Lecture 13: Viscous effects and phase separation kinetics

Linear non-equilibrium thermodynamics.

- Local thermodynamic equilibrium.
- Gradients in intensive variables, cause currents & fluxes of their conjugate variable.

current density

kinetic coefficients

Phenomenological laws: $\vec{J}_i = \sum_k L_{ik} \nabla \phi_k$ ← thermodynamic driving forces.

Microscopic time reversibility: $L_{ij} = L_{ji}$.

(Onsager recipracal relations)

- Entropy balance: $$\frac{\partial s}{\partial t} = -\nabla \cdot \vec{J}_s + \sigma$$ ← entropy production.

entropy density

entropy current density

$\sigma \geq 0$ (consequence of second law + imposing it locally)

Last lecture we only discussed energy and particle conservation

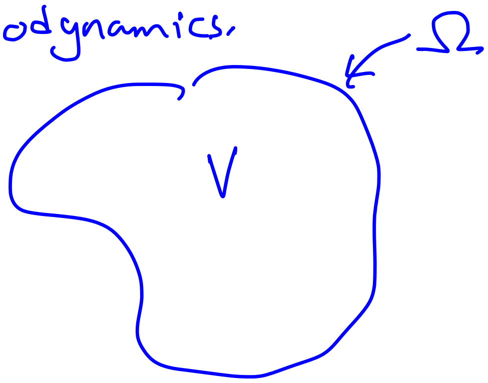
$$\frac{\partial \rho}{\partial t} + \nabla \cdot \vec{J}_\rho = 0 \qquad \vec{J}_\rho = L_{\rho\rho} \nabla\left(-\frac{\mu}{T}\right) + L_{\rho\epsilon} \nabla\left(\frac{1}{T}\right).$$

$$\frac{\partial \epsilon}{\partial t} + \nabla \cdot \vec{J}_\epsilon = 0 \qquad \vec{J}_\epsilon = L_{\epsilon\rho} \nabla\left(-\frac{\mu}{T}\right) + L_{\epsilon\epsilon} \nabla\left(\frac{1}{T}\right).$$

We implicitly assumed the absence of viscous effects, or fluid flow.

In this lecture, we will include such effects consistent with 1st & 2nd law.

First, we will focus on the first law of thermodynamics.



Consider n-component mixture

ρ_k : mass density of component k.

$$\frac{d}{dt} \int_V d\vec{r}\, \rho_k = \int_V \frac{\partial \rho_k}{\partial t}\, dV$$

$$\int_V d\vec{r}\,\frac{\partial \rho_k}{\partial t} = \underbrace{-\int_\Omega d\vec{S}\cdot(\rho_k \vec{v}_k)}_{\text{material flow of component } k \text{ into volume } V} \overset{\text{Gauß}}{=} -\int_V d\vec{r}\,\nabla\cdot(\rho_k \vec{v}_k)$$ valid for arbitrary V.

$$\Rightarrow \boxed{\begin{aligned} \frac{\partial \rho_k}{\partial t} &= -\nabla\cdot(\rho_k \vec{v}_k) \\ \frac{\partial \rho}{\partial t} &= -\nabla\cdot(\rho \vec{v}) \end{aligned}}$$

$k = 1, \ldots, n.$ Sum all n equations:

$\rho = \sum_{k=1}^{n} \rho_k$ total mass density.
(in this lecture not a number density !)

$\vec{v} = \rho^{-1} \sum_{k=1}^{n} \rho_k \vec{v}_k$ barycentric or centre-of-mass velocity.

conservation of mass

Can be augmented to include chemical reactions.

Alternatively, we can write:

$$\frac{D\rho_k}{Dt} = -\rho_k \nabla\cdot\vec{v} - \nabla\cdot\vec{J}_k \qquad \vec{J}_k = \rho_k(\vec{v}_k - \vec{v})$$ "diffusion flow"

$$\frac{D\rho}{Dt} = -\rho\,\nabla\cdot\vec{v} \qquad \frac{D}{Dt} = \frac{\partial}{\partial t} + \vec{v}\cdot\nabla$$

material derivative
or (barycentric) substantial time derivative.

Note that: $\sum_{k=1}^{n} \vec{J}_k = 0$ Only $n-1$ of n diffusion flows are independent.

