Phase transitions :

Part 1

We are all very familiar w/ phase transitions in our day to day life, but we don't always think about many interesting aspects

1) What is happening microscopically
2) what is happening macroscopically
3) how many phase transitions have "universal" properties that don't depend on the specific system

This is what has fascinated people from stat mech for ~100 years

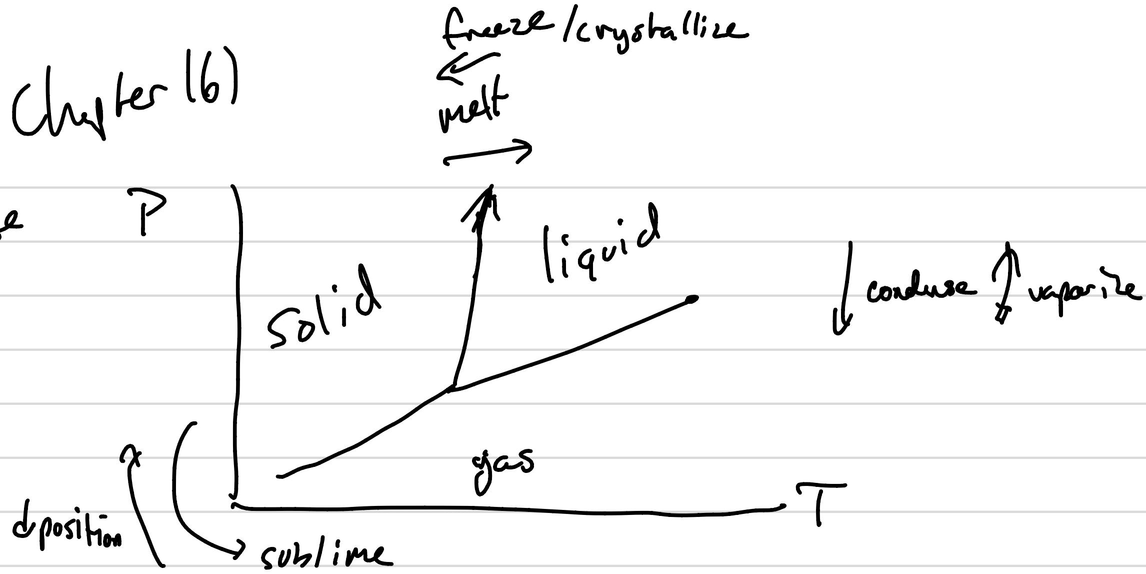
4 major modern areas of work:

1) How to sample/observe/predict phases in simulation
2) what happens in unusual environments, eg w/ confinement (water in a nanotube, protein...)
3) what is phase diagram for many components (lipids...)
4) What happens out of equilibrium?

We have to start w/ the basics to understand the more complex phenomena

(Tuckerman Chapter 16)

Basic Phase Diagram



Cross a line, discontinuity in some quantity: e.g. density

Ehrenfest: discontinuity in deriv. of free energy [density ~ $1/(\partial A/\partial P)$]

Modern definition: has to be latent heat at crossing

@ Far right, can go between phases w/o latent heat or weird behavior.

@ Critical point: 2nd order phase transition

Ehrenfest! Continuous in first deriv, but discontinuous change in second deriv.

Modern! "Continuous" phase transition, diverging susceptibility, powerlaw divergence of correlation length [Discuss more later]

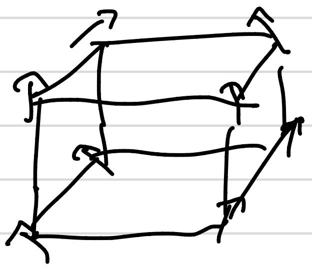
Typically, break symmetry in 1 direction

Liquid → solid, translational symmetry

Liquid → gas, 0 correlation length → finite correlation (g(r))

Need model systems to analyze to illustrate the important concepts and which can be "solved" on the computer or on paper

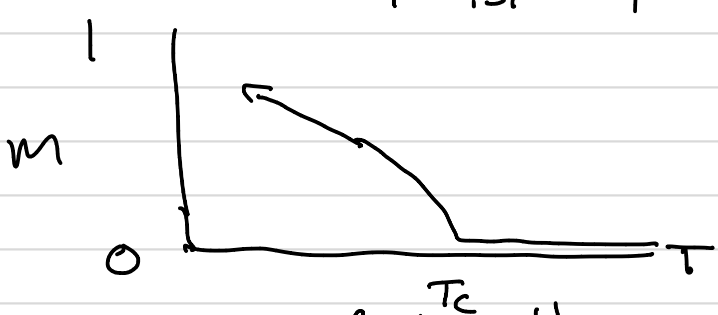
Magnetization Phenomenon:



spins on lattice, like being in same direction but entropy prevents ordering. Lower T or increasing B field has ordering Transition

