

# C5.3 Statistical Mechanics

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# Lecture 13: The Ising Model (I) – Definition and Applications

- A big thing in SM is models on networks and lattices.
- Such models have a variable at each site of some sort of networks (e.g., a regular grid) and a Hamiltonian or evolution law for each variable.
- Ising model has been used for many physical systems, including: **magnetism**, **binary alloys**, and **liquid-gas transition**.
  - It is the most extensively studied lattice model in physics.
  - Useful for lots of things (see preview Sethna p. 217).
- Simple system at the micro-level to study behaviour of large systems
- Work horse of statistical mechanics that also drove the development of renormalisation group theory (based on the observation that at coarser levels, the structure of e.g. the Ising model reproduces itself).

# Definition of the Ising model(s)

- A network (e.g., a lattice) of  $N$  sites  $i$  with a single 2-state DOF  $s_i \in \{-1, 1\}$  on each site:

- Hamiltonian is  $\mathcal{H} = - \sum_{ij} J_{ij} s_i s_j - h \sum_i s_i$

- $(J_{ij})$  is the **coupling matrix**:

- $J_{ij} = 0$ : sites  $i$  and  $j$  are **not interacting**;
- $J_{ij} > 0$ : interaction is **ferromagnetic**;
- $J_{ij} < 0$ : interaction is **anti-ferromagnetic**.

- **Nearest neighbour interaction (only)**

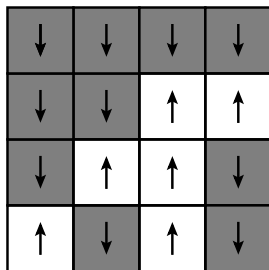
$$\begin{cases} J_{ij} = J = \text{const.}, & \text{if } i \text{ and } j \text{ are nearest neighbours} \\ 0, & \text{otherwise} \end{cases}$$

$$\Rightarrow \mathcal{H} = \sum_{\langle ij \rangle} J s_i s_j - h \sum_i s_i,$$

where  $\langle ij \rangle$  means that  $i$  and  $j$  are nearest neighbours.

- Example: Ising model on a 2D lattice (next page)

## Example: 2D Lattice



**Figure:**  $\uparrow \equiv +1 \equiv \text{light}$ ,  $\downarrow \equiv -1 \equiv \text{dark}$

- 4 centre squares have 4 nearest neighbours each;
- Non-corner edge ones have 3, and corner ones have 2.
- In finite systems, one can use periodic BCs so every square has 4 nearest neighbours.

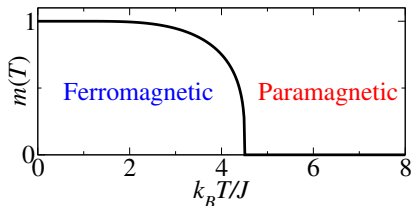
- Original use of Ising model.
- Each  $s_i$  is called a **spin**,  $h$  is the **external field**, and  $M := \sum_i s_i$  is the **magnetization**.
- This is where ferromagnetic ( $J_{ij} > 0$ ) and antiferromagnetic ( $J_{ij} < 0$ ) terminology comes from.
- Energy  $J_{ij}s_i s_j$  of 2 neighbouring spins is
  - $-J_{ij}$  if the spins are **parallel** (both  $+1$  or both  $-1$ )
  - $+J_{ij}$  if they are **antiparallel** (one  $+1$  and one  $-1$ ).

## Magnetism (2)

- Consider the nearest neighbour coupling matrix with

$$\begin{cases} J_{ij} = J, & \text{nearest neighbours} \\ 0, & \text{else} \end{cases}$$

- $J > 0$  favours parallel spins and these will mostly point in one direction [ferromagnetic phase];
- $J < 0$  favours anti-parallel spins and these will mostly orient themselves in a checkerboard pattern [anti-ferromagnetic phase];
- At high temperatures (for both signs of  $J$ ), we expect entropy to dominate: spins fluctuate wildly in a **paramagnetic phase** and the magnetization per spin  $m(T) \equiv \frac{M(T)}{N} \approx 0$ .
- There is a **phase transition** at a **critical temperature**  $T_c \approx 4.5$ .



