Statistical Mechanics
E0415

Fall 2023, lecture 6
Abrupt phase transitions

Take home… RG

“First, the lattice is sliced into 3x3 chunks. Then, each chunk is replaced with the more common state. Finally, the lattice is scaled down with 3 to obtain the original lattice. The final lattice looks the same as any of the chunks in the original lattice. There is self-similarity.” (KC: Fig. 1.14)

(1D percolation, the renormalized occupation probability after each coarse-graining step is smaller than in the previous step, if the original occupation probability is $0 < p <1$. Therefore, only for $p=0$ or $p=1$, the coarse-graining and renormalization has no effect, and the system remains fully empty ($p=0$) or fully occupied ($p=1$).

… percolation …

"Personally I think that the exponent for elasticity should be larger than for conductivity. Imagine that we measure the elasticity from up to down. The elasticity is not affected by anything that happens in the horizontal direction. The only thing that matters are the vertical springs. With conductivity also horizontal links matter. There are conducting paths that go some distance horizontally."

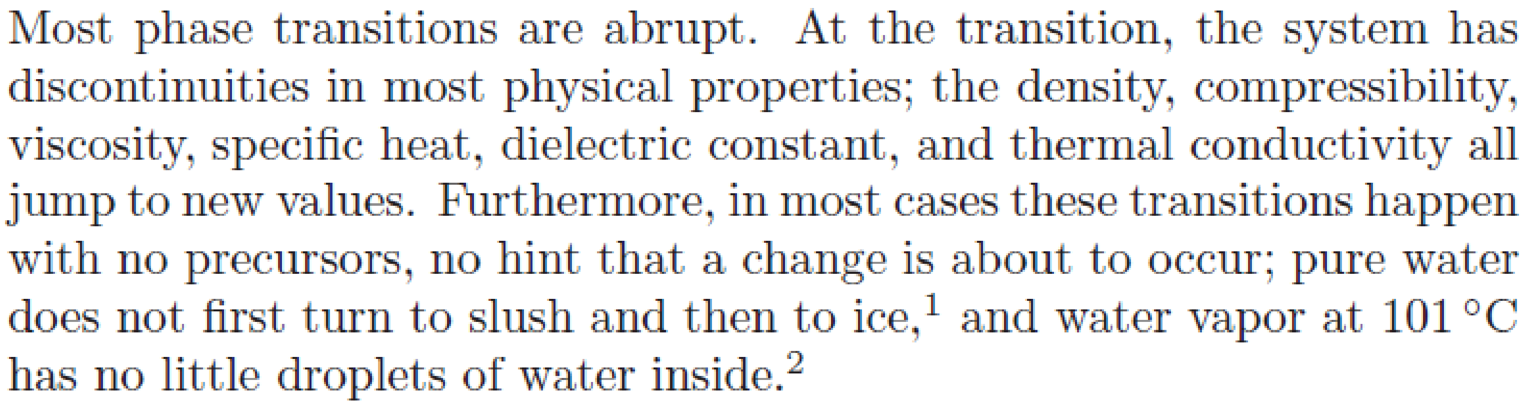
The main argument here is not easy,and depends on the # of constraints as a function of "p" and the consequences of that for the quantity at hand. In other words, if you add a bond to a marginally connected structure, what happens? **"Constraint counting".**

https://en.wikipedia.org/wiki/Structural_rigidity, 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,[1] and water vapor at 101 °C has no little droplets of water inside.[2]