Furthermore, we have balance of linear momentum:

$$\boxed{\rho \frac{D\vec{v}}{Dt} = -\nabla\cdot \underset{=}{P} + \sum_k \rho_k \vec{F}_k}$$

body forces.

$\llcorner$ pressure tensor
(minus the stress tensor)

Here, we assume that body forces are conservative: $\vec{F}_k = -\nabla \psi_k$

and we define potential energy density $\rho\psi := \sum_k \rho_k \psi_k$

Finally, we have the conservation of energy.

$$\boxed{\frac{\partial \rho e}{\partial t} = -\nabla\cdot\vec{J}_e}$$

Total specific energy: $e = \frac{1}{2}\vec{v}^2 + \psi + u$

kinetic energy of fluid

potential energy

specific internal energy.

We are interested in the part related to u.

Consider balance of linear momentum. Take inner product with $\vec{v}$ and rewrite

$$\rho\frac{D}{Dt}\left(\frac{1}{2}\vec{v}^2\right) = -\nabla\cdot\left(\underline{\underline{P}}\cdot\vec{v}\right) + \underline{\underline{P}}:\nabla\vec{v} + \sum_k \rho_k\vec{F}_k\cdot\vec{v}$$

$\underline{\underline{A}}:\underline{\underline{B}} = A_{\alpha\beta}B_{\beta\alpha}$ Since $\rho\frac{Da}{Dt} = \frac{\partial(a\rho)}{\partial t} + \nabla\cdot\left(a\rho\vec{v}\right)$ $\Big\} \Rightarrow$

$$\frac{\partial}{\partial t}\left(\frac{1}{2}\rho\vec{v}^2\right) = -\nabla\cdot\left(\underline{\frac{1}{2}\rho\vec{v}^2\vec{v}} + \boxed{\underline{\underline{P}}\cdot\vec{v}}\right) + \underline{\underline{P}}:\nabla v + \sum_k \rho_k\vec{F}_k\cdot\vec{v} \quad \text{(i).}$$

Since $\frac{\partial\psi_k}{\partial t} = 0$, it follows from mass conservation that

$$\frac{\partial}{\partial t}(\rho\psi) = -\nabla\cdot\left(\underline{\rho\psi\vec{v}} + \boxed{\sum_k \psi_k\vec{J}_k}\right) - \sum_k \rho_k\vec{F}_k\cdot\vec{v} - \sum_k \vec{J}_k\cdot\vec{F}_k. \quad \text{(ii).}$$

This motivates us to decompose:

$$\vec{J}_e = \rho e\vec{v} + \underline{\underline{P}}\cdot\vec{v} + \sum_k \psi_k\vec{J}_k + \vec{J}_q$$ which defines the heat flux.

Insertion of $\vec{J}_e$ in energy balance and using (i) & (ii):

$$\frac{\partial \rho u}{\partial t} = -\nabla\cdot\left(\rho u\vec{v} + \vec{J}_q\right) - \underline{\underline{P}}:\nabla\vec{v} + \sum_k \vec{J}_k\cdot\vec{F}_k.$$

internal energy not conserved!

We decompose: $\underline{\underline{P}} = p\,\mathbb{I} + \underline{\underline{\Pi}}$ ← viscous pressure tensor.

↑ hydrostatic pressure

Then equation for specific internal energy is:

$$\left.\begin{aligned} \rho\frac{Du}{Dt} &= -\nabla\cdot\vec{J}_q - p\,\nabla\cdot\vec{v} - \underline{\underline{\Pi}}:\nabla v + \sum_k \vec{J}_k\cdot\vec{F}_k \\ \rho\frac{Dq}{Dt} &= -\nabla\cdot\vec{J}_q \end{aligned}\right\}\Rightarrow$$

↑ added heat per unit mass

$$\boxed{\frac{Du}{Dt} = \frac{Dq}{Dt} - p\frac{Dv}{Dt} - v\,\underline{\underline{\Pi}}:\nabla\vec{v} + v\sum_k \vec{J}_k\cdot\vec{F}_k}$$

First law of thermodynamics with convection.

with $v = \rho^{-1}$ the specific volume (volume per unit mass).

What about the second law?

