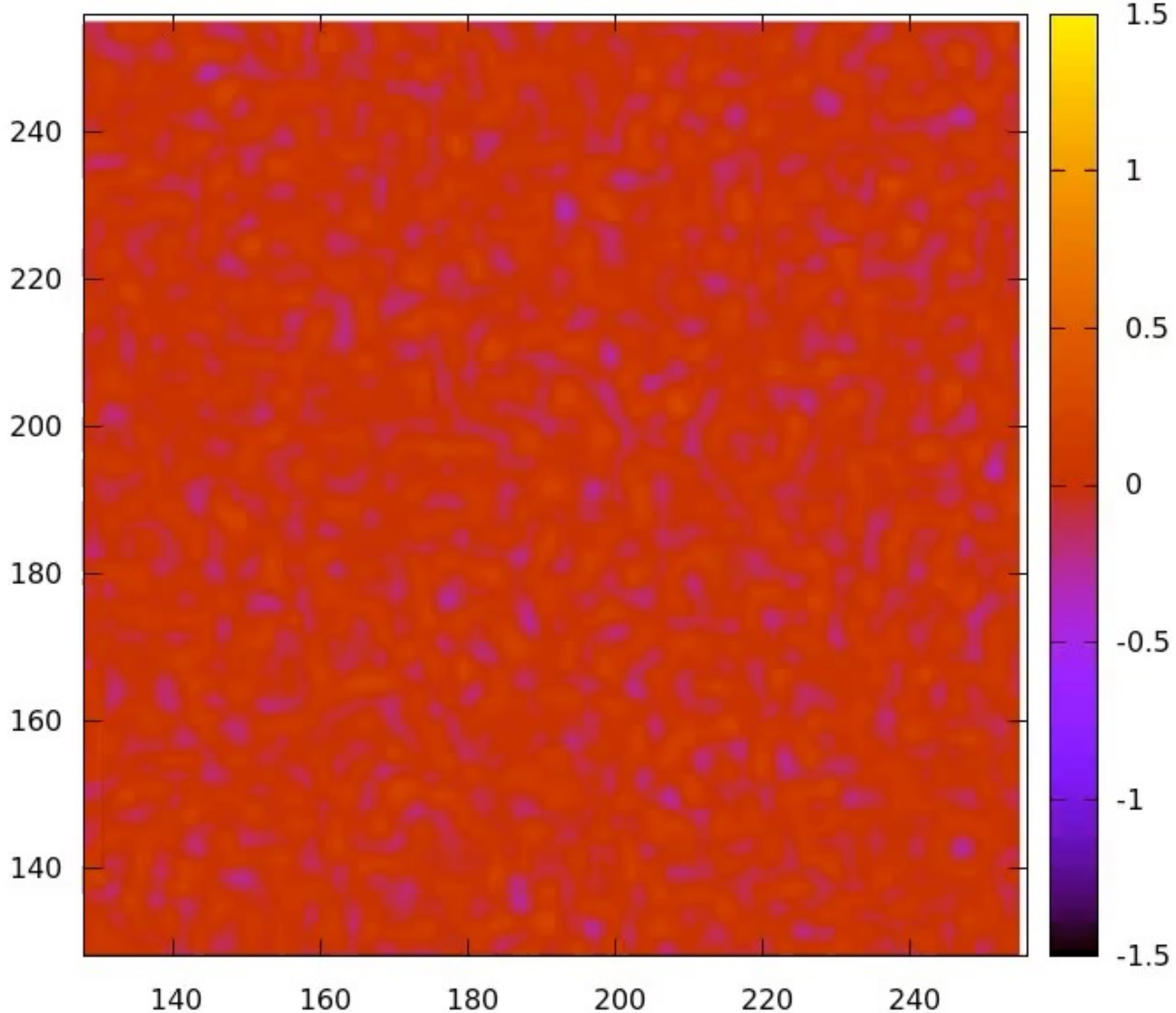
(a) Spinodal decomposition

- fuzzy domains first appear on length scale $L(0) = \pi/q^*$
- interfaces then sharpen
- local equilibrium reached between states of $\pm\phi_b$
- domain growth driven by area reduction: $L(t) \sim t^{1/3}$

  [Ostwald mechanism – explained later]

