

# Statistical Mechanics

## E0415

Fall 2020, lecture 6  
Abrupt phase transitions

# Take home... RG

Quickly simulating the coarsening of some random 1D system. The starting configuration has  $N = 3^5$  elements. At each step, each set is replaced by the majority vote.



... percolation ...

"Considering the conductivity and elasticity of this kind of system (with dimension  $d > 1$ ), I would expect that near the critical point the elastic modulus increase faster than the conductivity. .... Thus the elasticity would start increasing faster than the conductivity near the critical point, when the correlation length is not quite infinite yet."

The main argument here is not easy, and depends on the # of constraints as a function of "p" and the consequences of that for the quantity at hand. In other words, if you add a bond to a marginally connected structure, what happens? **"Constraint counting"**.

[https://en.wikipedia.org/wiki/Structural\\_rigidity](https://en.wikipedia.org/wiki/Structural_rigidity), and the great JC Maxwell

(This leads us quickly to some poorly understood problems in polymer physics, granular elasticity, mathematics, and biophysics... in 3D in particular)

# Why bother?

Says Sethna:

Most phase transitions are abrupt. At the transition, the system has discontinuities in most physical properties; the density, compressibility, viscosity, specific heat, dielectric constant, and thermal conductivity all jump to new values. Furthermore, in most cases these transitions happen with no precursors, no hint that a change is about to occur; pure water does not first turn to slush and then to ice,<sup>1</sup> and water vapor at 101 °C has no little droplets of water inside.<sup>2</sup>

# Stability and metastability

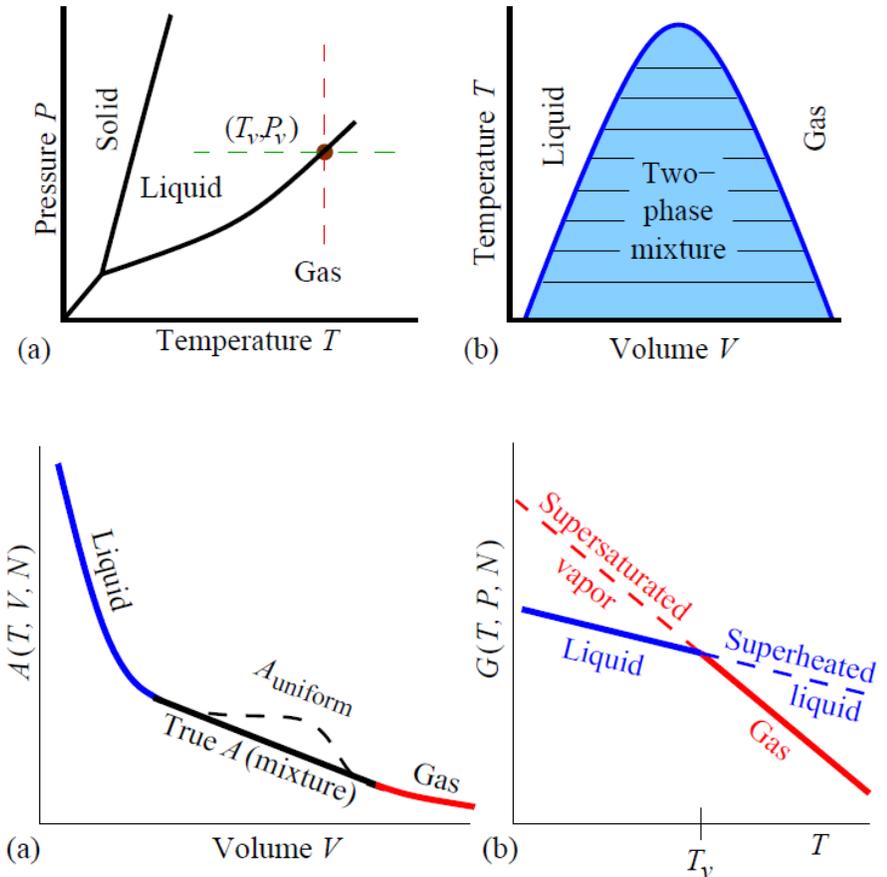
$$G(T, P, N) = E - TS + PV.$$

Gibbs: the phase with the lowest chemical potential  $\mu$  wins.

Co-existence (both phases present) in some region in  $V, T$ .