Ising magnetization in a 3D cubic lattice Ising model.

(Sethna 2020)

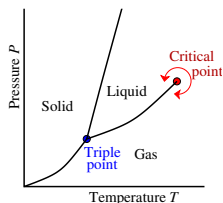


# Binary Alloys

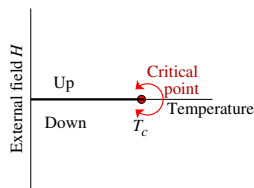
- Consider square lattice of atoms of type  $A$  and  $B$  ( $A = +1, B = -1$ ) of numbers  $N_A$  and  $N_B$  ( $N := N_A + N_B$ ).
- Interaction energies (i.e., bond strengths) are  $E_{AA}, E_{BB}, E_{AB}$ , and the numbers of such bonds are  $N_{AA}, N_{BB}, N_{AB}$ .
  - $\Rightarrow \mathcal{H} = -E_{AA}N_{AA} - E_{BB}N_{BB} - E_{AB}N_{AB}$ .
  - This is the nearest-neighbour Ising model with  $J = \frac{1}{4}(E_{AA} + E_{BB} - 2E_{AB})$  and  $h = E_{AA} - E_{BB}$  (see footnote 8 on (Sethna, pg.165)).
- A phase transition occurs from a high-temperature state (where the species freely interchange their positions) to a low-temperature stage (species are organised in an 'antiferromagnetic' i.e. 'checkerboard' style). For brass (1:1 Copper:Zinc) the transition is at  $733^\circ\text{C}$ .
- Can generalize by
  - including atomic relaxation effects
  - incorporating thermal fluctuations into  $\mathcal{H}$  to make it a free energy (see footnote 9 on (Sethna, pg. 165)),
  - or by considering more elaborate coupling such as large-range interactions.

- Ising model is also used to study liquid-gas transition.
  - In this **lattice gas** interpretation,  $s_i = +1$  for sites of atoms and  $s_i = -1$  for sites w/o atoms.
  - The gas has mostly  $s_i = -1$  spins (negative 'magnetization') and the liquid phase has mostly  $s_i = +1$ .
- Near gas phase, seems ok; but in "liquid" phase, it is really more like a crystal, so it is not a good model there.
- But Ising model is good for probing behaviour near a **critical point**.

# The critical point



$P$ - $T$  Phase diagram aka bifurcation diagram for a typical material (Sethna 2020)



$P$ - $T$  phase diagram for the Ising model (Sethna 2020)

- (1) solid/liquid boundary amounts to a change in symmetry and cannot end
- (2) gas/liquid boundary typically **does** end  
(One can go **continuously** from liquid phase to gas phase by increasing pressure above  $P_c$ , increasing temp. above  $T_c$ , then lowering  $P$  again.)
- The behaviour near the critical points in these two situations (realistic one above and model one below) is remarkably similar; this leads to the notion of **universality** [See chapter 12 of Sethna]. In many ways the behaviour at the liquid-gas critical point is described **exactly** by the 3D Ising model.

# Lecture 14: The Ising Model (II) – Analytic and computational solutions

# How to solve the Ising Model?

- 1 **1D case can be solved analytically.**
- 2 Be very clever: Onsager solved a 2D version (very technical) for square lattices; 3D is open even in square lattice.  
(For a treatment of the 2D version, see for example: M. L. Glasser (Am. J. Phys. 38, 1033 (1970)).)
- 3 Monte Carlo computational techniques.

