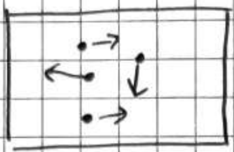
0 - Introduction

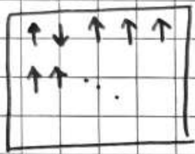
Dr Thomas
c.e.thomas@damtp.cam.ac.uk

e.g. gas



macroscopic variables:
Energy E
Volume V
pressure p
temperature T
entropy S

e.g. magnetic system
(spins on a lattice)



macroscopic variables:
Energy E
magnetisation M
External Field B
temperature T
entropy S

1 Fundamentals of statistical mechanics

1.1 Microcanonical ensemble

Consider an isolated system with a fixed energy E.
The schrödinger eq^n is $\hat{H}|\psi\rangle = E|\psi\rangle$

In this course, we will be interested in systems with many particles, $N \sim 10^{23}$. The wavefunction $|\psi\rangle$ is called the microstate - it tells us what all the particles are doing.

But macroscopic systems don't sit in a single state $|\psi\rangle$. Small perturbations ⇒ transitions to other states with the same energy. There are typically many such states. We'll use statistical methods.

Fundamental assumption: for an isolated system in equilibrium, all accesible microstates are equally likely ☺

"equilibrium" - system left alone for a long time, settles down and macroscopic quantities are time-independent "accessible" – states which can be reached by small perturbations (at fixed energy, for now)

Let $\Omega(E)$ = no. of states with energy E. ← i.e. dim^n of eigenspace of PQM

Prob. in a given state $|n\rangle$ with energy E is

$$p = \frac{1}{\Omega(E)}$$

Ω is typically very large, $\Omega \sim e^N$

Define <u>entropy</u> $S(E) = k_B \ln \Omega(E)$

where $k_B \approx 1.381 \times 10^{-23}\, JK^{-1}$ is <u>Boltzmann's constant</u>

<u>Note</u>: • Entropy is additive

For two systems with energies E_1, E_2

then $\Omega(E_1, E_2) = \Omega_1(E_1)\Omega_2(E_2)$

$\Rightarrow S(E_1, E_2) = S_1(E_1) + S_2(E_2)$

• $S \propto N$ – it's called an <u>extensive</u> quantity

as are V, E, M

Others like T, p, B are <u>intensive</u> quantities – don't depend on N

<u>2nd law of thermodynamics</u>

Take two non-interacting systems with energies E_1, E_2.

Bring them together so they can exchange energy.

$E_{total} = E_1 + E_2$ is fixed

No. of states in total is

$$\Omega(E_{total}) = \sum_{\substack{\{E_1, E_2 \\ E_1+E_2=E_{total}\}}} \Omega_1(E_1)\Omega_2(E_2)$$

$$= \sum_{\underset{\text{energies of 1}}{\overset{\uparrow}{\{E_i\}}}} \Omega_1(E_i)\Omega_2(E_{total}-E_i)$$

$$= \sum_{\{E_i\}} \exp\left(\frac{S_1(E_i)}{k_B} + \frac{S_2(E_{total}-E_i)}{k_B}\right)$$

$S \sim N \Rightarrow$ sum totally dominated by maximum value of the exponent at $E_i = E_*$

(overwhelmingly more likely to have $E_i = E_*$)

$$\left.\frac{\partial S_1}{\partial E}\right|_{E=E_*} - \left.\frac{\partial S_2}{\partial E}\right|_{E = E_{tot}-E_*} = 0$$

and $S(E_{total}) = k_B \ln \Omega(E_{total})$

$$\approx S_1(E_*) + S_2(E_{total} - E_*)$$

But E_* maximizes entropy

$$\Rightarrow \boxed{S(E_{total}) \geqslant S_1(E_1) + S_2(E_2)}$$

[This is blindingly obvious?]

This is the second law of thermodynamics:

entropy increases: whenever we remove constraints on a system the number of available states increases dramatically. The system will never return to its original state.

Define temperature T by

$$\boxed{\frac{1}{T} = \frac{\partial S}{\partial E}}$$

But why?

Defining property of temperature: if two systems have the same temperature T, then nothing happens when they are brought together.

But we've seen that the energy transfers such that the entropy is maximized. If we want no energy to be transferred, we must already have $E_1 = E_*$, and the condition becomes

$$\left.\frac{\partial S_1}{\partial E}\right|_{E=E_1} = \left.\frac{\partial S_2}{\partial E}\right|_{E=E_2}$$

i.e. $\frac{1}{T_1} = \frac{1}{T_2}$ as required.

Note: usually S increases with E, so $T > 0$

some model systems have S decreasing with E.

systems with finite no. of states or finite phase space.

e.g. spin systems, systems of confined vortices

In practice, these are coupled to other systems where S increases with E, so -ve temperature states are at best meta-stable, short lived.

Should think about negative temp as hotter than $T = \infty$ because $\frac{1}{T}$ is more natural than T.

Suppose systems are at slightly different temperatures.

Entropy change when they are brought together:

$$\delta S = \left.\frac{\partial S_1}{\partial E}\right|_{E=E_1} \delta E_1 + \left.\frac{\partial S_2}{\partial E}\right|_{E=E_2} \delta E_2$$

$$= \delta E_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \geqslant 0$$

If $T_1 > T_2$ then $\delta E_1 < 0$, and energy flows hot → cold.

<u>Note</u> we'll see that this defⁿ of temp coincides with temperature measured by an ideal gas thermometer later.

The <u>heat capacity</u> (at constant volume) is

$$C_V = \frac{\partial E}{\partial T}$$

This is something we can measure.

Provides link between theory and expt.