Now s is specific entropy.

$$\frac{\partial \rho s}{\partial t} = -\nabla\cdot\vec{J}_{s,tot} + \sigma \quad\Leftrightarrow\quad \rho\frac{Ds}{Dt} = -\nabla\cdot\vec{J}_s + \sigma$$

$\sigma \geq 0$

$\vec{J}_s = \vec{J}_{s,tot} - \rho s\vec{v}$.

Local equilibrium: $T\,ds = du + p\,dv - \sum_{k=1}^{n}\mu_k\,dc_k$.

with $c_k = \frac{\rho_k}{\rho}$ the mass fraction.

Local equilibrium: $T\frac{Ds}{Dt} = \frac{Du}{Dt} + p\frac{Dv}{Dt} - \sum_{k=1}^{n}\mu_k\frac{Dc_k}{Dt}$.

Furthermore $\rho\frac{Dc_k}{Dt} = -\nabla\cdot\vec{J}_k$

$$\vec{J}_s = \frac{1}{T}\left(\vec{J}_q - \sum_{k=1}^{n} \mu_k \vec{J}_k\right)$$

$$\sigma = \vec{J}_q \cdot \nabla\left(\frac{1}{T}\right) - \frac{1}{T}\sum_{k=1}^{n} \vec{J}_k \cdot \left(T \nabla \frac{\mu_k}{T} - \vec{F}_k\right) - \frac{1}{T}\underline{\underline{\Pi}} : \nabla \vec{v}.$$

Heat flux is not uniquely defined, see de Groot & Mazur pp 25-27.

What about viscous pressure tensor.

We take $\underline{\underline{\Pi}}$ s.t. $\Pi_{\alpha\beta} = \Pi_{\beta\alpha}$ (no sources of torque)

We can always decompose $\underline{\underline{\Pi}} = \frac{1}{3}\mathrm{tr}(\underline{\underline{\Pi}})\underline{\underline{1}} + \underset{\uparrow \text{ traceless symmetric.}}{\overset{\circ}{\underline{\underline{\Pi}}}}$

Similarly: $\nabla \vec{v} = \frac{1}{3}(\nabla\cdot\vec{v})\underline{\underline{1}} + \underset{\uparrow \text{ traceless part.}}{\overset{\circ}{\nabla}\vec{v}}$

then:

$$\underline{\underline{\Pi}} : \nabla \vec{v} = \overset{\circ}{\underline{\underline{\Pi}}} : \underset{\substack{\uparrow \\ \text{symmetric} \\ \text{traceless}}}{\nabla \overset{\circ}{\vec{v}}^{s}} + \underbrace{\frac{1}{3}\mathrm{tr}(\underline{\underline{\Pi}})}_{\pi} \nabla\cdot\vec{v}.$$

Now we see that the entropy production splits as

$$\sigma = \underbrace{\vec{J}_q \cdot \nabla\left(\frac{1}{T}\right) - \frac{1}{T}\sum_{k=1}^{n} \vec{J}_k \cdot \left(T \nabla \frac{\mu_k}{T} - \vec{F}_k\right)}_{\text{vectorial}} - \underbrace{\frac{1}{T}\overset{\circ}{\underline{\underline{\Pi}}} \cdot \nabla \overset{\circ}{\vec{v}}^{s}}_{\text{tensorial}} - \underbrace{\frac{1}{T}\pi \nabla\cdot\vec{v}}_{\text{scalar}}.$$

Thermodynamic fluxes do not depend on all components of thermodynami

forces ⟶ Curie symmetry principle.

Can be proven (not here) that fluxes and thermodynamic forces of different tensorial character do not mix!

We conclude that:

$$\vec{J}_q = L_{qq}\nabla\left(\frac{1}{T}\right) - \sum_{k=1}^{n} L_{qk}\left(\nabla\frac{\mu_k}{T} - \frac{\vec{F}_k}{T}\right)$$

(but no coupling with $\nabla\vec{v}$!)

$$\vec{J}_i = L_{iq}\nabla\left(\frac{1}{T}\right) - \sum_{k=1}^{n} L_{ik}\left(\nabla\frac{\mu_k}{T} - \frac{\vec{F}_k}{T}\right)$$

$$\overset{\circ}{\Pi}_{\alpha\beta} = -\frac{L}{T}\left(\nabla\overset{\circ}{\vec{v}}{}^{s}\right)_{\alpha\beta} = -\frac{L}{2T}\left(\partial_\alpha v_\beta + \partial_\beta v_\alpha - \frac{2}{3}\delta_{\alpha\beta}(\nabla\cdot\vec{v})\right)$$

$$\Pi = -l(\nabla\cdot\vec{v})/T.$$

Note all coefficients are scalars reflecting the underlying isotropic system! Generally they are tensors. Furthermore ORR: $L_{iq} = L_{qi}$

$L_{ik} = L_{ki}$.