# Ising 1D-Model – Transfer-Matrix Method

Ising Model with periodic boundary conditions

$$H(\sigma) = -J \sum_i s_i s_{i+1} - \frac{B}{2} \sum_i (s_i + s_{i+1}) \quad m(\sigma) = \frac{1}{N} \sum_{i=1}^N s_i$$

Transfer-Matrix Notation:

$$S_i = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{if } s_i = +1, \quad S_i = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad \text{if } s_i = -1,$$

$$T(s_i, s_{i+1}) = \exp \left[ \beta J s_i s_{i+1} + \frac{\beta}{2} B (s_i + s_{i+1}) \right] = S_i^t \underbrace{\begin{pmatrix} e^{\beta(J+B)} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-B)} \end{pmatrix}}_{\equiv \hat{T}} S_{i+1}.$$

Partition function:

$$\begin{aligned} Z(\beta) &= \sum_{\sigma \in \Sigma} e^{-\beta H(\sigma)} = \sum_{s_1=\pm 1} \dots \sum_{s_N=\pm 1} \prod_{i=1}^N T(s_i, s_{i+1}) \\ &= \sum_{s_1=\pm 1} \dots \sum_{s_N=\pm 1} S_1^t \hat{T} (S_2 S_2^t) \hat{T} \dots S_N^t \hat{T} S_1 \\ &= \sum_{s_1=\pm 1} S_1^t \hat{T}^N S_1 = \text{trace } \hat{T}^N = \Lambda_+^N + \Lambda_-^N \end{aligned}$$

Eigenvalues:

$$\Lambda_{\pm} = e^{\beta J} \left( \cosh(\beta B) \pm \sqrt{\sinh^2(\beta B) + e^{-4\beta J}} \right)$$

Average magnetisation

$$\mathbb{E}_{\beta, B}(m) = \frac{1}{N} \frac{\partial \ln(Z)}{\partial B} \longrightarrow \frac{\partial \ln(\Lambda_+)}{\partial B} = \frac{\sinh(\beta B)}{\sqrt{\sinh^2(\beta B) + e^{-4\beta J}}}$$

for  $N \rightarrow \infty$ .

# How to solve the Ising Model?

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(For a treatment of the 2D version, see for example: M. L. Glasser (Am. J. Phys. 38, 1033 (1970)).)
- 3 **Monte Carlo computational techniques.**

Some material courtesy Dirk Peschka

**Homework: Read section 8.2 in Sethna.**



How to compute the average

$$\mathbb{E}(f) = \sum_{\sigma} f(\sigma)p(\sigma)$$

of a random variable  $f$  with the probability distribution

$$p(\sigma) = \frac{\exp(-\beta H(\sigma))}{Z}$$

numerically?

**Problem:** Too many microstates!

**Ansatz:** Replace

$$\sum_{\sigma} f(\sigma)p(\sigma) \Rightarrow \frac{1}{N_{\text{mc}}} \sum_{n=1}^{N_{\text{mc}}} f(\sigma_n)$$

with the Markov chain  $\sigma_n$  transition rate  $p_{N,N-1} = P(\sigma_N|\sigma_{N-1})$ .

**Requirement:** The transition rate must lead to the distribution

$$p(\sigma) = Z^{-1} \exp(-\beta H).$$

**How to:** Metropolis Algorithm<sup>1</sup>

$$p_{N,N-1}(\sigma) = \min\left(1, \exp(-\beta\Delta H(\sigma))\right) \quad \Delta H(\sigma) = H(\sigma_N) - H(\sigma_{N-1})$$

Notice: Subsequently, the realisation  $f(\sigma_n)$  will be called a measurement.

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<sup>1</sup>N. Metropolis, A. Rosenbluth, M. Rosenbluth, A. Teller und E. Teller: Equation of State Calculations by Fast Computing Machines. (doi:10.1063/1.1699114)

# The Monte-Carlo Method: The heat bath algorithm

2D-Case – 1D very similar.

- Pick a site  $i = (x, y)$  at random
- Check how many neighbour spins are pointing up:

$$m_i = \sum_{j:\langle ij \rangle} s_j = 4, 2, 0, -2, -4$$

for 4, 3, 2, 1, 0 neighbours up, respectively.