Write $S = S(E)$ and invert temp. defⁿ to think of $E = E(T)$, then,

$$\frac{\partial S}{\partial T} = \frac{\partial S}{\partial E}\frac{\partial E}{\partial T} = \frac{C_V}{T}$$

$$\Rightarrow \Delta S = \int_{T_1}^{T_2} \frac{C_V(T)}{T}\, dT$$

gives us a handle on entropy differences from $C_V(T)$

<u>Note</u>:
$$\frac{\partial^2 S}{\partial E^2} = \frac{\partial}{\partial T}\left(\frac{\partial S}{\partial E}\right)\frac{\partial T}{\partial E}$$
$$= -\frac{1}{T^2}\cdot\frac{1}{C_V}$$

$\Rightarrow$ maximal entropy if $C_V > 0$

$C_V > 0 \Rightarrow$ energy increases with temp.

$\Rightarrow$ slope of $S(E)$ decreases with temp

<u>An example</u>: <u>Two state system</u>

consider a system of N non-interacting particles, each with two possible states; for convenience call these spin up, spin down

$|\uparrow\rangle$, $|\downarrow\rangle$

$E_\uparrow = \varepsilon$, $E_\downarrow = 0$

If system has $N_\uparrow$ particles with spin up, and $N_\downarrow = N - N_\uparrow$ with spin down, total energy is $E = N_\uparrow \varepsilon$

$\Omega(E)$ = no. of states with total energy E

$$= \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow!\,(N-N_\uparrow)!}$$

and so $S(E) = k_B \Big(\ln(N!) - \ln(N_\uparrow!) - \ln((N-N_\uparrow)!)\Big)$

For large N, approximate using Stirling's formula:

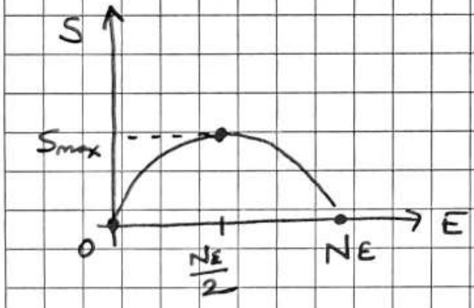
$$\ln(N!) = \underbrace{N\log N - N}_{\text{only relevant ones}} + \frac{1}{2}\ln N + \frac{1}{2}\log 2\pi + O\left(\frac{1}{N}\right)$$

$$\therefore\ S(E) = k_B\left(N\log N - \cancelto{0}{N} - N_\uparrow \log N_\uparrow - (N-N_\uparrow)\log(N-N_\uparrow)\right)$$

$$= k_B\left[-(N-N_\uparrow)\ln\left(\frac{N-N_\uparrow}{N}\right) - N_\uparrow \ln\left(\frac{N_\uparrow}{N}\right)\right]$$

$$= -k_B\left[N\left(1-\frac{E}{N\varepsilon}\right)\ln\left(1-\frac{E}{N\varepsilon}\right) + N\frac{E}{N\varepsilon}\ln\left(\frac{E}{N\varepsilon}\right)\right]$$

A graph of $S(E)$ looks like



max at $E = \frac{1}{2}N\varepsilon$

when $S(E) = Nk_B \ln 2$

The temperature is $\dfrac{1}{T} = \dfrac{\partial S}{\partial E} = \dfrac{k_B}{\varepsilon}\ln\left(\dfrac{N\varepsilon}{E} - 1\right)$ ← doubt? no

Suppose the system is at temp. T

Inverting this, fraction of particles with spin up is:

$$\frac{N_\uparrow}{N} = \frac{E}{N\varepsilon} = \frac{1}{e^{\varepsilon/k_B T} + 1}$$

$\left(\frac{N_\uparrow}{N} \to \frac{1}{2} \text{ as } T \to \infty,\quad \frac{N_\uparrow}{N} \to 0 \text{ as } T \to 0\right)$

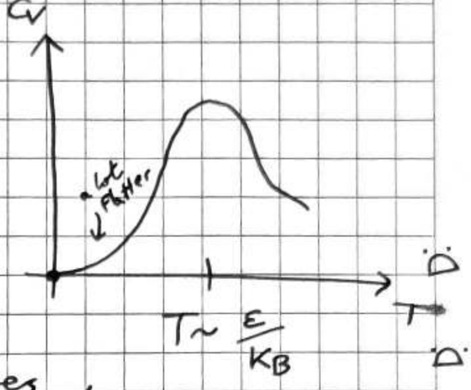
Note: $\frac{N_\uparrow}{N} > \frac{1}{2}$ corresponds to negative temperatures e.g. Two State System (cont.)

$$S(E) = -k_B N \left[\left(1-\frac{E}{N\varepsilon}\right)\ln\left(1-\frac{E}{N\varepsilon}\right) + \frac{E}{N\varepsilon}\ln\left(\frac{E}{N\varepsilon}\right) \right]$$

$$\frac{N_\uparrow}{N} = \frac{E}{N\varepsilon} = \frac{1}{e^{\varepsilon/k_BT}+1}$$

Heat capacity (express as a f^n of T)

$$c_V = \frac{\partial E}{\partial T} = \frac{N\varepsilon^2}{k_BT^2}\frac{e^{\varepsilon/k_BT}}{\left(e^{\varepsilon/k_BT}+1\right)^2}$$



Note: • $c_V \propto N$ (extensive)

- As $T \to 0$, $c \sim e^{-\varepsilon/k_BT}$ which goes to 0 exponentially

This is due to an energy gap

- As $T \to \infty$, $c_V \to 0$ at a power-law rate
- This effect is tiny in real solids – swamped by phonons/electrons

Pressure, volume and the First Law

We now consider other external parameters. One of the most important is volume V. Very often the no. of states will depend on V (e.g. whenever particles can move around)

$$S(E,V) = k_B \ln \Omega(E,V)$$

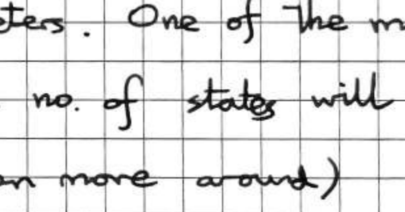
We still have $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V$

We can also define pressure $p = T\left(\frac{\partial S}{\partial V}\right)_E$

Consider two systems with pressures p_1, p_2.