Stability and metastability

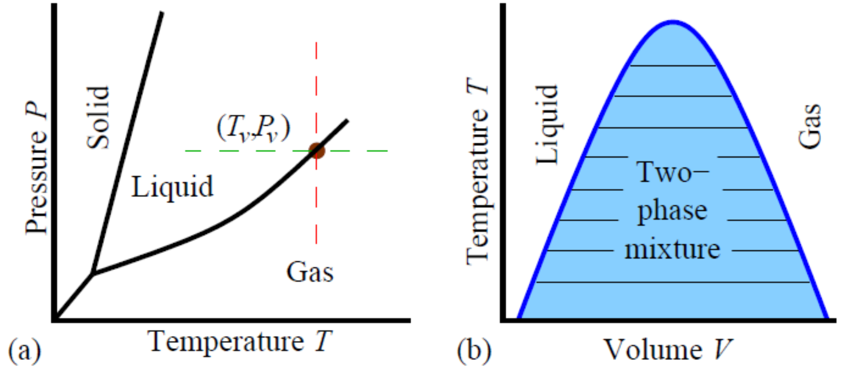
$$G(T, P, N) = E - TS + PV.$$

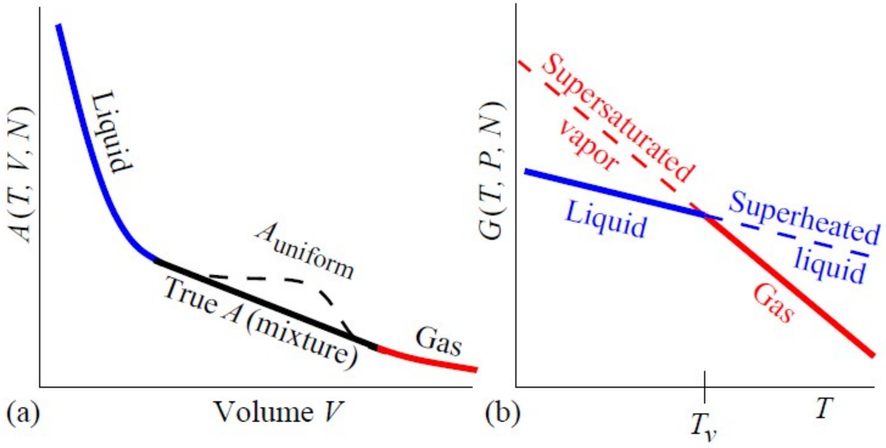
Gibbs: the phase with the lowest chemical potential μ wins.

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

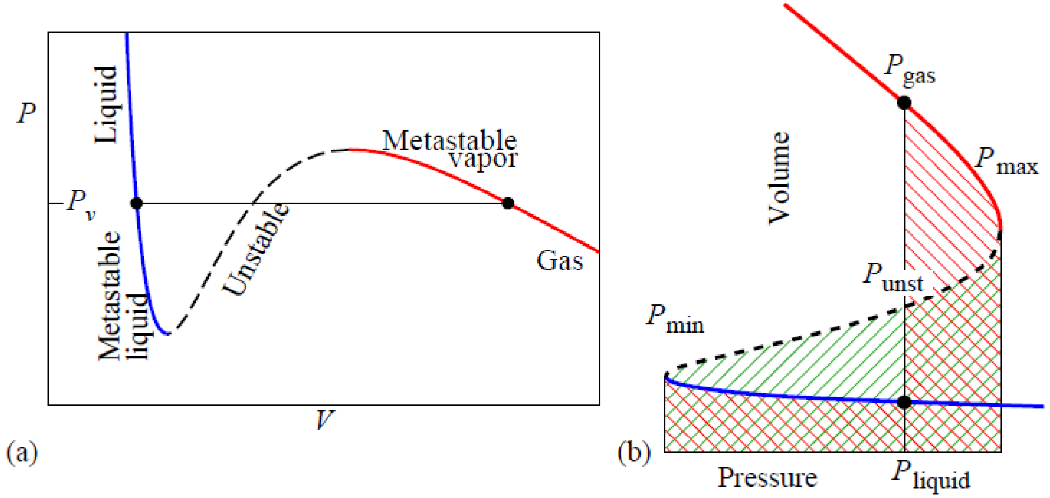
At constant number N and temperature T

$$\Delta G = \int_{P_{\mathrm{liq}}}^{P_{\mathrm{gas}}} V(P)\,\mathrm{d}P = 0.$$

so we have

$$\Delta G = \int_{P_{\mathrm{liq}}}^{P_{\mathrm{min}}} V(P)\,\mathrm{d}P + \int_{P_{\mathrm{min}}}^{P_{\mathrm{unst}}} V(P)\,\mathrm{d}P + \int_{P_{\mathrm{unst}}}^{P_{\mathrm{max}}} V(P)\,\mathrm{d}P + \int_{P_{\mathrm{max}}}^{P_{\mathrm{gas}}} V(P)\,\mathrm{d}P,$$