- Calculate  $E_+ = -Jm_i - H$  and  $E_- = Jm_i + H$ , the energy for the spin  $i$  to be  $+1$  or  $-1$  given its current environment.
- Set spin  $i$  up with probability (reminder: Here and earlier,  $\beta = 1/k_B T$ )

$$\frac{\exp(-\beta \mathbf{E}_+)}{\exp(-\beta E_+) + \exp(-\beta E_-)}$$

and down with probability.

$$\frac{\exp(-\beta \mathbf{E}_-)}{\exp(-\beta E_+) + \exp(-\beta E_-)}$$

# Numerics 1D – Code

```
% ising1d.m
nx          = 50; % N
monte_carlo_steps = 100; % N_mc
monte_carlo_substeps = 100;

beta = 0.5; % 1/(k*T)
j     = 1.0; % Coupling parameter
B     = 0.1; % external field

s=2*round(rand(nx, 1))-1;
for n1=1:monte_carlo_steps
    for n2=1:monte_carlo_substeps
        s=mc1d(s,j,B,beta,nx );
    end
    m(n1)=mean(s(:));
end
plot(m)

% Function: mc1d.m
% Markov step P(n+1,n)
% 1D linear mesh, length nx

function s=mc1d(s,j,B,beta,nx )

for x=1:nx

    % neighbouring positions
    xm1 = mod(x-2+nx,nx)+1;
    xp1 = mod(x,nx)+1;

    % neighbouring spins
    s1=s(xm1 );    s2=s(xp1 );

    % heat bath algorithm for p = exp(-beta*H):
    % set s=+1 if rand < w=exp(bA)/(exp(bA)+exp(-bA))
    % otherwise s=-1
    A=j*(s1+s2 )+B;
    w=exp(beta*A)/(exp(beta*A)+exp(-beta*A));
    s(x )=(rand(1)<w)*2-1;

end
```

# Numerics 2D – Code

```
% ising2d.m
nx          = 50; % N
ny          = 50;
monte_carlo_steps = 100; % N_mc
monte_carlo_substeps = 100;
```

```
beta = 0.5; % 1/(k*T)
j     = 1.0; % Coupling parameter
B     = 0.1; % external field
```

```
s=2*round(rand(nx,ny))-1;
for n1=1:monte_carlo_steps
    for n2=1:monte_carlo_substeps
        s=mc2d(s,j,B,beta,nx,ny);
    end
    m(n1)=mean(s(:));
end
plot(m)
```

```
% Function: mc2d.m
% Markov Step P(n+1,n)
% 2D mesh size (nx) x (ny)
```

```
function s=mc2d(s,j,B,beta,nx,ny)
```

```
for x=1:nx
    for y=1:ny
```

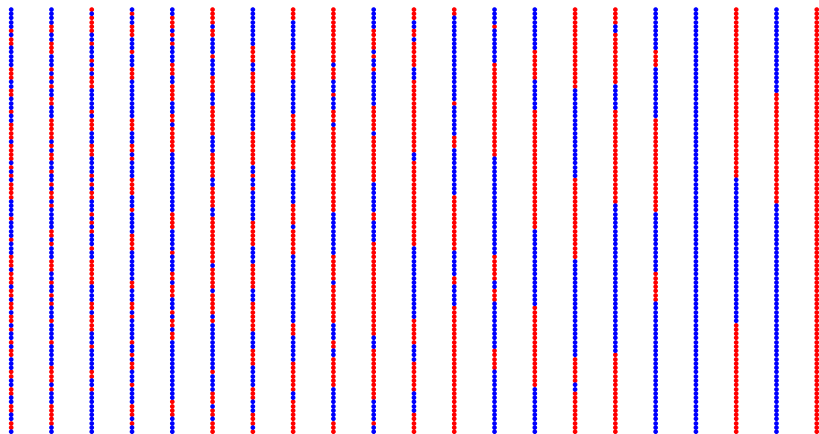
```
        % neighbouring positions
        xm1 = mod(x-2+nx,nx)+1;
        xp1 = mod(x,nx)+1;
        ym1 = mod(y-2+ny,ny)+1;
        yp1 = mod(y,ny)+1;
```

```
        % neighbouring spins
        s1=s(xm1,y );    s2=s(xp1,y );
        s3=s(x ,ym1);    s4=s(x ,yp1);
```

```
        % heat bath algorithm for p = exp(-beta*H):
        % set s=+1 if rand < w=exp(bA)/(exp(bA)+exp(-bA))
        % otherwise s=-1
        A=j*(s1+s2+s3+s4)+B;
        w=exp(beta*A)/(exp(beta*A)+exp(-beta*A));
        s(x,y)=(rand(1)<w)*2-1;
```