Phase Separation Kinetics

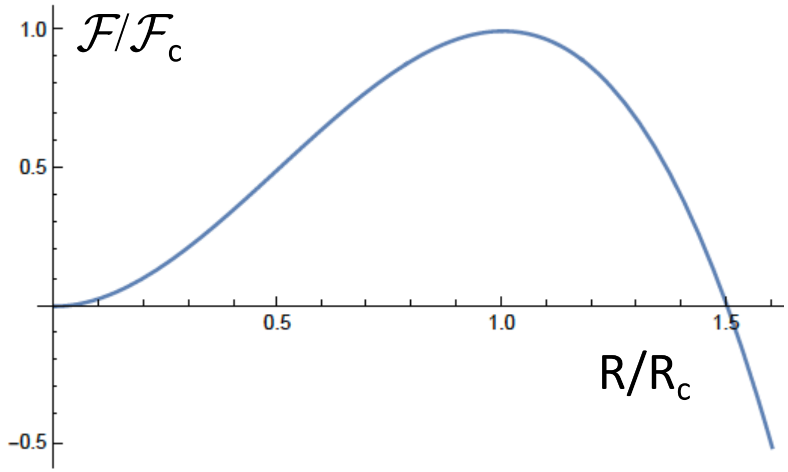
(a) Spinodal decomposition

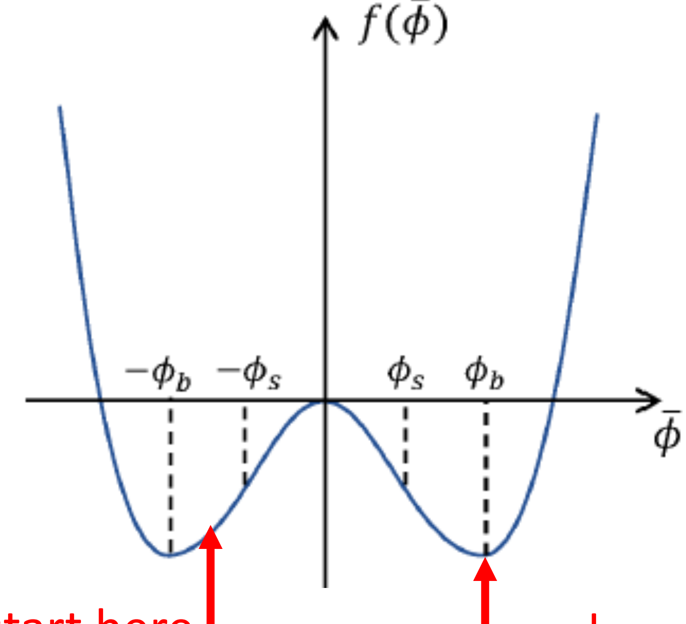


Phase Separation Kinetics

(b) Nucleation and growth (3D)