Put them together so volume can change (total vol. fixed)

(Same temperature T)



Entropy of combined system is maximal only if $\left.\frac{\partial S_1}{\partial V}\right|_{V=V_1} = \left.\frac{\partial S_2}{\partial V}\right|_{V=V_2}$

$$p_1/T = p_2/T$$ i.e. $p_1 = p_2$ as expected

Back to a single system, we can write

$$S = S(E, V)$$

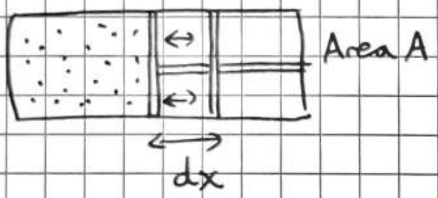
$$\therefore \; dS = \left(\frac{\partial S}{\partial E}\right)_V dE + \left(\frac{\partial S}{\partial V}\right)_E dV$$

$$= \frac{1}{T} dE + \frac{P}{T} dV$$

$$\therefore \quad \boxed{dE = TdS - pdV}$$ 1st law of thermodynamics

Expresses conservation of energy

$-pdV$ = work done <u>on</u> the system



work done = Force × dx

$= -pA\,dx$ (+ve if we push in)

$= -p\,dV$

TdS = interpreted as energy transferred <u>to</u> the system in the form of <u>heat</u>

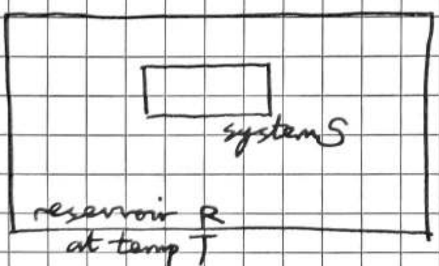
(A lot of the section on thermodynamics will be devoted to understanding this)

1.2 – Canonical ensemble

The microcanonical ensemble describes systems at fixed E.

Here we will describe systems at fixed temperature T.

Consider the following setup:



The reservoir R has fixed temperature T (heat bath). It is in thermal equilibrium with the system S.

The energy of S is negligible compared to the energy of R.

Let $|n\rangle$ denote the states of S with energy E_n.

The number of (micro) states of the combined system is:

$$\Omega(E_{total}) = \sum_{\underset{\nwarrow}{n}} \Omega_R(E_{total} - E_n)$$

sum over all the states of S, not energies

$$= \sum_n \exp\left(\frac{S_R(E_{total}-E_n)}{k_B}\right)$$

$$\approx \sum_n \exp\left(\frac{S_R(E_{total})}{k_B} - \underbrace{\frac{\partial S_R}{\partial E}\bigg|_{E=E_{total}}}_{1/T}\frac{E_n}{k_B}\right)$$

$E_n \ll E_{total}$ $\therefore$ Taylor exp^n

$$= \exp\left(\frac{S_R(E_{total})}{k_B}\right)\sum_n \exp\left(-\frac{E_n}{k_BT}\right)$$

Now apply fundamental assumption to $S+R$: each of these states is equally likely

No. of states of $S+R$, above $\Omega(E_{total})$, s.t. S is in state $|n\rangle$ is $\exp\left(\frac{S_R(E_{total})}{k_B}\right)\exp\left(-\frac{E_n}{k_BT}\right)$

$\therefore$ Prob(S in $|n\rangle$) $\propto \exp\left(-\frac{E_n}{k_BT}\right)$

i.e. $P(n) = \dfrac{e^{-E_n/k_BT}}{\sum_m e^{-E_m/k_BT}}$ ← normalis^n

Note:
- very small prob to be in state with $E_n \gg k_BT$
- reasonable prob to be in state with $E_n \lesssim k_BT$

Define $\beta = \dfrac{1}{k_BT}$, $\underset{\uparrow}{Z} = \sum_m e^{-\beta E_m}$

"partition function"

It contains all the information we need about the system $Z(\beta)$

$$\boxed{P(n) = \frac{e^{-\beta E_n}}{Z}}$$

Boltzmann distribution

Claim: For two independent systems at the same temperature,

$$Z = Z_1 Z_2$$

Proof:

$$Z(\beta) = \sum_{n,m} e^{-\beta(E_n^1 + E_m^2)}$$

$$= \sum_{n,m} e^{-\beta E_n^1} e^{-\beta E_m^2}$$

$$= \left(\sum_n e^{-\beta E_n^1}\right)\left(\sum_m e^{-\beta E_m^2}\right)$$

$$= Z_1(\beta) Z_2(\beta). \qquad \square$$

Energy The average energy is

$$\langle E \rangle = \sum_n p(n) E_n$$

$$= \sum_n E_n e^{-\beta E_n} / Z$$

$$= \frac{-1}{Z} \cdot \frac{\partial Z}{\partial \beta} = \frac{-\partial}{\partial \beta} \ln Z$$

The spread of energies is given by the variance

$$(\Delta E)^2 = \langle E^2 \rangle - \langle E \rangle^2$$

$$= \frac{\partial^2}{\partial \beta^2} \ln Z .$$

The heat capacity is

$$C_V = \frac{\partial \langle E \rangle}{\partial T}$$

On Ex Sheet show: $(\Delta E)^2 = k_B T^2 C_V$

Note $\langle E \rangle \propto N$, $C_V \propto N$ (extensive)

$$\Rightarrow \Delta E / E \sim \sqrt{N}/N = \frac{1}{\sqrt{N}} \to 0 \text{ as } N \to \infty$$

(called the thermodynamic limit)

The fluctuations around the average value are very small in this limit. We can usually ignore them and we will write $\langle E \rangle = E$.

$\Rightarrow$ canonical ensemble is equivalent to the microcanonical ensemble

Example Back to the 2-state system.