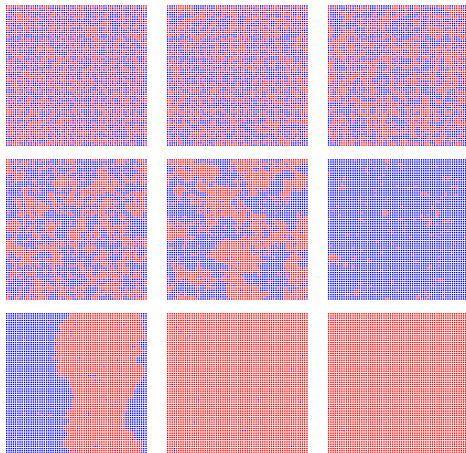
```
    end
end
```

# Numerics 1D – Typical micro states



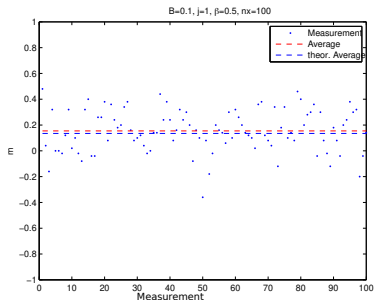
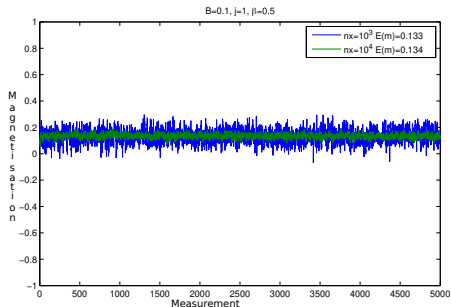
Typical states with  $\beta = 0.0, \beta = 0.1, \dots, \beta = 1.9, \beta = 2.0$   
( $\beta = 1/(k_B T)$ )

# Numerics 2D – Typical micro states



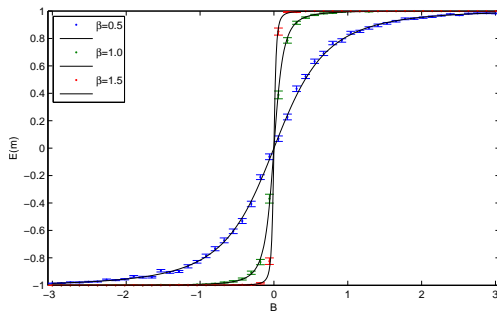
Typical states with  $\beta = 0.0, \dots, \beta = 0.8$

# Numerics 1D – The magnetisation as a random variable



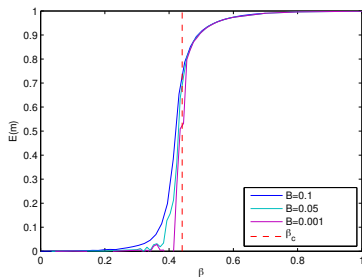


# Numerics 1D – dependence on $B$ and $\beta$

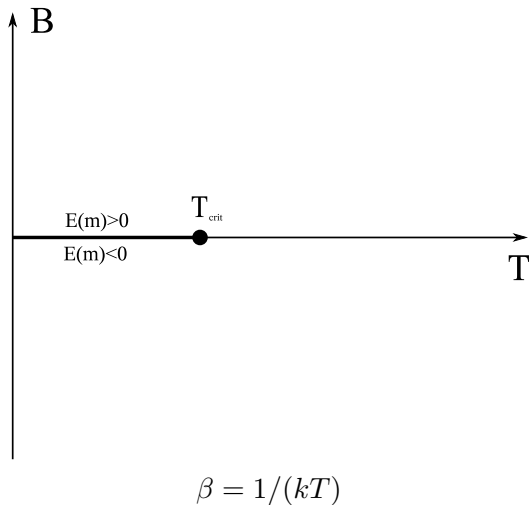


$$\mathbb{E}_{\beta, B}(m) = \frac{\sinh(\beta B)}{\sqrt{\sinh^2(\beta B) + e^{-4\beta J}}}$$