Discontinuity in FE (constant pressure) means for the derivative of Gibbs FE, or  $\left. \frac{\partial G}{\partial T} \right|_{P,N} = -S$  that there is an entropy difference due to latent heat:  $\Delta S = LN/T_v$ .

“First-order transitions” –  $L$  latent heat per particle.



# Maxwell construction

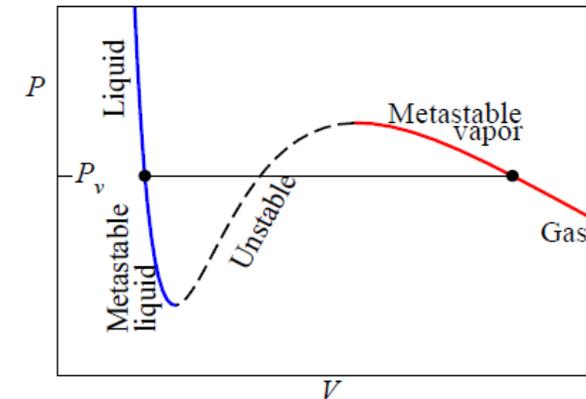
At constant number  $N$  and temperature  $T$

$$\Delta G = \int_{P_{\text{liq}}}^{P_{\text{gas}}} V(P) dP = 0.$$

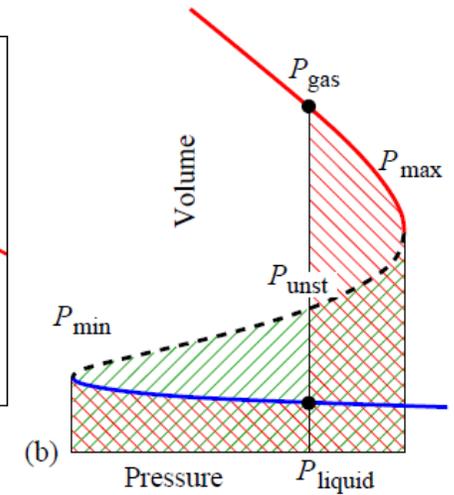
so we have

$$\begin{aligned} \Delta G = & \int_{P_{\text{liq}}}^{P_{\text{min}}} V(P) dP + \int_{P_{\text{min}}}^{P_{\text{unst}}} V(P) dP \\ & + \int_{P_{\text{unst}}}^{P_{\text{max}}} V(P) dP + \int_{P_{\text{max}}}^{P_{\text{gas}}} V(P) dP, \end{aligned}$$

2 positive and 2 negative contributions define  $P_v$  and  $P_{\text{unst}}$



(a)



(b)

# Nucleation or critical droplets

Try to go below the phase transition by a  $\Delta T$  – where does the liquid come to a gas?

Free energy difference per molecule due to the droplet vs. the cost of the surface: surface tension.

[One makes here lots of hidden assumptions... geometry, surface tension...]

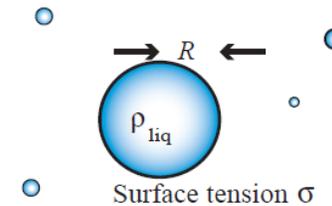


Fig. 11.4 Vapor bubble. The nucleation of a new phase happens through a rare thermal fluctuation, where a droplet of the new phase forms of sufficient size to get it over the free energy barrier of Fig. 11.5.

$$\begin{aligned}\Delta\mu &= (G_{\text{gas}} - G_{\text{liq}})/N = \left( \frac{\partial(G_{\text{gas}} - G_{\text{liq}})}{\partial T} \Big|_{P,N} (T - T_v) \right) / N \\ &= \Delta S \Delta T / N = (LN/T_v)(\Delta T/N) = L\Delta T/T_v.\end{aligned}\quad (11.6)$$

# Critical radius

Write the total FE as a function of  $R$ : critical radius and a barrier height come out of this.

Fate of a droplet depends on... in particular  $\Delta T$ .

This is “homogeneous” (in space) nucleation, with rate  $\Gamma$ .