$\mathcal{F} = \gamma\, 4\pi R^2 - \delta\, f''(\phi_b)\, 4\pi R^3/3$





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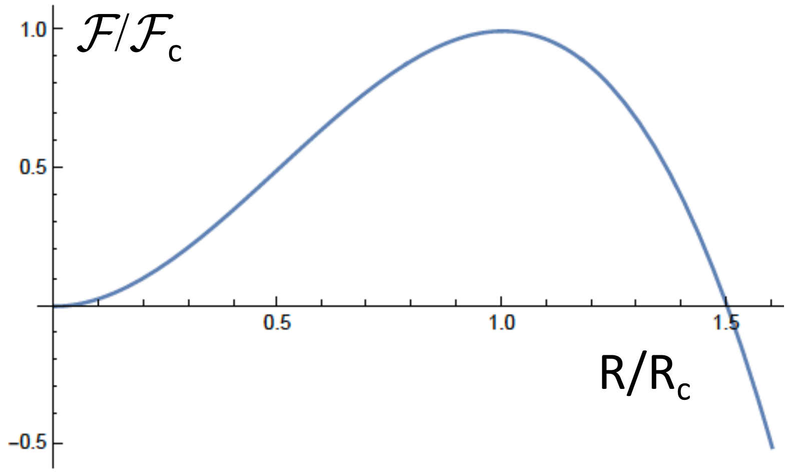
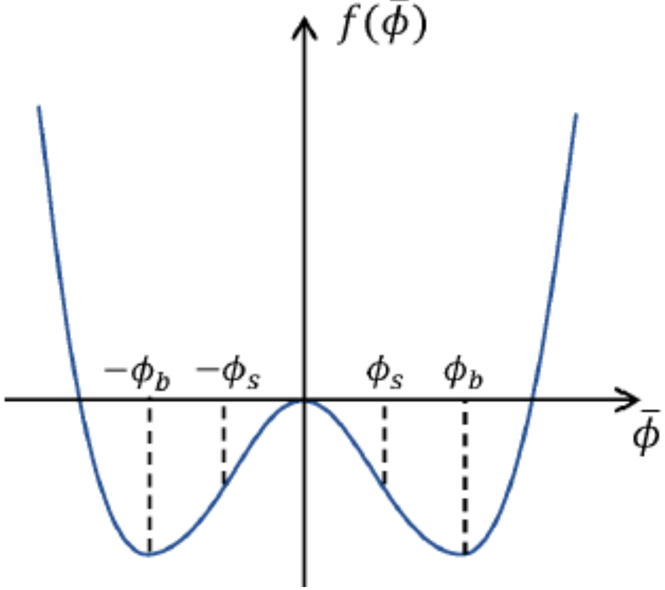
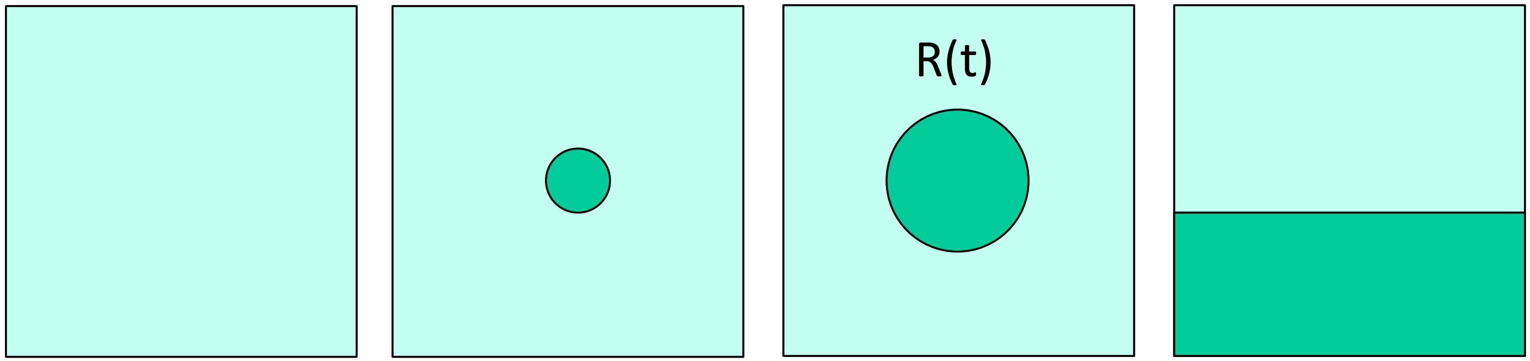




noise driven rare event

nucleation rate ∝ $\exp[-\beta\mathcal{F}_c]$



Phase Separation Kinetics:

(c) Late stages: $\mathcal{F} = \gamma A \Rightarrow$ interface-driven coarsening

Key idea: Laplace pressure at curved interfaces changes μ there

$\Rightarrow$ Large droplets grow while small droplets shrink

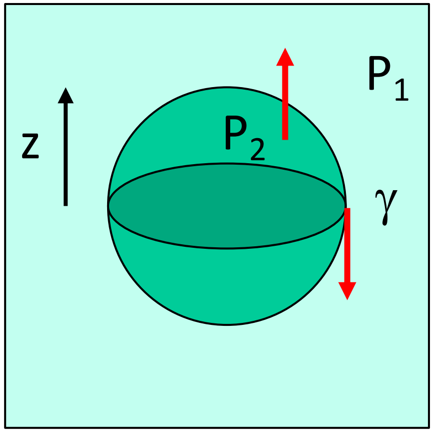
$\Rightarrow$ Material moves from bumps to hollows

A(t) decreases via "Ostwald ripening"