# Numerics 2D – The magnetisation as a random variable.



# Phase Diagram



# Lecture 15: Phase Transitions

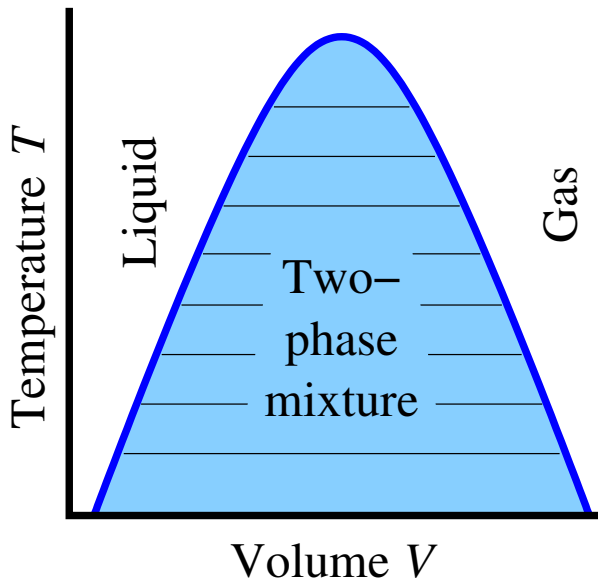
# Illustration of abrupt phase transitions

- Most phase transitions are abrupt; at the transition, the system has discontinuities in most physical properties
- Also, in most cases, these transitions happen with no indication that a change is about to occur: Pure water turns directly to ice- not to slush first and then to ice.

## Illustration of abrupt phase transitions (continued)

- However, boiling away a pan of water is not abrupt- this is because one is not controlling the temperature directly but rather is adding energy at a constant rate.
  - Consider insulated, flexible container of  $H_2O$  at fixed pressure and we slowly add energy to it.
  - When system first reaches liquid-gas transition, a small bubble of gas forms at the top; the bubble grows gradually, inflating and filling the container over a range of energies.
  - The transition from liquid to gas at fixed energy passes through an intermediate **two-phase region**; the temperature of the system stays constant until the last liquid is gone.
- Alternatively, one can see a two-phase region by fixing the temperature and varying (e.g. increasing) the volume.

# Phase Diagram



(Sethna 2020 – All figures in this lecture from Sethna's book)

# Gibbs free energy

- To avoid two-phase mixtures, let us fix (control) the pressure and temperature of the system. Such systems are well described by the Gibbs free energy  $G$ ,

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

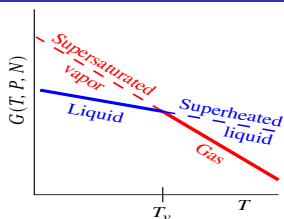
using, for the second equality, Euler relation  $E = TS - PV + \mu N$ , (see exercise 6.9 in Sethna).

- A transition for such a system occurs spontaneously if it decreases the total Gibbs  $G$  free energy.
- System can lower  $G$  by moving material to the phase with the lower chemical potential.  $\Rightarrow$  state with lower chemical potential is favoured, and the phase transition occurs when  $\mu_{\text{liq}} = \mu_{\text{gas}}$ .
- Using thermodynamic shorthand  $dE = TdS - PdV + \mu dN$  gives  $dG = -SdT + VdP + \mu dN$ .
- Varying temperature at fixed pressure and number of particles gives

$$\left. \frac{\partial G}{\partial T} \right|_{P, N} = -S \quad (\star)$$



# Latent heat



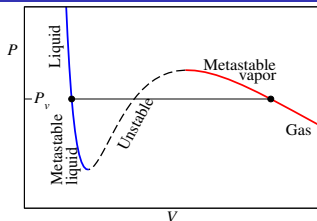
- The difference in the slopes of the 2 lines is given by the difference in entropies between the liquid and the gas (see  $(\star)$ ).
- The thermodynamic definition of entropy says  $\Delta S = \frac{Q}{T}$  that the entropy difference is

$$\Delta S = \frac{LN}{T_v},$$

where  $L$  is the **latent heat** per particle, and  $T_v$  the transition temperature.

