Statistical Mechanics
E0415

Fall 2022, lecture 6
Abrupt phase transitions

Take home… RG

“In the case of 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, if the course-graining is iterated for long enough, the occupation probability will finally be $p'=0$, i.e., all lattice sites will become empty. For the original occupation probability of $p=0$ 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 …

"I think that elastic modulus should increase faster in percolation transitions than conductivity. This is because of the dimensions (length, time, mass,etc.) of these two quantities. Conductivity is proportional to the area of the cross section and inversely proportional to the length. In addition, elastic modulus depends on the surface perpendicular to the applied stress. So, for example, consider an elastic string (almost 1D), then renormalization does not affect the area of the cross section of the string and the elastic modulus should not change but conductivity could decrease since the length increases. Of course, whether these quantities actually increase or decrease depends on what method one uses to coarse-grain the system"

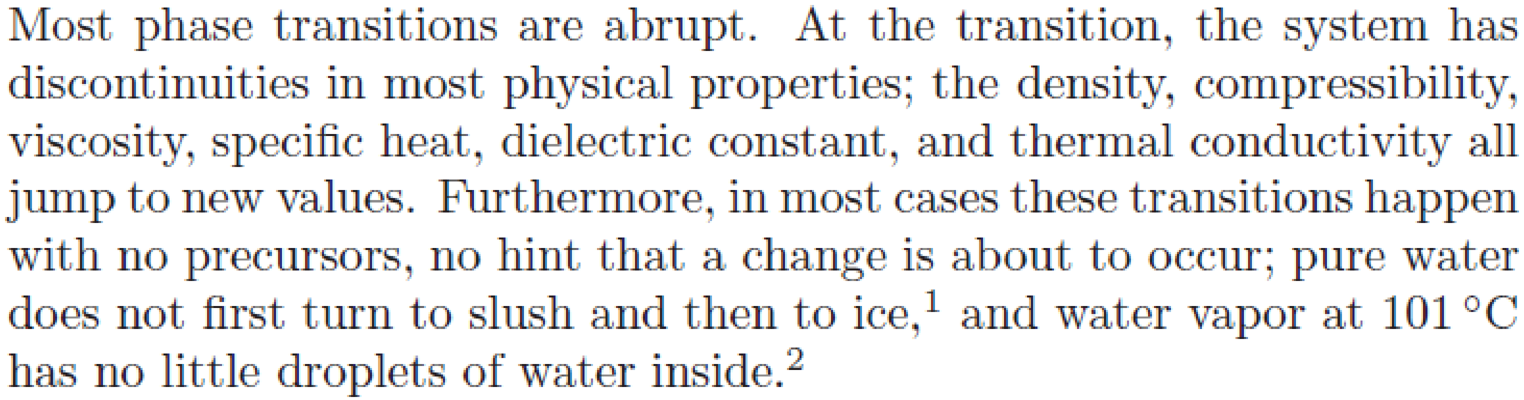
The main argument here is not easy,and depends on the # of constraints as a function of "p" and the consequences of that for the quantity at hand. In other words, if you add a bond to a marginally connected structure, what happens? **"Constraint counting".**

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

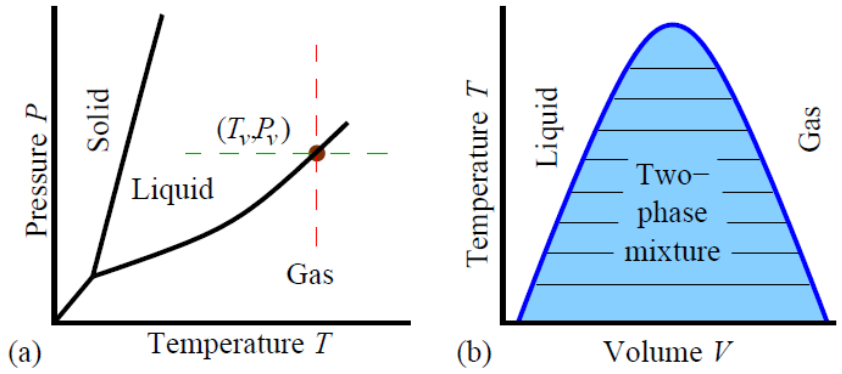
$$G(T, P, N) = E - TS + PV.$$

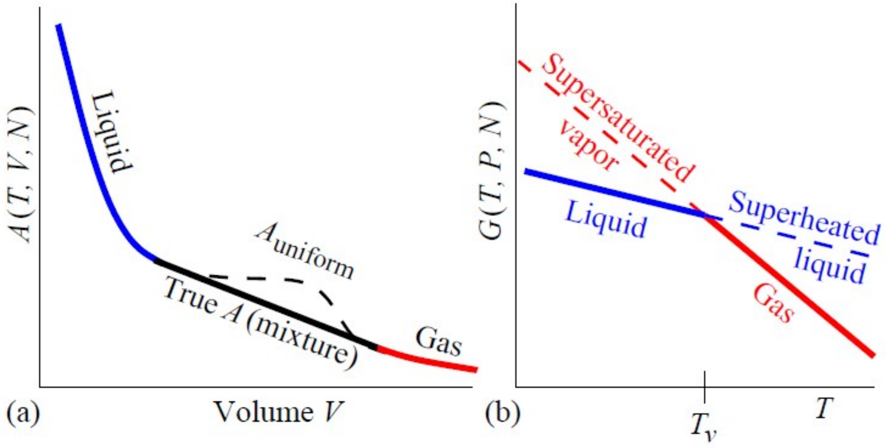
Gibbs: the phase with the lowest chemical potential μ wins.