Due to the Curie principle, we have moreover that scalar, vectorial, and tensorial parts of σ are separately positive definite.

It is insightful to focus on a one-component isotropic system: ($\vec{F}_k = 0\ \forall k$)

$$\frac{\partial\rho}{\partial t} = -\nabla\cdot(\rho\vec{v})$$

Continuity equation.

$$\rho\frac{Dv}{Dt} = -\nabla p + \eta_s\nabla^2\vec{v} + \left(\frac{1}{3}\eta_s + \eta_b\right)\nabla(\nabla\cdot\vec{v})$$

Navier-Stokes

$$\rho\frac{Du}{Dt} = \lambda\nabla^2 T - p\nabla\cdot\vec{v} + \underbrace{2\eta_s(\overset{\circ}{\nabla}\vec{v})^s : (\overset{\circ}{\nabla}\vec{v})^s + \eta_b(\nabla\cdot\vec{v})^2}_{\text{Rayleigh dissipation function}}$$

Equations of thermohydrodynamics.

Here $\eta_s = \frac{L}{2T}$ shear viscosity.

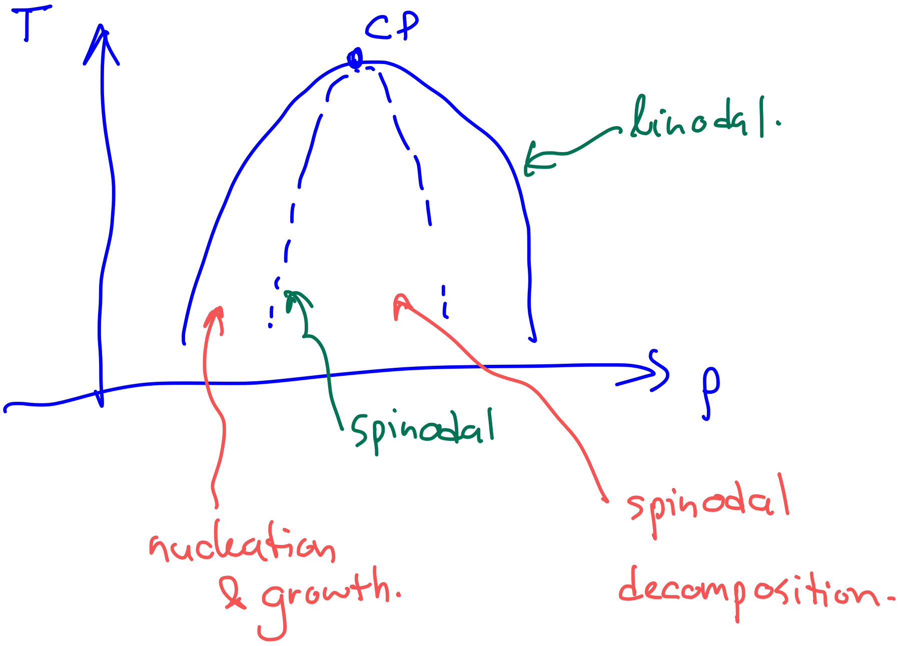
$\eta_b = \frac{l}{T}$ bulk viscosity. ! No diffusion!

$\lambda = \frac{L_{qq}}{T^2}$ heat conductivity.

Above should be supplemented by $p = p(\rho,T)$ and $u = u(\rho,T)$.