For a single particle with $E_\uparrow = \varepsilon$, $E_\downarrow = 0$,

$$Z_1 = e^{-\beta E_\downarrow} + e^{-\beta E_\uparrow} = 1 + e^{-\beta\varepsilon}$$
$$= 2e^{-\beta\varepsilon/2}\cosh\left(\frac{\beta\varepsilon}{2}\right)$$

For N particles,

$$Z = Z_1^N = 2^N e^{-\beta N\varepsilon/2}\cosh^N\left(\frac{\beta\varepsilon}{2}\right)$$

$$\rightarrow \langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z = \frac{N\varepsilon}{2}\left(1 - \tanh(\beta\varepsilon/2)\right)$$

With some algebra, can show this is the same result as before. ☺

Entropy We want to define entropy in the canonical ensemble (or any ensemble) with prob. dist^n $p(n)$

Consider W copies of the system (W very large). Think of collection of W copies as sitting in the microcanonical ensemble.

No. of systems in state $|n\rangle$ is $p(n)W$.

No. of ways of arranging states among all copies is

$$\Omega = \frac{W!}{\prod_n (p(n)W)!}$$

$$\Rightarrow S_W = k_B \ln\Omega$$
$$= -k_B W \sum_n p(n)\ln p(n) \qquad \text{(using Stirling's formula)}$$

This is the entropy for W copies, but entropy is additive. So for a single copy of the system,

$$S = -k_B \sum_n p(n)\ln p(n)$$

This is the <u>Gibbs entropy</u>

(a.k.a. Shannon entropy, von Neumann entropy)

It holds for any prob. dist^{n}

<u>Note</u> In the microcanonical ensemble, $p(n) = \frac{1}{\Omega(E)}$ if $E_n = E$

$$\Rightarrow S = -k_B \sum_{n|E_n=E} \frac{1}{\Omega(E)} \ln\left(\frac{1}{\Omega(E)}\right) = k_B \ln \Omega(E) \qquad \ddot{o}$$

in agreement with before.

In canonical ensemble,

$$S = k_B \frac{\partial}{\partial T}\left(T \ln Z\right)$$

(proof on ex sheet 1)

Free energy

When $T=0$, the ground state is determined by minimising the energy.

What about $T>0$?

<u>Claim</u> The most likely energy of the system is determined by minimising the (Helmholtz) <u>free energy</u>:

$$F = E - TS$$

(note: "free" means "vaailabe")

<u>Proof</u> The prob. that the system is at eregy E is

$$p(E) = \sum_{n|E_n=E} p(n) = \underset{\substack{\uparrow \\ \text{No. of states of} \\ \text{S w/energy E}}}{\Omega_S(E)}\, p(n) = \Omega_S(E)\, e^{-\beta E}/Z$$

$$p(E) = e^{S/k_B}\, e^{-E/k_BT}/Z = \frac{1}{Z}\exp\left(\frac{-F}{k_BT}\right)$$

where $F = E - TS$. So done since $T > 0$. $\square$

mathematically, F is (T times) a Legendre transf^n of $S(E,V)$

$$F = E - TS$$

$$\Rightarrow dF = dE - TdS - SdT$$

$$= -pdV - SdT$$

$\therefore$ more natural to think of $F = F(T,V)$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \quad , \quad p = -\left(\frac{\partial F}{\partial V}\right)_T$$

Claim $F = -k_B T \ln Z$

Pf (outline) $F = E - TS$

$$= k_B T^2 \frac{\partial}{\partial T} \ln Z \quad - k_B T \frac{\partial}{\partial T}(T \ln Z)$$

$$= -k_B T \ln Z. \qquad \square$$

$\therefore Z = e^{-\beta F}$

1.3 - Chemical Potential

When there are conserved quantities, the accessible states are restricted to those where the quantities have the correct values.

e.g. particle number N

electric charge Q

In this section we'll consider N. In the microcanonical ensemble:

$$S(E,V,N) = k_B \ln \Omega(E,V,N)$$

Define the <u>chemical potential</u>

$$\mu = -T \frac{\partial S}{\partial N}$$

Suppose two systems can exchange particles; using the same argument as before $\Rightarrow \mu_1 = \mu_2$ in equilibrium

First Law of thermodynamics becomes

$$dE = T\,dS - p\,dV + \mu\,dN$$

μ = energy cost to add 1 more particle to the system at fixed S and V.

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}$$

$$\lceil \left(\frac{\partial S}{\partial N}\right)_{E,V} \left(\frac{\partial N}{\partial E}\right)_{S,V} \left(\frac{\partial E}{\partial S}\right)_{N,V} = -1$$

$$\left(-\frac{\mu}{T}\right) T \left(\frac{\partial N}{\partial E}\right)_{S,V} = -1 \rfloor$$

Expression for dF becomes

$$dF = -S\,dT - p\,dV + \mu\,dN$$

Grand Canonical Ensemble

Suppose we have a system where the particle no. can fluctuate, surrounded by a reservoir at constant μ and T.

Prob. that system is in microstate $|n\rangle$ with energy E_n and particle number N_n is $p(n) = e^{-\beta(E_n - \mu N_n)}/Z$

where $Z(T, \mu, V) = \sum_n e^{-\beta(E_n - \mu N_n)}$
is the <u>grand partition function</u>.