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

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

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





Maxwell construction

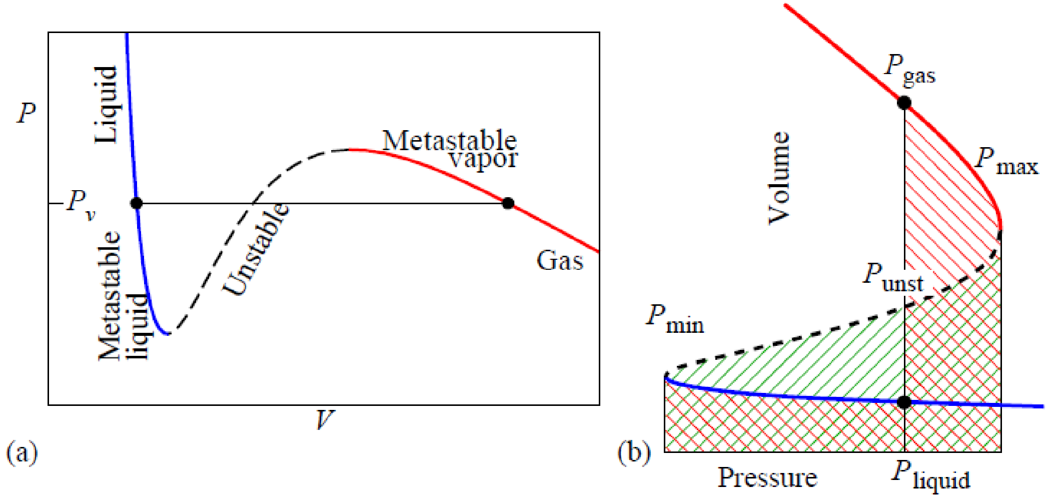
At constant number N and temperature T

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

so we have

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

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…]

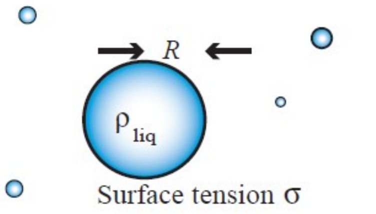


Fig. 11.4 Vapor bubble. The nucleation of a new phase happens through a rare thermal fluctuation, where a droplet of the new phase forms of sufficient size to get it over the free energy barrier of Fig. 11.5.

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

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.

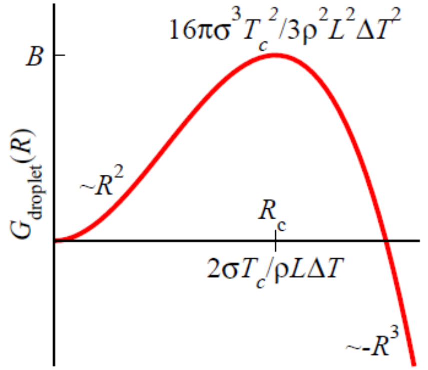
$$\Gamma = (\text{prefactors})e^{-B/k_B T}.$$

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

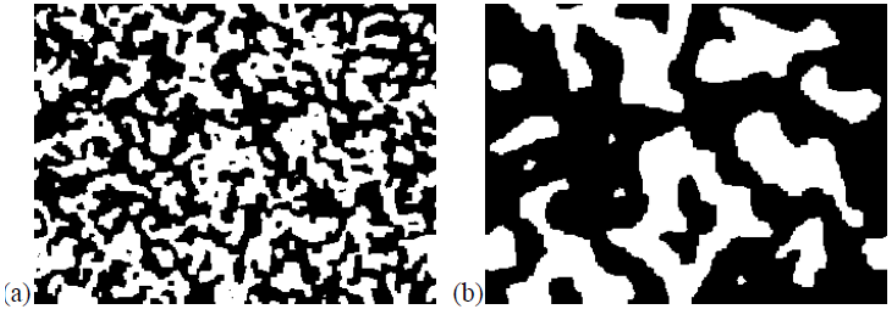
$$\left.\frac{\partial G_{\text{droplet}}}{\partial R}\right|_{R_c} = 8\pi\sigma R_c - 4\pi\rho_{\text{liq}}(L\Delta T/T_v)R_c^2 = 0,$$

