Lecture 12: Viscous effects and phase separation kinetics

Linear non-equilibrium thermodynamics.

• Local thermodynamic equilibrium.

• Gradients in intensive variables, cause currents & fluxes of their conjugate variable.

Phenomenological laws: $\vec{j}_i = \sum_k L_{ik} \nabla \phi_k$

current density

kinetic coefficients

ϕ_k thermodynamic driving forces.

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

(Onsager reciprocal relations)

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

entropy density

entropy current density

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

Past lecture we only discussed energy and particle conservation

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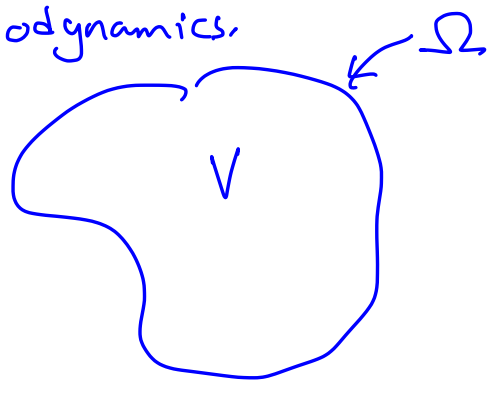
$$\frac{\partial \varepsilon}{\partial t} + \nabla \cdot \vec{j}_\varepsilon = 0 \qquad \vec{j}_\varepsilon = L_{\varepsilon\rho} \nabla \left(-\frac{\mu}{T}\right) + L_{\varepsilon\varepsilon} \nabla \left(\frac{1}{T}\right).$$

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.

Ω

V

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

$$\int_V d\vec{r} \, \frac{\partial \rho_k}{\partial t} = -\int_\Omega d\vec{S} \cdot (\rho_k \vec{v}_k) \overset{\text{Gauß}}{=} -\int_V d\vec{r} \, \nabla \cdot (\rho_k \vec{v}_k) \qquad \text{valid for arbitrary } V.$$

$\underbrace{\qquad\qquad\qquad}$ material flow of component k into volume V

$$\Rightarrow \boxed{\begin{array}{l} \dfrac{\partial \rho_k}{\partial t} = -\nabla \cdot (\rho_k \vec{v}_k) \\[4mm] \dfrac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \vec{v}) \end{array}} \qquad k = 1, \dots, n.$$

conservation of mass

$\text{Sum all } n \text{ equations:}$

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

$$\vec{v} = \rho^{-1} \sum_{k=1}^{n} \rho_k \vec{v}_k \qquad \begin{array}{l}\text{barycentric} \\ \text{or centre-of-mass} \\ \text{velocity.}\end{array}$$

Can be augmented to include chemical reactions.

Alternatively, we can write:

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

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

material derivative
or (barycentric) substantial time derivative.

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

Furthermore, we have balance of linear momentum:

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

— 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 $\quad \rho \psi := \sum_k \rho_k \psi_k$

Finally, we have the conservation of energy.

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

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

kinetic energy of fluid

potential energy

$\nwarrow$ 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

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

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

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

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

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

This motivates us to decompose:

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

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

$$\frac{\partial \rho u}{\partial t} = -\nabla \cdot (\rho u \vec{v} + \vec{j}_q) - \underline{\underline{P}} : \nabla \vec{v} + \sum_k \vec{j}_k \cdot \vec{F}_k. \quad \text{!}$$

internal energy not conserved !

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

↑ hydrostatic pressure

Then equation for specific internal energy is:

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

$$\rho \frac{Dq}{Dt} = -\nabla \cdot \vec{J}_q$$

↑ added heat per unit mass

$\Bigg\} \Rightarrow$

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

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.

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

$$\sigma \geq 0 \qquad\qquad \vec{J}_s = \vec{J}_{s,tot} - \rho s \vec{v}.$$

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

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

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

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

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

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

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 $\underline{\underline{\Pi}} = \frac{1}{3}\mathrm{tr}\left(\underline{\underline{\Pi}}\right)\underline{\underline{1}} + \overset{\circ}{\underline{\underline{\Pi}}}$

↳ traceless symmetric.