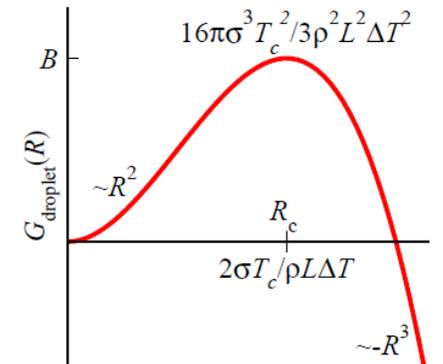
$$\Gamma = (\text{prefactors})e^{-B/k_B T}.$$

$$G_{\text{droplet}}(R) = \sigma A - V \rho_{\text{liq}} \Delta \mu = 4\pi R^2 \sigma - \left(\frac{4}{3}\pi R^3\right) \rho_{\text{liq}} (L \Delta T / T_v).$$

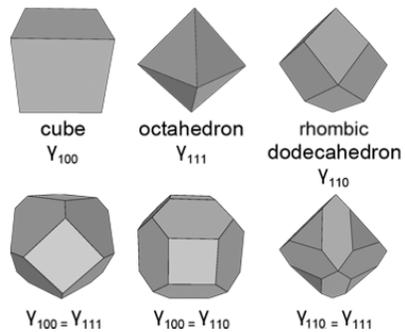
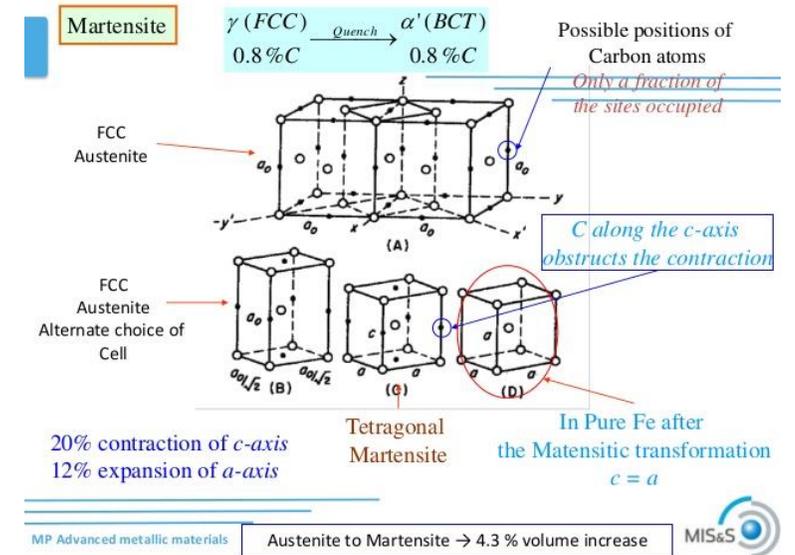
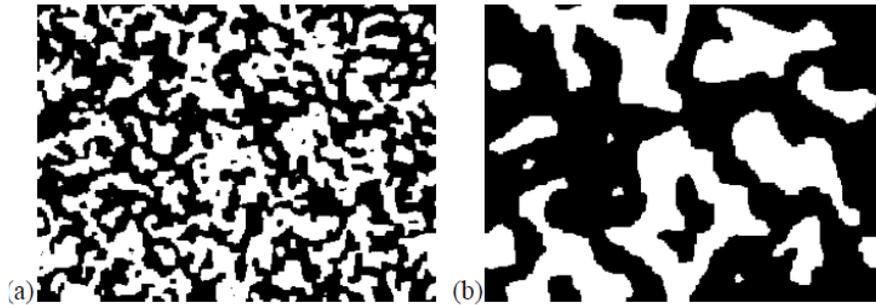
$$\left. \frac{\partial G_{\text{droplet}}}{\partial R} \right|_{R_c} = 8\pi \sigma R_c - 4\pi \rho_{\text{liq}} (L \Delta T / T_v) R_c^2 = 0,$$

$$R_c = \frac{2\sigma T_v}{\rho_{\text{liq}} L \Delta T},$$

$$B = \frac{16\pi \sigma^3 T_v^2}{3\rho_{\text{liq}}^2 L^2} \frac{1}{(\Delta T)^2}.$$



# Morphology of phases or coarsening



## Nanoparticle shapes by using Wulff constructions and first-principles calculations

Georgios D. Barmparis, Zbigniew Lodziana, Nuria Lopez et al.

Beilstein J. Nanotechnol. 2015, 6, 361–368.

doi:10.3762/bjnano.6.35

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# Two mechanisms for coarsening

Conserved vs. non-conserved.