It can be shown that:

$$\langle E \rangle - \mu \langle N \rangle = -\frac{\partial}{\partial \beta} \ln Z$$

$$\langle N \rangle = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Z$$

$$(\Delta N)^2 = \frac{1}{\beta^2} \frac{\partial^2}{\partial \mu^2} \ln Z$$

Also $\frac{(\Delta N)}{\langle N \rangle} \sim \frac{1}{\sqrt{\langle N \rangle}}$

$\Rightarrow$ *fluctuations negligible as $\langle N \rangle \longrightarrow \infty$*

All three ensembles coincide in the termodynamic limit.
The <u>grand canonical potential</u> is

$$\Phi = F - \mu N$$

$$\therefore \ d\Phi = -S\,dT - p\,dV - N\,d\mu$$

and so $\Phi = \Phi(T, \mu, V)$.
We can show that

$$\Phi = -k_B T \ln Z \qquad \text{(proof as before)}$$

$$Z = e^{-\beta \Phi} \qquad \text{c.f. } Z = e^{-\beta F}$$

Extensive vs Intensive Quantities

Recall that an extensive quantity scales proportionally to the size of the system: e.g. N, V, E, S

This can be written as

$$S(\lambda E, \lambda V, \lambda N) = \lambda S(E, V, N)$$

An intensive quantity is independent of the size of the system, e.g. $\frac{1}{T} = \frac{\partial S}{\partial E}$, $p = T\frac{\partial S}{\partial V}$, $\mu = -T\frac{\partial S}{\partial N}$

$F = E - TS$ is extensive

$\Rightarrow F(T, \lambda V, \lambda N) = \lambda F(T, V, N)$

↳ Lots of ways to solve

e.g. $F \sim V^{n+1}/N^n$

$\Phi = F - \mu N$ is extensive

$\Rightarrow \Phi(T, \lambda V, \mu) = \lambda \Phi(T, V, \mu)$

↳ only one way to solve

$\Phi \propto V$

$$\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu} = -p$$

$$\Rightarrow \Phi = -p(T, \mu) V$$

§ 2 Classical Gases

2.1 Classical partition function

The quantum partition function is

$$Z = \sum_{\text{states}} e^{-\beta E}$$

In classical mechanics, the state of a system is specified by a point in phase space.

The energy is the Hamiltonian.

e.g. for a particle moving in $\mathbb{R}^3$,

$$H = \underset{\substack{\nearrow \\ \text{momentum}}}{\frac{1}{2m}|\underline{p}|^2} + \underset{\substack{\nwarrow \\ \text{position}}}{V(\underline{q})}$$

This motivates the classical partition function for a single particle,

$$Z_1 = \frac{1}{h^3}\int d^3p\, d^3q\ e^{-\beta H}$$

Notes:
- This can be derived from the quantum partition function. (see §2.1.1 of David Tong's notes)
- The factor of $\frac{1}{h^3}$ is needed on dimensional grounds, so that Z is dimensionless:
  $$[h] = [pq] = \text{action} = \text{Js}$$
- h doesn't ~~depend~~ appear in any measurable quantity because these are $\sim \frac{d}{dX}\ln Z$
- The correct value of h can be found by deriving from the quantum partition function: $h = 2\pi\hbar$, Planck's const.

§ 2.2 Ideal Gas

Gas = N particles in a box of volume V

Ideal = non-interacting particles

$$H = \frac{|\underline{p}|^2}{2m}$$

$$Z_1(V,T) = \frac{1}{(2\pi\hbar)^3}\int d^3q\, d^3p\, \exp\left(\frac{-\beta|\underline{p}|^2}{2m}\right)$$

$$= \frac{V}{(2\pi\hbar)^3}\int d^3p\, \exp\left(-\frac{\beta|\underline{p}|^2}{2m}\right)$$

Gaussian integral $\int_{-\infty}^{\infty} e^{-ax^2}dx = \sqrt{\frac{\pi}{a}}$

$$= \frac{V}{(2\pi\hbar)^3}\left(\frac{2m\pi}{\beta}\right)^{3/2}$$

$$= V\left(\frac{k_B T m}{2\pi\hbar^2}\right)^{3/2}$$

$$\equiv \frac{V}{\lambda^3}$$

where $\lambda = \left(\frac{2\pi\hbar^2}{k_B T m}\right)^{1/2}$ is the thermal de Broglie wavelength.

$[\lambda] = \text{length}$

For N particles,

$$Z(N,V,T) = Z_1^N = V^N/\lambda^{3N}$$

Compute pressure :

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{\partial}{\partial V}(k_B T \ln Z) = \frac{N k_B T}{V}$$

This is the ideal gas law.

(Works well for gases at low densities where interactions between particles are unimportant.)

Our definition of temperature is the same as the temperature measured by an ideal gas thermometer.

The average energy is

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z = \frac{3}{2} N \frac{1}{\beta} = \frac{3}{2} N k_B T = \underset{\substack{\uparrow \\ \text{no. of} \\ \text{degrees} \\ \text{of freedom}}}{3N} \cdot \left(\tfrac{1}{2} k_B T\right)$$

Equipartition of energy

— any classical system at temperature T has $\frac{1}{2} k_B T$ energy per degree of freedom.

Note : $E = \frac{p^2}{2m} \Rightarrow \langle p \rangle \sim \sqrt{m k_B T}$

$\lambda \sim \frac{h}{\langle p \rangle}$ i.e. de Broglie wavelength

Heat capacity

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2} N k_B$$

Boltzmann constant

Recall $k_B \approx 1.381 \times 10^{-23}\ \mathrm{J\,K^{-1}}$

Conversion factor between energy and temperature, but why is it so small ?

$$\underset{\substack{\uparrow \\ \text{for reasonable} \\ p, V, T \text{ these are} \\ \approx 10^2}}{\frac{pV}{T}} = N k_B$$

$\therefore N k_B$ must be a reasonable quantity

N big $\Rightarrow k_B$ small,

telling us that atoms are very small

Entropy and the Gibbs Paradox

We said $Z = Z_1^N$.

But this isn't quite right ; quantum particles are indistinguishable ; swapping two particles gives us back the same state (up to a minus sign)

$\therefore Z = Z_1^N$ overcounts the states

$$Z_{\substack{\text{ideal}\\ \text{gas}}} = \frac{Z_1^N}{N!} = \frac{V^N}{N!\,\lambda^{3N}}$$

This doesn't affect p or $\langle E \rangle$, but it does affect the entropy:

$$S = \frac{\partial}{\partial T}\left(k_B T \ln Z\right)$$

$$= \frac{3}{2} N k_B + k_B \ln Z$$

$$\big\downarrow \text{Stirling}$$

$$= N k_B \left(\frac{5}{2} + \ln\left(\frac{V}{N \lambda^3} \right) \right)$$

This is the <u>Sackur – Tetrode equation</u>.