Similarly: $\nabla\vec{v} = \frac{1}{3}(\nabla\cdot\vec{v})\underline{\underline{1}} + \overset{\circ}{\nabla\vec{v}}$

↳ traceless part.

then:

$$\underline{\underline{\Pi}} : \nabla\vec{v} = \overset{\circ}{\underline{\underline{\Pi}}} : \overset{\circ}{\nabla\vec{v}}{}^{s} + \frac{1}{3}\mathrm{tr}\left(\underline{\underline{\Pi}}\right)\nabla\cdot\vec{v}.$$

↳ symmetric traceless   ↳ Π

Now we see that the entropy production splits as

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

⎵ vectorial ⎵   ⎵ tensorial ⎵   ⎵ scalar ⎵

Thermodynamic fluxes do not depend on all components of thermodynamic forces ⟶ Curie symmetry principle.

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

We conclude that:

$$\vec{J}_q = L_{qq}\nabla\left(\frac{1}{T}\right) - \sum_{k=1}^{n} L_{qk}\left(\nabla\frac{\mu_k}{T} - \frac{\vec{F}_k}{T}\right) \quad \text{(but no coupling with } \nabla\vec{v}\text{!)}$$

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

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

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

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: $(\vec{F}_k = 0\ \forall k)$

$$\frac{\partial \rho}{\partial t} = -\nabla\cdot(\rho\vec{v}) \qquad \text{Continuity equation.}$$

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

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

$$\underbrace{\qquad\qquad\qquad\qquad\qquad\qquad}_{\text{Rayleigh dissipation function}}$$

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

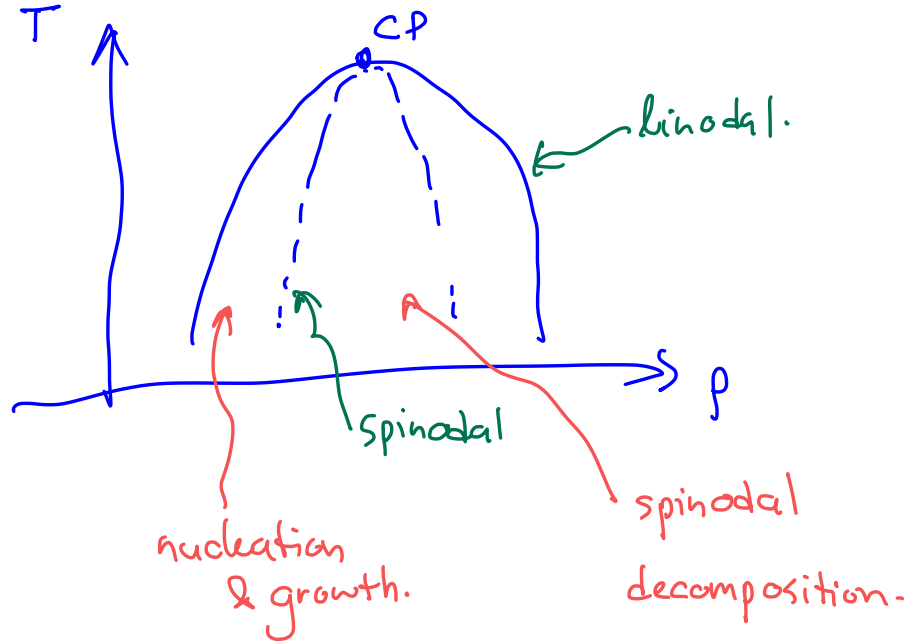$\eta_b = \frac{\ell}{T}$ bulk viscosity. ! No diffusion !