- Abrupt phase transitions have jumps in the first derivatives of their free energies.
  - Discuss old terminology: first vs. second order transition. (Footnote 7 in Sethna.)

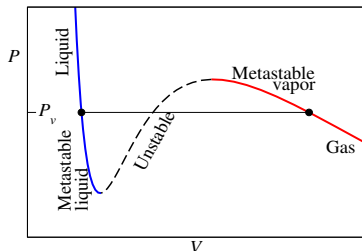
# Maxwell Construction



**Figure:** Pressure vs. volume as we expand/compress material at constant temperature. The dots represent points where pressures and chemical potentials are equal and gas and liquid coexist.

- Liquid (gas) turns metastable as  $V$  increases (decreases) when the pressure reaches the vapour pressure  $P_v$  for that volume.
- Metastable states are well defined only near vapor pressure, where nucleation is slow and lifetime of the state is long (but finite!)
- Dashed line in (a) shows a completely unstable region: a mixture of molecules prepared uniformly in space in this region will spontaneously separate into (a finely inter-tangled network of) the two phases.

# Questions

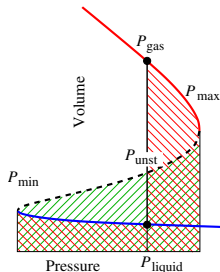


- What is the **vapour pressure**  $P_v$ ?  
(Answer: The pressure at which the liquid and the gas (vapour) phase coexist i.e. are in equilibrium with each other.)
- How can we find the vapour pressure  $P_v$  at which liquid and gas coexist at this temperature?

# Coexistence line

- Coexistence line occurs when Gibbs free energies agree:  $G_{\text{liq}} = G_{\text{gas}}$ ;  $dG = -SdT + VdP + \mu dN$ , so at constant temperature and number of molecules we get

$$\begin{aligned} \Delta G &= \int_C V(P)dP \\ &= \underbrace{\int_{P_{\text{liq}}}^{P_{\text{min}}} V(P)dP}_{<0} + \underbrace{\int_{P_{\text{min}}}^{P_{\text{unst}}} V(P)dP}_{>0} + \underbrace{\int_{P_{\text{unst}}}^{P_{\text{max}}} V(P)dP}_{>0} + \underbrace{\int_{P_{\text{max}}}^{P_{\text{gas}}} V(P)dP}_{<0} \end{aligned}$$



- Note  $P_{\text{liq}} = P_{\text{unst}} = P_{\text{gas}}$  at coexistence, but volumes are different! Hence the path integral is non-zero.
- First 2 terms subtract to give the **lower left hatched area** and last 2 terms subtract to give **minus** the area in the **upper right hatched area**.
- $\implies$  the 2 areas must be equal at the vapor pressure. This is called the **Maxwell equal-area construction**.

## Part 2

# Nucleation: Critical Droplet Theory

# Nucleation: Critical Droplet Theory

- On a humid night, as temperature drops, the air can become supersaturated with water vapour. **How does this metastable vapour turn into drops of dew or tiny water droplets to make up fog or clouds?**
- The Gibbs free energy (hence chemical potential) difference between gas and liquid grows as temperature decreases below  $T_v$ . Estimate:

$$\left. \frac{\partial G}{\partial T} \right|_{P,N} = -S \quad \text{and} \quad \Delta S = \frac{LN}{T_v}$$
$$\Rightarrow \Delta\mu = \frac{(G_{\text{gas}} - G_{\text{liq}})}{N} = \frac{1}{N} \left( \left. \frac{\partial(G_{\text{gas}} - G_{\text{liq}})}{\partial T} \right|_{P,N} \Delta T \right)$$
$$= \frac{\Delta S \Delta T}{N} = \left( \frac{LN}{T_v} \right) \left( \frac{\Delta T}{N} \right) = \frac{L\Delta T}{T_v}$$

- Supersaturation means  $\Delta\mu > 0$ , so why doesn't vapour just condense to liquid (releasing heat) beforehand?
- The obstacle impeding the formation of droplets is the **surface tension**.