Phase Separation Kinetics

(c) Late stages: $\mathcal{F} = \gamma A \Rightarrow$ interface-driven coarsening

Laplace: force balance on upper half of liquid droplet



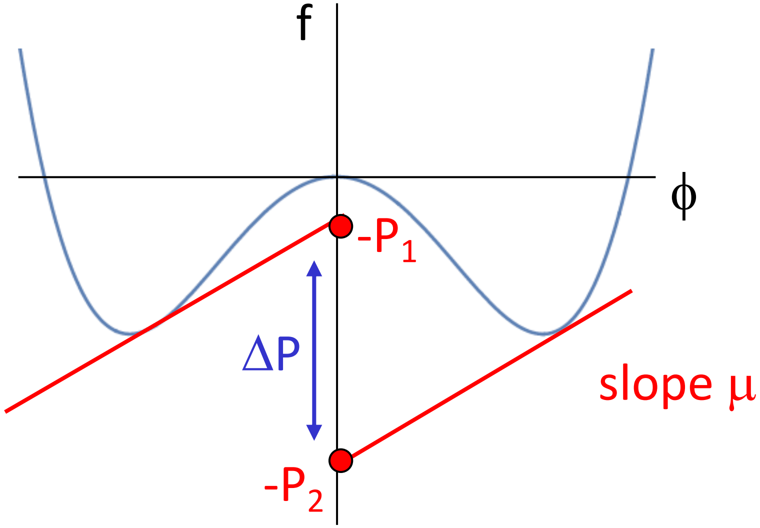
$$(P_2 - P_1)\pi R^2 \hat{z} = 2\pi R \gamma \hat{z}$$

$$\Rightarrow P_2 = P_1 + \frac{\gamma}{R}(d-1)$$ in d dimensions

Thermodynamics: $P = \mu\phi - f$

Local equilibrium requires

$$\mu_1 = \mu_2 = \mu_I(R) \equiv \frac{\gamma(d-1)}{\phi_b R}$$

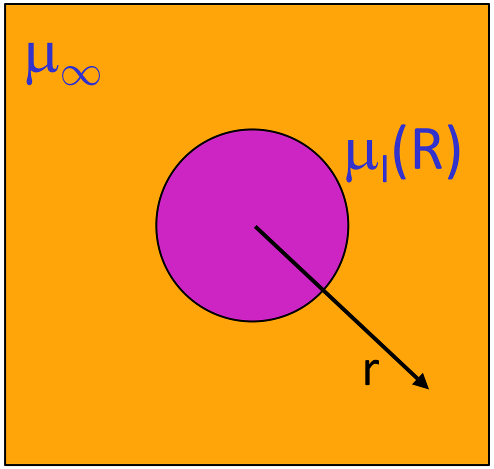


Phase Separation Kinetics

(c) Late stages: $\mathcal{F} = \gamma A \Rightarrow$ interface-driven coarsening

One droplet in vapour at ambient $\mu = \mu_\infty$

- static equilibrium if $\mu_\infty = \mu_I$
- otherwise $\dot{R} \neq 0$: growth or evaporation



Timescale separation: $$\dot{\phi} = \nabla^2 \mu \simeq 0$$

Solve Laplace equation: $$\mu(r) = \mu_\infty + \frac{\mu_I - \mu_\infty}{r}$$

Current at droplet surface: $$J = -\nabla \mu|_R = \frac{\mu_\infty - \mu_I}{R^2}$$