2 positive and 2 negative contributions define P_v and P_{unst}



Nucleation or critical droplets

Try to go below the phase transition by a ΔT – 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…]

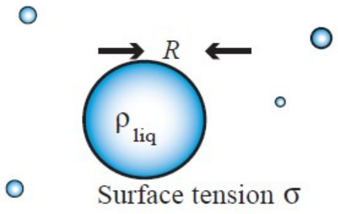


Fig. 11.4 Vapor bubble. The nucleation of a new phase happens through a rare thermal fluctuation, where a droplet of the new phase forms of sufficient size to get it over the free energy barrier of Fig. 11.5.

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

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 ΔT.

This is “homogeneous” (in space) nucleation, with rate Γ.

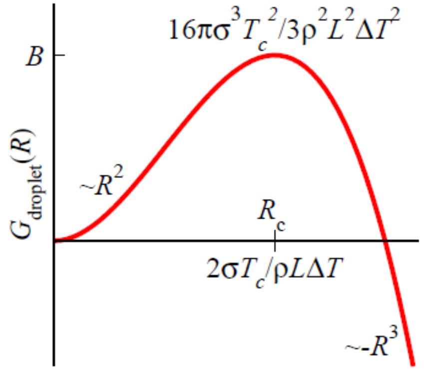
$$\Gamma = (\text{prefactors})\mathrm{e}^{-B/k_B T}.$$

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

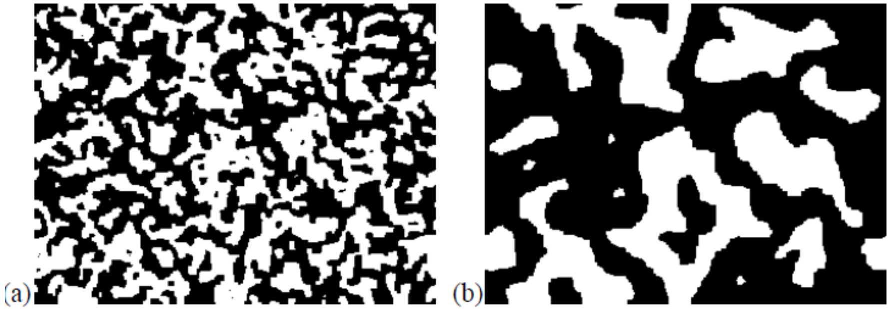
$$\left.\frac{\partial G_{\text{droplet}}}{\partial R}\right|_{R_c} = 8\pi\sigma R_c - 4\pi\rho_{\text{liq}}(L\Delta T/T_v)R_c^2 = 0,$$

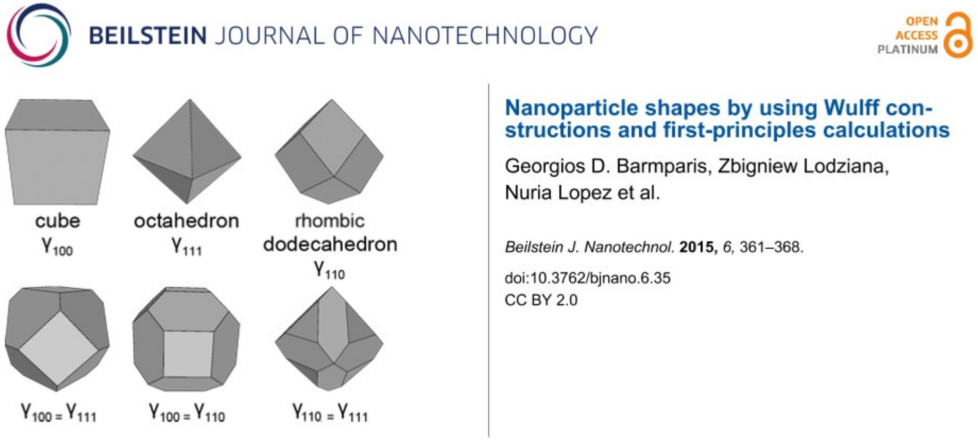
$$R_c = \frac{2\sigma T_v}{\rho_{\text{liq}} L\Delta T},$$

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



Morphology of phases or coarsening





BEILSTEIN JOURNAL OF NANOTECHNOLOGY

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.