Spinodal decomposition

Recall typical phase diagram of a system that can undergo condensation:



To describe spinodal decomposition, we take purely diffusive isothermal dynamics:

$$\frac{\partial \rho}{\partial t} = D \nabla \cdot \left[\rho \nabla \beta \mu \right]$$

lets interpret this as the intrinsic chemical potential.

$$= D \nabla \cdot \left[\rho \nabla \frac{\delta \beta F}{\delta \rho(\vec{r})} \right]$$

Dynamical density functional theory

Lets take a square-gradient approximation:

$$F[\rho] = \int d\vec{r}\left[f(\rho(\vec{r})) + \kappa|\nabla\rho(\vec{r})|^2\right]. \qquad \kappa \text{ constant.}$$

$$\beta\mu(\vec{r},t) = \frac{\partial f(\rho(\vec{r},t))}{\partial\rho(\vec{r},t)} - 2\kappa\nabla^2\rho(\vec{r},t).$$

$$\Rightarrow \boxed{\frac{\partial\rho}{\partial t} = D\nabla\cdot\left[\rho(\vec{r},t)\frac{\partial^2 f(\rho(\vec{r},t))}{\partial\rho(\vec{r},t)^2}\nabla\rho(\vec{r},t) - 2\kappa\rho(\vec{r},t)\nabla\left(\nabla^2\rho(\vec{r},t)\right)\right]}$$

Cahn-Hilliard equation.

Linearise: $\rho(\vec{r},t) = \underbrace{\rho_0}_{\substack{\text{constant}\\ \text{bulk density.}}} + \delta\rho(\vec{r},t) \qquad |\delta\rho(\vec{r},t)| \ll \rho_0$

$$\frac{\partial}{\partial t}\delta\rho(\vec{r},t) = D\left[\rho_0\frac{\partial^2 f(\rho_0)}{\partial\rho_0^2}\nabla^2\delta\rho(\vec{r},t) - 2\kappa\rho_0(\vec{r},t)\nabla^4\delta\rho(\vec{r},t)\right]$$

We solve in Fourier space: $\delta\tilde{\rho}(\vec{k},t) = \int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}}\,\delta\rho(\vec{r},t)$

$$\Rightarrow \frac{\partial}{\partial t}\delta\tilde{\rho}(\vec{k},t) = -Dk^2\left[\rho_0 f''(\rho_0) + 2\kappa\rho_0 k^2\right]\delta\tilde{\rho}(\vec{k},t)$$

Solution: $\dfrac{\delta\tilde{\rho}(\vec{k},t)}{\delta\tilde{\rho}(\vec{k},0)} = \exp\left[R(k)t\right].$

$$\boxed{R(k) = -\underbrace{D\rho_0 f''(\rho_0)}_{:= D_{coop}}\left[1 + \frac{2\kappa k^2}{f''(\rho_0)}\right]k^2}$$

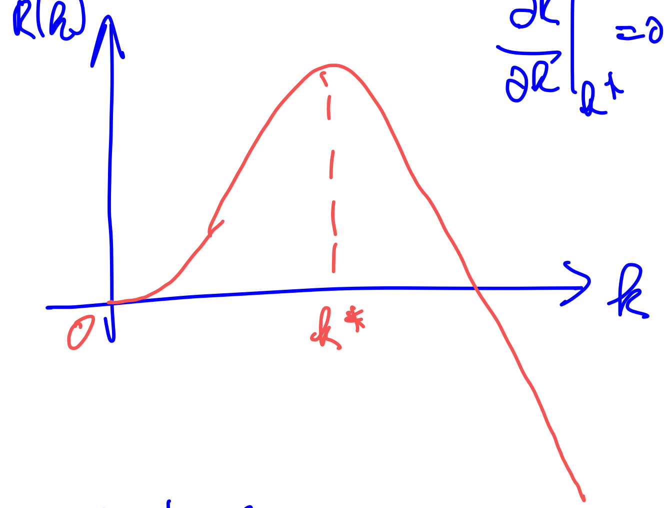
"cooperative diffusion constant"

Note within spinodal $D_{coop} < 0$ ("uphill diffusion")

Within spinodal: fluctuations amplify ($R>0$ for some k).

Outside spinodal $R<0$ fluctuations relax.