In classical mechanics, considering mixing of gases,

$$Z = Z_1^N / N!$$

is needed, but it wasn't understood why.
This is the Gibbs paradox.

Last time: ideal classical gases

$$Z_{\text{ideal}} = \frac{V^N}{N!\,\lambda^{3N}} \quad , \quad \lambda = \sqrt{\frac{2\pi\hbar^2}{mk_BT}}$$

Ideal gas in the grand canonical ensemble

$$\mathcal{Z}_{\text{ideal}}(\mu,V,T) = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_{\text{ideal}}(N,V,T)$$

$$= \sum_{N=0}^{\infty} \frac{1}{N!}\left(e^{\beta\mu}\frac{V}{\lambda^3}\right)^N$$

$$= \exp\left(\frac{e^{\beta\mu}V}{\lambda^3}\right)$$

Average no. of particles is

$$N = \frac{1}{\beta}\frac{\partial}{\partial\mu}(\ln\mathcal{Z}) = \frac{e^{\beta\mu}V}{\lambda^3}$$

$$\frac{\Delta N}{\langle N\rangle} = \frac{1}{\sqrt{N}} \rightarrow 0 \text{ as } N\rightarrow\infty$$

$$\therefore \mu = k_BT\ln\left(\frac{N\lambda^3}{V}\right)$$

For a classical gas we must have $\lambda \ll \left(\frac{V}{N}\right)^{1/3}$
Otherwise quantum effects become important.

$$\therefore \mu < 0$$

Note: $\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}$

Adding a particle increases S, so must reduce E to compensate at fixed S.

Compute equation of state:

Use $-pV = \Phi = -k_BT\ln\mathcal{Z}$

$$\Rightarrow pV = \frac{e^{\beta\mu}V}{\lambda^3}k_BT = Nk_BT$$

2.3 Maxwell Distribution

How fast are atoms in a gas moving?

They are not all travelling at the same speed and we'd like to understand the distribution of speeds.

One-particle partition function:

$$Z_1 = \frac{1}{(2\pi\hbar)^3} \int d^3q \int d^3p \; e^{-\beta p^2/2m}$$

$$= \frac{m^3 V}{(2\pi\hbar)^3} \int \underset{\nwarrow p=mv}{d^3v} \; e^{-\beta m v^2/2}$$

$$= \frac{4\pi m^3 V}{(2\pi\hbar)^3} \int dv \; v^2 e^{-\beta m v^2/2}$$

$$\sim \sum_{\text{speeds } v} \text{prob}(v)$$

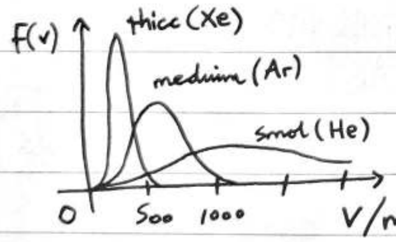
$$\left(\text{c.f. } Z = \sum_{\text{states}} \text{prob}(\text{state}) \right)$$

The prob. that the particle has speed between v, $v+dv$ is

$$f(v)\,dv \quad \text{where} \quad f(v) = \underset{\substack{\uparrow \\ \text{normalisation}}}{\mathcal{N}} v^2 e^{-\beta m v^2/2}$$

$$\int_0^\infty dv\, f(v) = 1 \implies \mathcal{N} = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2}$$

This is called the Maxwell distribution.



Check: average v^2

$$\langle v^2 \rangle = \int_0^\infty dv \; v^2 f(v)$$

$$= \mathcal{N} \int_0^\infty v^4 e^{-mv^2/2k_BT} dv$$

$$= \frac{3}{2} \frac{2k_BT}{m} = 3\frac{k_BT}{m}$$

agrees with $E = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T$

2.4 – Diatomic Gas

Consider a molecule made of two atoms

As well as translational motion, it can also:

- rotate – this is only relevant about the two axes perp to symm axis
- vibrate – along the axis of symmetry

Assume these modes are independent.

For one particle:

$$Z_1 = Z_{trans} Z_{rot} Z_{vib}$$

Rotations

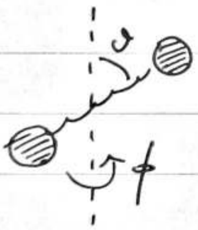
$$L_{rot} = \frac{I}{2}\left(\dot\theta^2 + \sin^2\theta\,\dot\phi^2\right)$$

Lasagnian

moment of inertia

$$\Rightarrow \text{momenta } p_\theta - \frac{\partial L}{\partial\dot\theta} = I\dot\theta$$

$$p_\phi = \frac{\partial L}{\partial\dot\phi} = I\sin^2\theta\,\dot\phi$$



$$\therefore H_{rot} = \dot\theta p_\theta + \dot\phi p_\phi - L$$

$$= \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I\sin^2\theta}$$

$$\therefore Z_{rot} = \frac{1}{(2\pi\hbar)^2}\int d\theta\int d\phi\int dp_\theta\int dp_\phi\; e^{-\beta H_{rot}}$$

$$= \frac{2\pi}{(2\pi\hbar)^2}\int d\theta\,\sqrt{\frac{2\pi I}{\beta}}\sqrt{\frac{2\pi I\sin^2\theta}{\beta}}$$

$$= 2Ik_BT/\hbar^2$$

$$\therefore \langle E_{rot}\rangle = -\frac{\partial}{\partial\beta}\ln Z_{rot} = \frac{1}{\beta} - k_BT$$