Surface tension drives in the latter the process, resulting in a “RW”-like scaling.  $\beta = 1/2$ .

$$\tau = \frac{\partial F_{\text{surface}}}{\partial R} / (4\pi R^2) = 2\sigma/R.$$

$$\frac{dR}{dt} = -\eta\tau = -\eta\frac{2\sigma}{R}.$$

$$L(t) \sim R_0 = \sqrt{4\sigma\eta t} \propto \sqrt{t}.$$

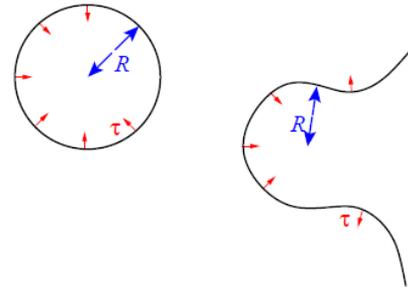


Fig. 11.8 Curvature-driven interface motion. The surface tension  $\sigma$  at the interface produces a traction (force per unit area)  $\tau = 2\sigma\kappa$  that is proportional to the local mean curvature of the surface  $\kappa$  at that point. The coarsening morphology has a characteristic length  $R$ , so it has a characteristic mean curvature  $\kappa \sim 1/R$ . For non-conserved order parameters, these forces will lead to a length scale  $L(t) \sim t^{1/2}$ .

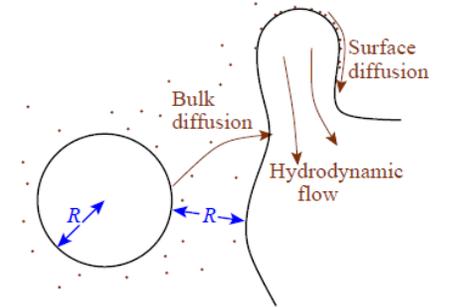


Fig. 11.9 Coarsening for conserved order parameter. Differences in local mean curvature drives the growth in the case of a conserved order parameter. Atoms will diffuse from regions of high positive curvature to regions of low or negative curvature. Bulk diffusion dominates on long length scales ( $L(t) \sim t^{1/3}$ ); surface diffusion can be important when the scales are small ( $L(t) \sim t^{1/4}$ ). For liquids, hydrodynamic flow makes things more complicated [134].

# Coarsening for conserved systems

Now this is driven by inhomogeneities in the chemical potential.

The coarsening time is computed by the time for a droplet to vanish.  $\beta = 1/3$ .

Caveats: this is a 3D argument. The barriers can be higher (surface coarsening, more complex mass transport mechanisms). Random systems: FE / V,  $\sigma$  may change.

$$v = \gamma \nabla \mu \Rightarrow J = \rho v = \rho \gamma \nabla \mu$$

$$\Delta \mu = \frac{dF_{\text{surface}}}{dR} / \frac{dN}{dR} = (8\pi\sigma R) / (4\pi R^2 \rho) = \frac{2\sigma}{R\rho}, \quad J \sim \rho \gamma \frac{\Delta \mu}{\Delta R} \sim \frac{2\gamma\sigma}{R^2}.$$

$$\begin{aligned} \frac{dV_{\text{droplet}}}{dt} &= \frac{4}{3}\pi \left( 3R^2 \frac{dR}{dt} \right) \\ &= - \frac{A_{\text{droplet}} J}{\rho} = -(4\pi R^2) \frac{2\gamma\sigma}{\rho R^2} = - \frac{8\pi\gamma\sigma}{\rho}, \\ \frac{dR}{dt} &= - \frac{2\gamma\sigma}{\rho} \frac{1}{R^2}, \\ \int_{R_0}^0 R^2 dR &= \int_0^{t_f} - \frac{2\gamma\sigma}{\rho} dt, \\ \frac{R_0^3}{3} &= \frac{2\gamma\sigma}{\rho} t_f, \end{aligned}$$

$$L(t) \sim R_0 = \left( \frac{6\gamma\sigma}{\rho} t \right)^{1/3} \propto t^{1/3}.$$

# Take home

We concentrate on Sethna Ch 11 and abrupt phase transitions. The Chapter is about three things. Why there is metastability (and thus abrupt transitions), how the metastability is broken (nucleation) and the signatures such as snowflakes (and their shape due to the growth process). Read the Chapter and check the particular focus topics from the lecture summary.

The take home problem is as follows. Check the problem 11.9 on snowflake growth. It argues for the flake to have six-fold symmetry. Now the question is, a popular claim is that no two flakes have equal shapes. Why is that so? To have a bit more insight check out the Wikipedia article on snowflakes and a good site is <http://www.snowcrystals.com/science/science.html>.