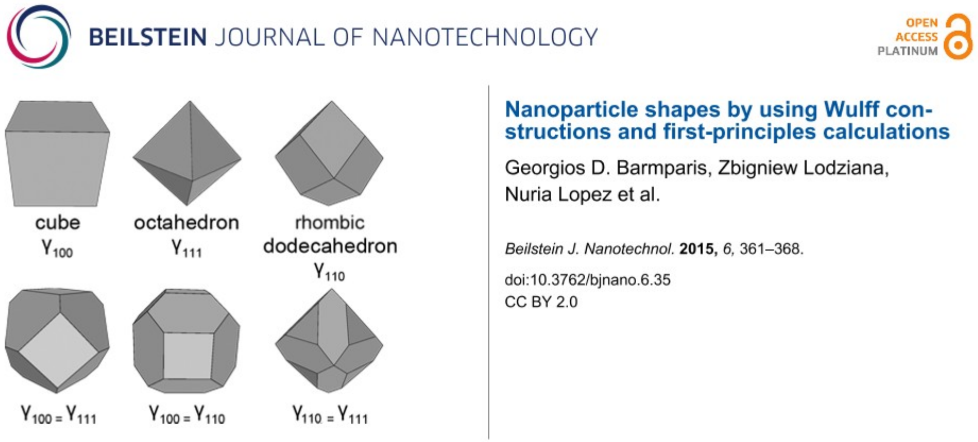
$$R_c = \frac{2\sigma T_v}{\rho_{\text{liq}} L \Delta T},$$

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



Morphology of phases or coarsening

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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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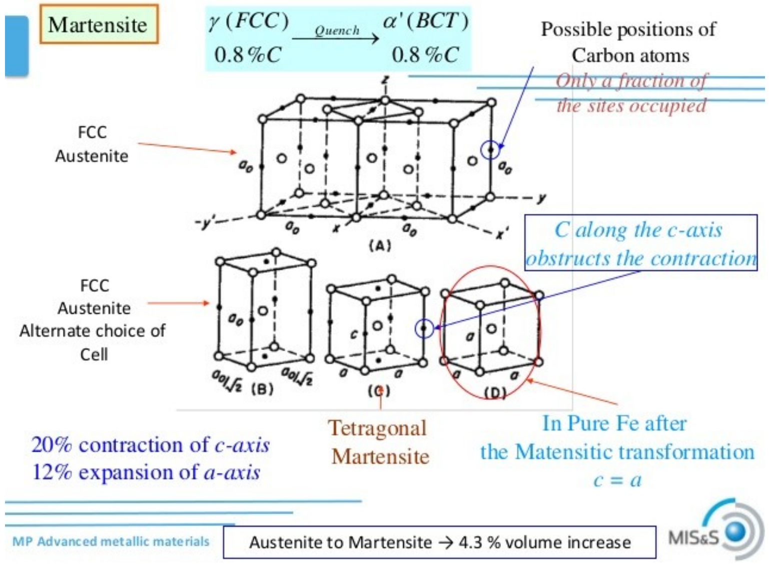
Martensite

$\gamma\,(FCC) \xrightarrow{Quench} \alpha'\,(BCT)$

$0.8\,\%C \qquad 0.8\,\%C$

Possible positions of Carbon atoms

Only a fraction of the sites occupied

FCC Austenite

FCC Austenite Alternate choice of Cell

C along the c-axis obstructs the contraction

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

Tetragonal Martensite

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

MP Advanced metallic materials

Austenite to Martensite → 4.3 % volume increase

Two mechanisms for coarsening

Conserved vs. non-conserved.

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

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

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

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

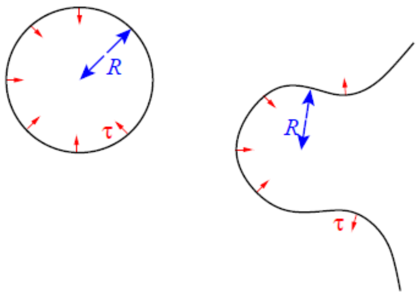

Fig. 11.8 Curvature-driven interface motion. The surface tension σ at the interface produces a traction (force per unit area) $\tau = 2\sigma\kappa$ that is proportional to the local mean curvature of the surface κ at that point. The coarsening morphology has a characteristic length R, so it has a characteristic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

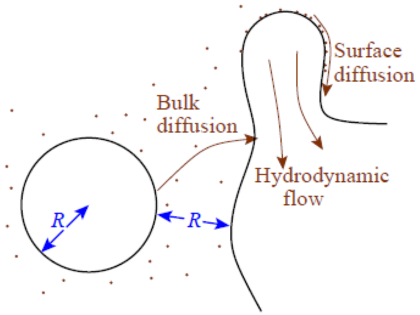

Fig. 11.9 Coarsening for conserved order parameter. Differences in local mean curvature drives the growth in the case of a conserved order parameter. Atoms will diffuse from regions of high positive curvature to regions of low or negative curvature. Bulk diffusion dominates on long length scales ($L(t)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