Conservation of ϕ: $$2\phi_b \dot{R} = -J(R, \mu_\infty)$$

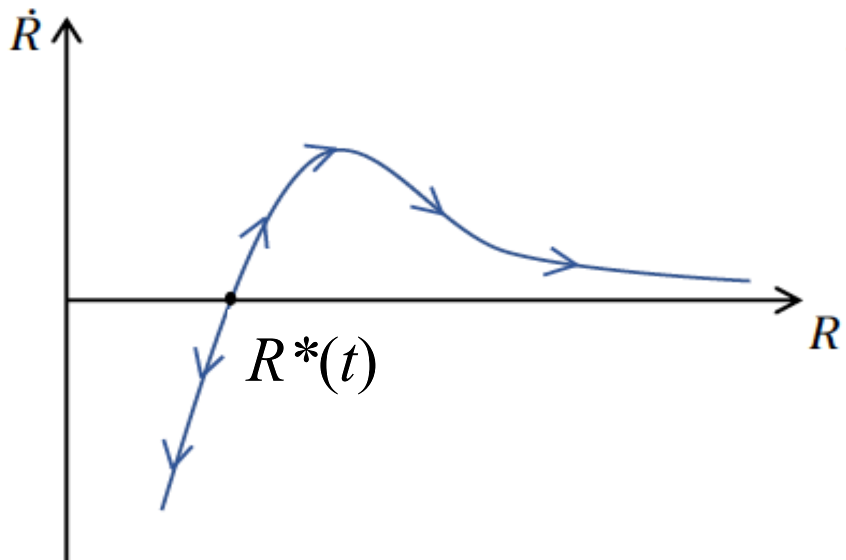
Phase Separation Kinetics

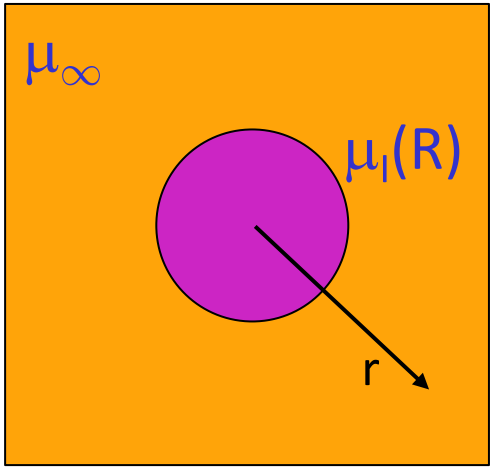
(c) Late stages: $\mathcal{F} = \gamma A \Rightarrow$ interface-driven coarsening

Multiple droplets: Ostwald process

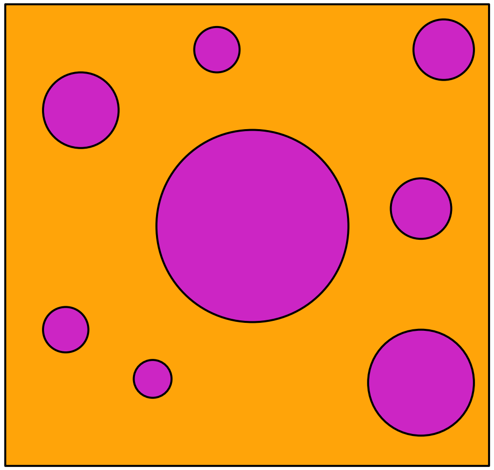
- $\mu_\infty \approx \mu_l(R^*)$ with R^* a typical droplet size
- for $R > R^*$ growth; $R < R^*$ evaporation

$$\dot{R} = \frac{J}{2\phi_b} = \frac{\gamma}{2\phi_b^2}\left[\frac{1}{R^*} - \frac{1}{R}\right]$$





approximating



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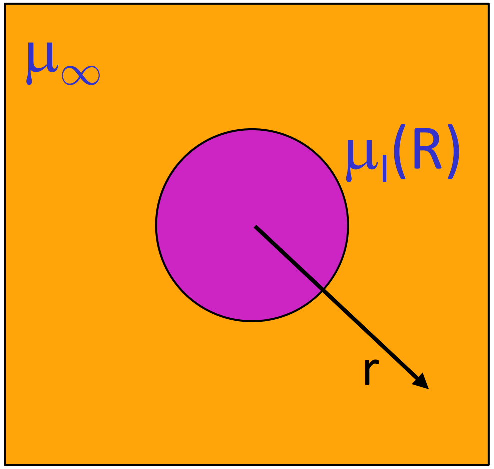
- for $R > R^*$ growth; $R < R^*$ evaporation

$$\dot{R} = \frac{J}{2\phi_b} = \frac{\gamma}{2\phi_b^2}\left[\frac{1}{R^*} - \frac{1}{R}\right]$$

- Mean domain size $L \sim R^*$ grows as

$$\dot{L} \propto \frac{\gamma}{\phi_b^2 L^2} \Rightarrow L(t) \propto \left(\frac{\gamma t}{\phi_b^2}\right)^{1/3}$$

- This holds also for late-stage spinodal



approximating