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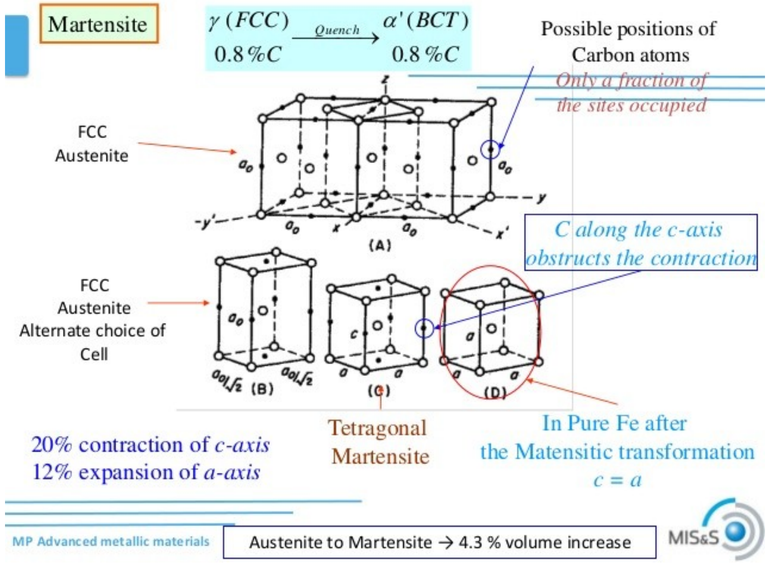

Martensite

$\gamma\,(FCC) \xrightarrow{Quench} \alpha'\,(BCT)$
$0.8\,\%C \qquad 0.8\,\%C$

Possible positions of Carbon atoms

Only a fraction of the sites occupied

FCC Austenite

C along the c-axis obstructs the contraction

FCC Austenite Alternate choice of Cell

Tetragonal Martensite

20% contraction of *c-axis*
12% expansion of *a-axis*

In Pure Fe after
the Matensitic transformation
$c = a$

MP Advanced metallic materials

Austenite to Martensite → 4.3 % volume increase

MIS&S

Two mechanisms for coarsening

Conserved vs. non-conserved.

Surface tension drives in the latter the process, resulting in a “RW”-like scaling. β = ½.

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

$$\frac{\mathrm{d}R}{\mathrm{d}t} = -\eta\tau = -\eta\frac{2\sigma}{R}.$$

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

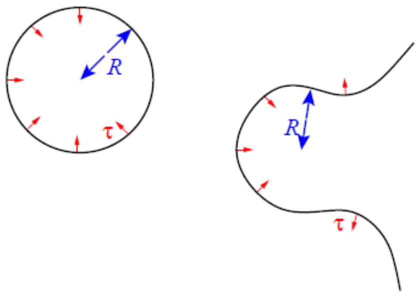

Fig. 11.8 Curvature-driven interface motion. The surface tension σ at the interface produces a traction (force per unit area) $\tau = 2\sigma\kappa$ that is proportional to the local mean curvature of the surface κ at that point. The coarsening morphology has a characteristic length R, so it has a characteristic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

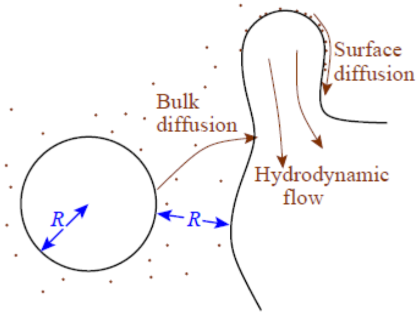

Fig. 11.9 Coarsening for conserved order parameter. Differences in local mean curvature drives the growth in the case of a conserved order parameter. Atoms will diffuse from regions of high positive curvature to regions of low or negative curvature. Bulk diffusion dominates on long length scales ($L(t) \sim t^{1/3}$); 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].

Take home 6

Study the material for the week: Sethna chapter 11. Then, answer the following question(s).

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.