- Surface tension is given by

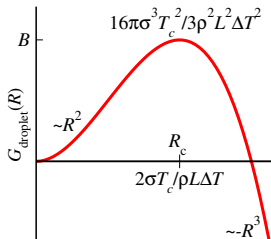
$$\begin{aligned} \sigma &= \text{Gibbs free energy per unit area of interface between liquid and gas} \\ &\left[ = \frac{G_{\ell g} - \frac{1}{2}(G_{\ell\ell} + G_{g g})}{A} \quad (\text{See footnote 12 in Sethna section 11.3}) \right] \end{aligned}$$

- Gibbs free energy grows as the area  $A$  and bulk free energy gain grows as volume  $V$ , so tiny droplets cost the system more than they gain.

# Energy barrier & Critical droplet radius

- Consider spherical droplet of radius  $R$ ; the surface Gibbs free energy is  $\sigma A$ ; if the liquid has  $\rho_{\text{liq}}$  particles per unit volume and each particle provides a free energy gain of  $\Delta\mu = \frac{L\Delta T}{T_v}$  then the bulk free energy gain is  $V\rho_{\text{liq}}$ .

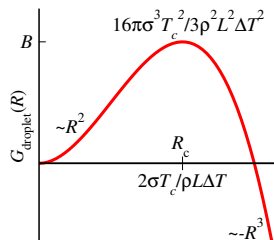
$$\therefore G_{\text{droplet}}(R) = \sigma A - V\rho_{\text{liq}}\Delta\mu = 4\pi R^2\sigma - \left(\frac{4}{3}\pi R^3\right)\rho_{\text{liq}}\frac{L\Delta T}{T_v}$$



- The gas remains a gas until a rare thermal fluctuation pays the critical energy cost to reach the top of the barrier, making a **critical droplet**.



## Energy barrier & Critical droplet radius (2)



- One finds the critical droplet radius  $R_c$  and the height of free energy barrier  $B$  by maximizing  $G(R)$ :

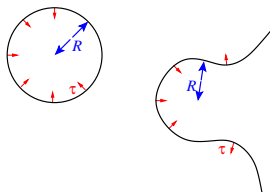
$$\left. \frac{\partial G_{\text{droplet}}}{\partial R} \right|_{R_c} = 8\pi\sigma R_c - 4\pi\rho_{\text{liq}} \left( \frac{L\Delta T}{T_v} \right) r_c^2 = 0$$
$$\Rightarrow R_c = \frac{2\sigma T_v}{\rho_{\text{liq}} L \Delta T}, \quad B = \frac{16\pi\sigma^3 T_v^2}{3\rho_{\text{liq}}^2 L^2} \frac{1}{(\Delta T)^2}$$

# Nucleation rates

- The net droplet nucleation rate per volume is  $\Gamma = (\text{const.}) \times \exp\left(\frac{-B}{k_B T}\right)$ .
- Note the following:
  - Critical droplet radius  $R_c \propto \frac{1}{\Delta T}$ ; if you undercool the gas by a tiny amount, you need a large droplet to overcome the surface tension.
  - $B \propto \frac{1}{(\Delta T)^2}$ : The energy barrier for nucleation diverges at  $T_v$ .
- Critical droplet theory calculates the rare fluctuations that take us over the energy barrier (Read note 14 in Sethna, section 11.3)
- The rates we have calculated are for **homogenous nucleation**, the rate of forming a new phase in a clean system w/o boundaries.
- Since nucleation is suppressed very strongly by surface tension, the system tries to bypass at least part of the free energy barrier; this is why droplets usually form on grass or your windows rather than forming in the air and dropping down.

# Coarsening

- Tiny objects merging into bigger ones (e.g., salad dressing after one stops shaking, and numerous examples in materials science and geophysics).
- This can also be seen in abstract situation like the Ising model



**Figure:** Snapshot of a coarsening system; most features here have a characteristic length scale of radius  $R \sim L(t)$ ,  $L(t)$  =time dependent length scale of the smallest features.

- Coarsening involves the smaller features shrinking to zero, leaving only the larger scales behind.
- Coarsening is driven by surface tension: the system can lower its free energy by lowering the interfacial area between different domains.