∴ For trans. + rot (not vib)

$$\langle E\rangle = \tfrac{5}{2}k_BTN, \qquad C_V = \tfrac{5}{2}k_BN$$

Vibrations

Treat as a harmonic oscillator

$$H_{vib} = \frac{p_z^2}{2m} + \frac{1}{2} m \underset{\uparrow \text{ natural frequency}}{\omega^2} \underset{\nwarrow \text{ displacement from equi}}{z^2}$$

$$\therefore \; Z_{vib} = \frac{1}{2\pi\hbar} \int dz \int dp_z \; e^{-\beta H_{vib}}$$

$$= \frac{1}{2\pi\hbar} \sqrt{\frac{2\pi m}{\beta}} \sqrt{\frac{2\pi}{\beta m \omega^2}}$$

$$= k_B T / \hbar\omega$$

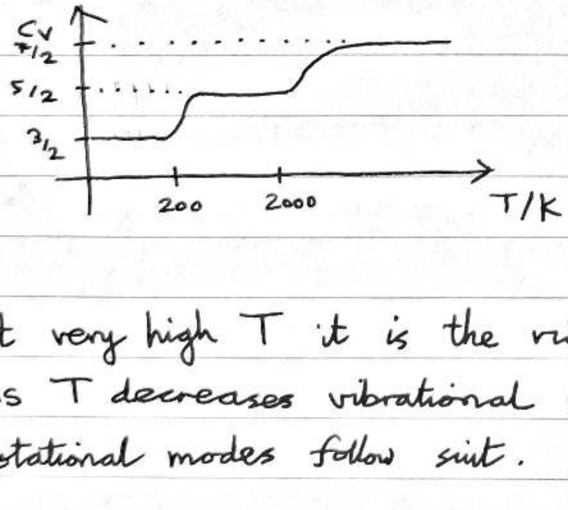
$$\langle E_{vib} \rangle = \frac{1}{\beta} = k_B T$$

$\therefore$ For trans. + rot. + vib.

$$\langle E \rangle = \frac{7}{2} N k_B T \quad \Rightarrow \quad C_V = \frac{7}{2} N k_B$$

But this is not what is observed in experiment

E.g. for H_2



At very high T it is the right answer.
As T decreases vibrational modes 'freeze out', then the rotational modes follow suit.

This was a big puzzle. It turns out that this 'freezing' of modes is a quantum effect, the first time quantum effects appeared in experiment. (We'll return to this later.)

Ideal gas = no interactions

$\Rightarrow \quad pV = Nk_BT$

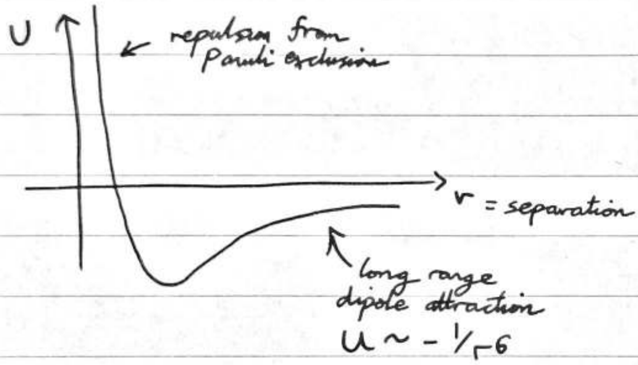
This is valid for low densities ; small N/V

A general equation of state can be written as an expansion in the density,

$$p/k_BT = \frac{N}{V} + B_2(T)\left(\frac{N}{V}\right)^2 + B_3(T)\left(\frac{N}{V}\right)^3 + \cdots$$

- This is the virial expansion.
- Coefficients $B_i(T)$ are virial coefficients.
- Goal : compute $B_i(T)$ from first principles.

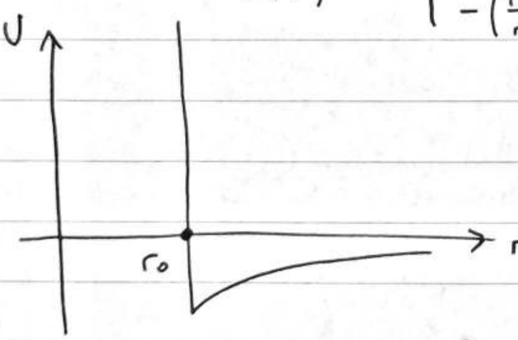
Potential between neutral atoms:



[One atom gets a dipole p_1 from fluctuations $\Rightarrow$ E-field $\sim \frac{p_1}{r^3}$ $\Rightarrow$ polarises 2nd atom $\Rightarrow p_2 \sim \frac{p_1}{r^3} \Rightarrow U \sim \frac{p_1 p_2}{r^3} \sim \frac{1}{r^6}$]

E.g. $U(r) \sim \left(\frac{r_0}{r}\right)^{12} - \left(\frac{r_0}{r}\right)^6$ Lennard-Jones potential

We'll use $U(r) = \begin{cases} \infty, & r < r_0 \\ -\left(\frac{r_0}{r}\right)^6 U_0, & r > r_0 \end{cases}$



Hamiltonian is

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i>j} U(r_{ij})$$

$$\uparrow \; r_{ij} = |\underline{r}_i - \underline{r}_j|$$

The partition function doesn't factorize ⇒ hard to do calculations

$$Z(N,V,T) = \frac{1}{N!}\frac{1}{(2\pi\hbar)^{3N}} \int \prod_{i=1}^{N} d^3p_i\, d^3r_i \; e^{-\beta H}$$

$$= \frac{1}{N!}\frac{1}{(2\pi\hbar)^{3N}} \left(\int \prod_{i=1}^{N} d^3p_i \, e^{-p_i^2/2mk_BT} \right) \left(\int \prod_{i=1}^{N} d^3r_i \; e^{-\beta \sum_{k<j} U(r_{jk})} \right)$$

$$= \frac{1}{N!\,\lambda^{3N}} \int \prod_i d^3r_i \; e^{-\beta \sum_{j<k} U(r_{jk})} \qquad \boxed{\lambda = \sqrt{\frac{2\pi\hbar^2}{mk_BT}}}$$