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

$$= D \nabla \cdot \left[\rho \nabla \frac{\delta \beta F}{\delta \rho(\vec{r})} \right] \qquad \text{Dynamical density functional theory}$$

Lets take a square-gradient approximation:

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

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

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

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: $\boxed{\begin{array}{l} \dfrac{\delta\tilde{\rho}(\vec{k},t)}{\delta\tilde{\rho}(\vec{k},0)} = \exp\left[R(k)t \right]. \\[2em] R(k) = -D\rho_0 f''(\rho_0)\left[1 + \dfrac{2\kappa k^2}{f''(\rho_0)} \right]k^2 \end{array}}$

$:= D_{coop}.$
"cooperative diffusion constant"

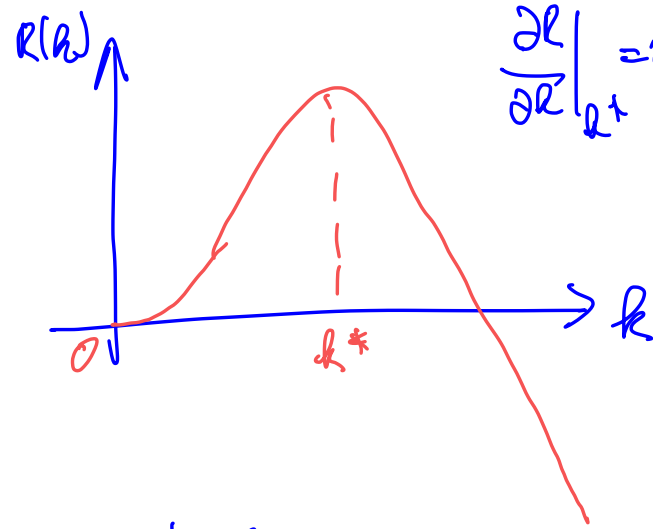Note within spinodal $D_{coop} < 0$ ("uphill diffusion")

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

Outside spinodal $R < 0$ fluctuations relax.

Growth rate $R(k)$

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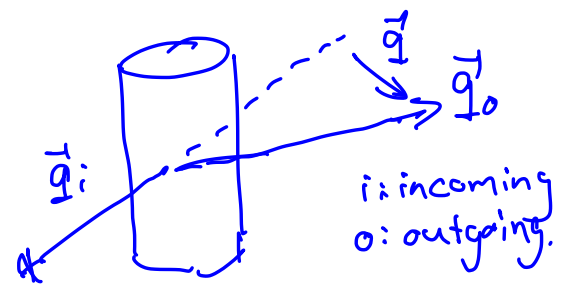
$$\sim \xi^{-1}.$$

Deeper the quench

$$\Rightarrow k_* \uparrow$$

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

$$\Rightarrow \text{finer the structure}$$

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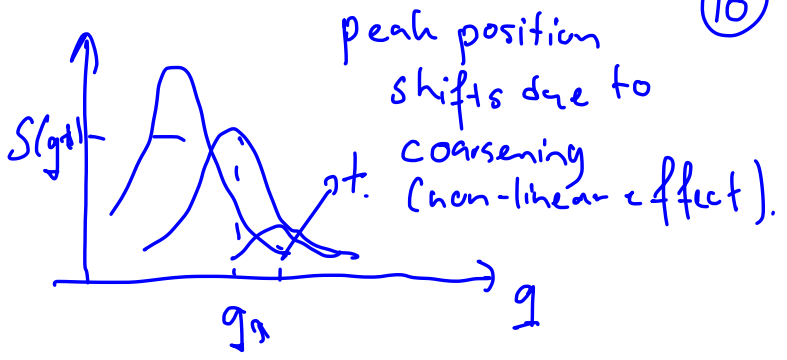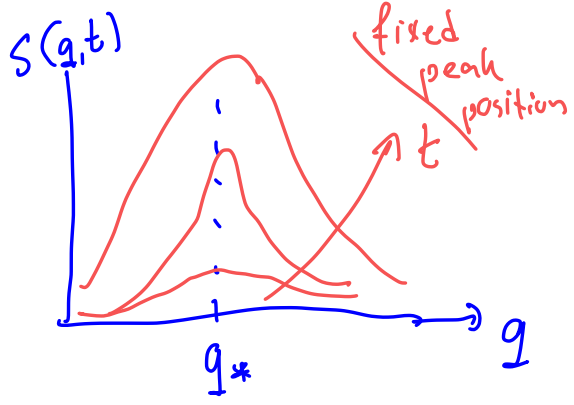
Experimental determination via scattering

i: incoming
o: outgoing.

scattered intensity:

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

"dynamical structure factor"

$$S(\vec{q}, t) = \langle \delta \tilde{\rho}(\vec{q}, t) \, \delta \tilde{\rho}(-\vec{q}, 0) \rangle$$
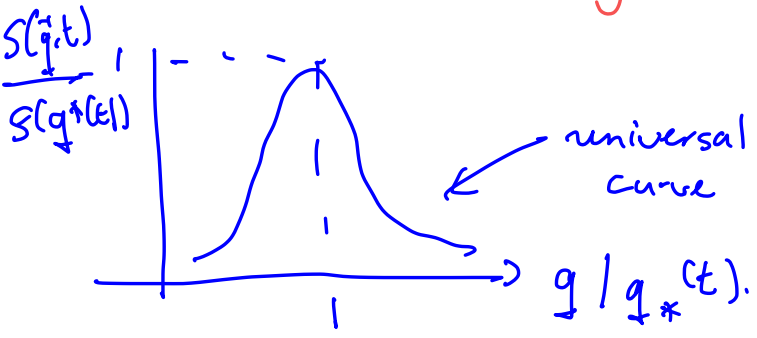
One can show that (Onsager regression hypothesis)

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

$S(q,t)$

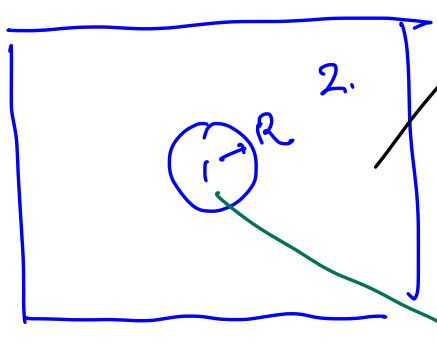~fixed peak position~

t

$q*$

q

$S(q,t)$

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

q_s

q

Linear Cahn-Hillard theory

$\dfrac{S(q,t)}{S(q*(t))}$

universal curve

$g / q_*(t)$.

Experiment.

Domain size grows!

Dynamical scale invariance.

(Slides!)

Nucleation and growth.

2.

$\rightarrow R$

supercooled / supersaturated mixture.

droplet (nucleus) of new phase:

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

- Mixed state locally stable, but globally unstable.
  Locally stable $\iff$ linearly stable.

- Relaxation to equilibrium requires non-linear $\hat{=}$ large spontaneous
  fluctuation or external perturbation.

- Rate of formation can be estimated from thermodynamic arguments

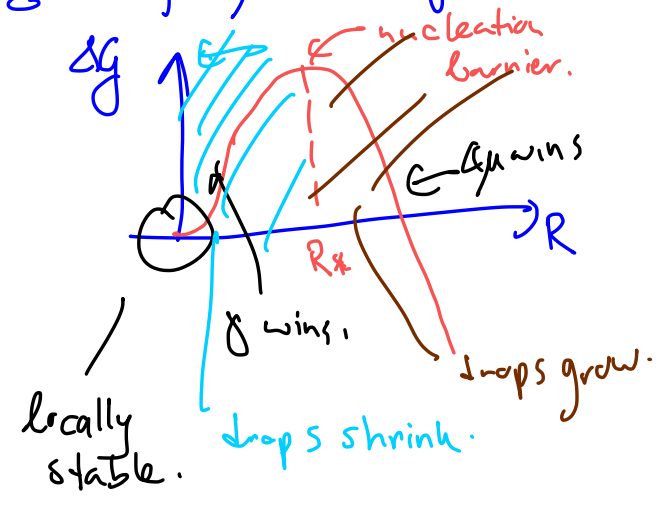Work done to create drop: $\Delta G = N_1 \Delta \mu + \gamma A$

# of A particles in drop.

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

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

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

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

nucleation barrier.

$-\Delta\mu$ wins

γ wins.

locally stable.

drops shrink.

drops grow.

Critical nucleus: $\dfrac{\partial \Delta G}{\partial R}\Big|_{R_*} = 0$

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

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

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

$\Delta G_* = \dfrac{16\pi\gamma^3}{3\rho_1^2 \Delta\mu^2}$ (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. $\mathcal{J} = K \rho_0 e^{-\beta \Delta G^*}$

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.

ΔG

quench depth.

R