Growth rate $R(k)$



$$\frac{\partial R}{\partial k}\Big|_{k^*} = 0 \Rightarrow k_* = \left(\frac{-f''(\rho_0)}{4\kappa}\right)^{1/2} \sim \xi^{-1}.$$

Deeper the quench

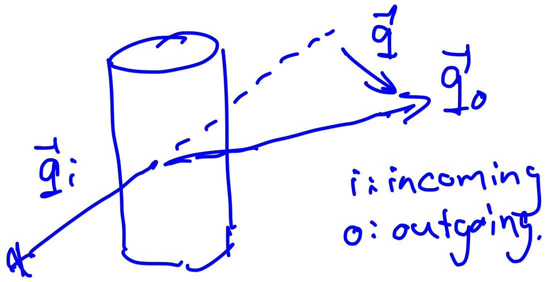
$\Rightarrow k_* \uparrow$

Typical length scale: k_*^{-1} (domain size)

$\Rightarrow$ finer the structure

Quench in unstable region produces instabilities that grow exponentially with time with one characteristic length scale that grows more quickly than others

Experimental determination via scattering



scattered intensity:

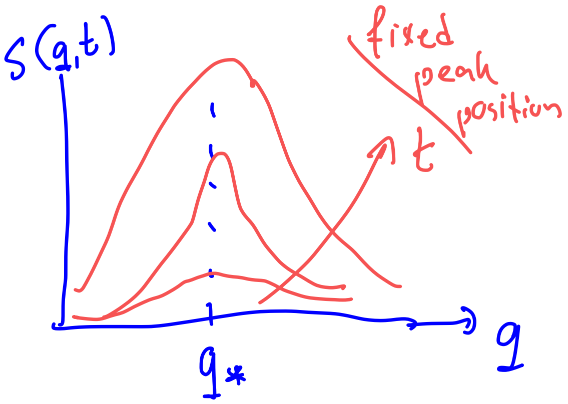
$$I(\vec{q},t) \propto S(\vec{q},t)$$

"dynamical structure factor"

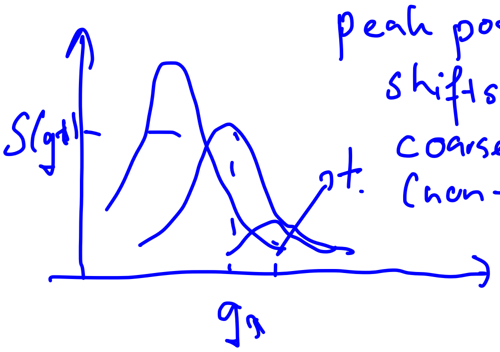
$$S(\vec{q},t) = \langle \delta\tilde{\rho}(\vec{q},t)\,\delta\tilde{\rho}(-\vec{q},0)\rangle$$

One can show that (Onsager regression hypothesis)

$$S(\vec{q},t) = S(\vec{q},0)\,e^{R(\vec{q})t}.$$



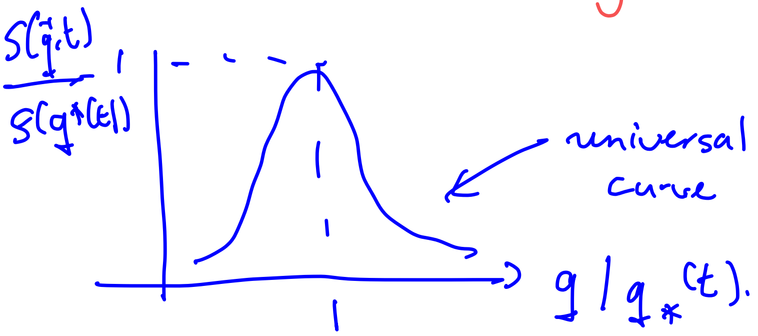
Linear Cahn-Hillard theory



peak position shifts due to coarsening (non-linear effect).

Experiment.