Need "order parameter" to describe a phase transition, a quantity that distinguishes the phases. $\rho - \rho_L$ works for Liquid gas or Liquid solid, 0 when a Liquid, nonzero otherwise

Here, $M = \left| \left\langle \sum_{i=1}^{N} \sigma_i \right\rangle \right|$ $m = M/N$ is Magnetization



no field, "spontaneous magnetization"

T_c is curie temp, Pierre Currie studied this transition

Can we "derive" this result. Have to start w/ Hamiltonian in canonical ensemble and get $Z(N, V, T)$ to compute M

"Real" Hamiltonian:

$$\hat{\mathcal{H}} = -\tfrac{1}{2}\sum_{i,j} \hat{\sigma}_i \cdot \underbrace{J_{ij}}_{\text{coupling tensor}} \cdot \sigma_j - \sum_i \gamma B \cdot \hat{S}_i \quad \text{"} -\sum_i \vec{h}\cdot\vec{\sigma}_i \text{"} \qquad h = \frac{\gamma\hbar B}{2}$$

where $\hat{S}_i = \hbar/2\, \hat{\sigma}_i$ ← pauli matrix

Approximation, consider only z direction & field in z-direction, then

$$H = -\frac{1}{2}\sum_{i,j} J_{ij}\sigma_i\sigma_j - \sum_i h\sigma_i \quad , \quad \sigma_i = \{\pm 1/2\}$$

if we make the further approx that coupling is short ranged $J_{ij} = \begin{cases} J, & i \,\&\, j \text{ neighboring sites} \\ 0 & \text{otherwise}\end{cases}$

$$H = -\underbrace{J/2}_{\text{2 for double counting}} \sum_{\langle i,j\rangle} s_i s_j - \sum_i h s_i \quad s_i \in (-1,1)$$ ← Ising Model

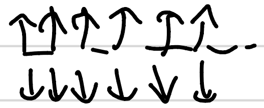
(Invented by Lenz, gave to grad student Ising to study in 1924)

We can solve in 1d, approx & exact. Onsager (1944) solved 2d exactly, no one has done 3d yet...

if $J > 0$, like to align, and $h > 0$, like to align facing up, $h < 0$, down

w/ $h = 0$, $\mathcal{H}$ is min when all up or all down

So configuration $\cdots\uparrow\uparrow\uparrow\uparrow\downarrow\downarrow\downarrow\downarrow\cdots$ has $M = 0$, and $\mathcal{E} = \underbrace{-NJ}_{E_{min}} + J$, so interface has cost only 1 in N, hence only at $T = 0$ do you expect full phase trans in 2d:



interface typically of size $N^{1/2}$ and this is big enough cost to stabilize ordered state ("surface tension")

Still can learn a lot from 1d ising model, including mapping all sorts of physical problems to it, like adsorption to a surface or folding of peptides

So what is $Z(N,V,T)$?

Lets rewrite $H = -J\sum_{i=1}^{N-1} s_i s_{i+1} - h\sum_{i=1}^{N} s_i$

we can add periodic boundary conditions, $s_{N+1} = s_1$ and write in a more symmetric way

$$\mathcal{H} = -J\sum_{i=1}^{N} s_i s_{i+1} - \frac{h}{2}\sum_{i=1}^{N}(s_i + s_{i+1})$$

$$= \sum_{i=1}^{N}\left(-J s_i s_{i+1} - \frac{h}{2}(s_i + s_{i+1})\right)$$

$$Z = \sum_{\nu} e^{-\beta E_\nu}$$

$$= \sum_{s_1}\sum_{s_2}\cdots\sum_{s_N}\exp\left(+\beta\sum_{i=1}^{N}\left(J s_i s_{i+1} + \frac{h}{2}(s_i + s_{i+1})\right)\right)$$

for $h = 0$

$$= \sum_{s_1, s_2, \ldots, s_N} e^{\beta J s_1 s_2} e^{\beta J s_2 s_3} \cdots e^{\beta J s_N s_1}$$

Defect variables

Let $s_j' = s_j s_{j-1}$, can only be ± 1, but 2 ways

$$= 2 \sum_{\sigma_1', \sigma_N' = 1}^{2} e^{\beta J \sigma_i'} = 2 \left(\sum_{\sigma=1}^{2} e^{\beta J \sigma} \right)^N = 2 \left(e^{\beta J} + e^{-\beta J} \right)^N$$

$$= 2 (2 \cosh(\beta J))^N$$

$$f = F/N = -k_B T/N \log Z = -\frac{1}{\beta} \log[2\cosh(\beta J)] + \text{const}$$