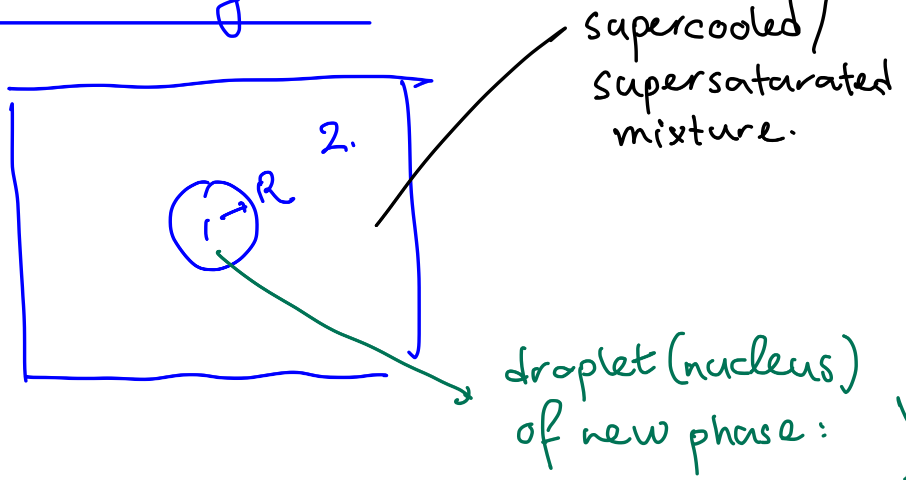
Domain size grows!



Dynamical scale invariance.

(Slides!)

Nucleation and growth.



$V = \frac{4}{3}\pi R^3$
$A = 4\pi R^2$.

- Mixed state locally stable, but globally unstable.
  Locally stable $\not\Leftarrow\Rightarrow$ linearly stable.
- Relaxation to equilibrium requires non-linear = large spontaneous fluctuation or external perturbation.
- Rate of formation can be estimated from thermodynamic arguments

Work done to create drop: $\Delta G = N_1 \Delta\mu + \gamma A$

\# of A particles in drop.

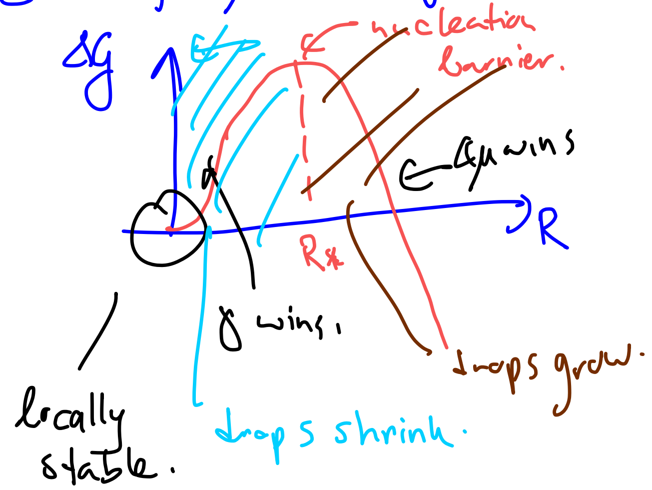
Note that:
- Free energy gain $\Delta\mu < 0$
- $\gamma A > 0$ free energy loss.

$\Big\} \Rightarrow$ competition.

$\gamma, \Delta\mu$ computable from model free energy!

$$\Rightarrow \Delta G = \frac{4}{3}\pi R^3 \underbrace{\left(\frac{N_1}{\frac{4}{3}\pi R^3}\right)}_{\equiv \rho_1} \Delta\mu + 4\pi R^2 \gamma = \frac{4}{3}\pi R^3 \rho_1 \Delta\mu + 4\pi R^2 \gamma.$$

$\equiv \rho_1$ density of A in drop, set by thermodynamics



Critical nucleus: $\left.\frac{\partial \Delta G}{\partial R}\right|_{R_*} = 0$

$\Rightarrow R_* = 0$ (local minimum)

$R_* = -\frac{2\gamma}{\rho_1 \Delta\mu}$ (maximum).

Hence: $N_* = \frac{32}{3}\pi \frac{\gamma^3}{\rho_1^2 |\Delta\mu|^3}$ (size critical nucleus)

$\Delta G_* = \frac{16\pi\gamma^3}{3\rho_1^2 \Delta\mu^2}$ (nucleation barrier).

Note: (i) Near binodal: $\Delta\mu \to 0 \Rightarrow N_* \to \infty \wedge \Delta G_* \to \infty$.

(ii) Near spinodal: $\gamma \to 0 \Rightarrow N_* \to 0$

Steady-state nucleation rate. $J = K \rho_0 \boxed{e^{-\beta\Delta G^*}}$

Boltzmann factor accounting for probability that a critical nucleus is formed.

#nuclei per unit volume per second.

attempt frequency.

initial concentration.

$\beta\Delta G^* \uparrow \Rightarrow$ slower nucleation.