Define Meyer f function

$$f(r) = e^{-\beta U(r)} - 1$$

$$\Rightarrow f(r) = -1 \quad \text{for } r < r_0$$

$$f(r) \longrightarrow 0 \quad \text{as } r \to \infty$$

Define $f_{ij} = f(r_{ij})$

$$\Rightarrow Z = \frac{1}{N!\,\lambda^{3N}} \int \prod_i d^3r_i \prod_{j>k} (1 + f_{jk})$$

$$= \frac{1}{N!\,\lambda^{3N}} \int \prod_i d^3r_i \left(1 + \sum_{j>k} f_{jk} + \sum_{\substack{j>k \\ l>m}} f_{jk} f_{lm} + \cdots \right)$$

- first term $\int \prod_i d^3r_i = V^N$
- each of the terms with one f is the same, e.g.

$$\int \prod_{i=1}^{N} d^3r_i \, f_{12} = V^{N-2} \int d^3r_1\, d^3r_2 \, f_{12} \qquad \text{change to } (\underline{r}_1, \underline{r}_2) \mapsto (\underline{r}_1, \underline{r}_2 - \underline{r}_1)$$

$$= V^{N-1} \int d^3r \, f(r)$$

A term like this for each pair ⇒ $\frac{1}{2}N(N-1) \approx \frac{1}{2}N^2$ terms

$$Z(N,V,T) \approx \frac{V^N}{N!\,\lambda^{3N}}\left(1 + \frac{1}{2}\frac{N^2}{V}\int d^3r\, f(r)\right)$$

$$= Z_{ideal}\left(1 + \frac{N}{2V}\int d^3r\, f(r)\right)^N$$

$$F = -k_B T \ln Z$$

$$= F_{ideal} - k_B T N \ln\left(1 + \frac{N}{2V}\int d^3r\, f(r)\right)$$

Expanding $\ln(1+x) \approx x$

$$\Rightarrow p = -\frac{\partial F}{\partial V} = \frac{N k_B T}{V}\left(1 - \frac{N}{2V}\int d^3r\, f(r) + \cdots\right)$$

$$\Rightarrow \frac{pV}{N k_B T} = 1 - \underbrace{\frac{N}{2V}\int d^3r\, f(r)}_{\text{second virial 'coefficient'}} + \cdots$$

<u>Examples</u> · repulsion: $U(r) > 0 \;\forall r$

$\Rightarrow f(r) = e^{-\beta U(r)} - 1 < 0$

$\Rightarrow$ pressure increases ✓

· attraction: $U(r) < 0 \;\forall r$

$\Rightarrow f(r) = e^{-\beta U(r)} - 1 > 0$

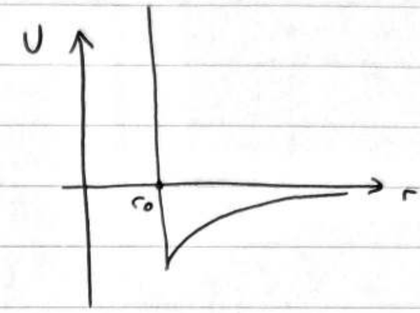
$\Rightarrow$ pressure decreases ✓

Last time: interacting gas

$$\frac{pV}{Nk_BT} = 1 - \frac{N}{2V}\int d^3r\, f(r) + \cdots$$

$$f(r) = e^{-\beta U(r)} - 1$$

$$U(r) = \begin{cases} \infty & \text{for } r<r_0 , \\ -U_0\left(\frac{r_0}{r}\right)^6 & \text{for } r>r_0 . \end{cases}$$



$$\therefore \int d^3r\, f(r) = \int_0^{r_0} d^3r\,(-1)$$

$$+ \int_{r_0}^{\infty} d^3r \left(\exp\left[\beta U_0\left(\frac{r_0}{r}\right)^6\right] - 1\right)$$

At high temperatures, $\beta U_0 \ll 1$

$$\exp\left[\beta U_0\left(\tfrac{r_0}{r}\right)^6\right] \approx 1 + \beta U_0\left(\tfrac{r_0}{r}\right)^6$$

$$\therefore \int d^3r\, f(r) \approx -4\pi\int_0^{r_0} r^2 dr + 4\pi\int_{r_0}^{\infty} \frac{U_0}{K_BT} r_0^6\, r^{-4}\, dr$$

$$= \frac{4\pi r_0^3}{3}\left(-1 + \frac{U_0}{K_BT}\right)$$

$$\therefore \frac{pV}{NK_BT} = 1 - \frac{N}{V}\left(\frac{a}{K_BT} - b\right)$$ where $a = \frac{2\pi r_0^3 U_0}{3}$, $b = \frac{2\pi r_0^3}{3}$

We can rewrite this as

$$K_BT = \frac{V}{N}\left(p + \frac{N^2}{V^2}a\right)\left(1 + \frac{Nb}{V}\right)^{-1}$$

$$\approx \frac{V}{N}\left(p + \frac{N^2}{V^2}a\right)\left(1 - \frac{Nb}{V}\right)$$

$$\boxed{k_BT \approx \left(p + \frac{N^2}{V^2}a\right)\left(\frac{V}{N} - b\right)}$$

This is the van der Waals equation of state

Can also write as

$$p = \underbrace{\frac{NK_BT}{V - bN}}_{\text{reduced volume due to hard atoms}} - \frac{aN^2}{V^2} \leftarrow \text{reduced pressure due to attractive forces between atoms}$$

Note : 

$\left[b = \frac{2\pi r_0^3}{3} \right]$

Volume of atom $= \frac{4\pi}{3}\left(\frac{r_0}{2}\right)^3 \neq b$

But excluded volume around each atom $= \Omega = \frac{4\pi}{3} r_0^3 = 2b$

Why?

Total cfg space

$$= \frac{1}{N!} V(V-\Omega)(V-2\Omega)\cdots(V-N\Omega)$$

$$= \frac{1}{N!} V^{N+1}\left(1 - \frac{N^2}{2}\frac{\Omega}{V} + \cdots\right)$$

$$\approx \frac{1}{N!} V\left(V - \frac{N\Omega}{2}\right)^N$$

3 - Quantum Gases

3.1 - Density of States

Consider a gas in a box with sides of Length L

$\Rightarrow V = L^3$ (volume)

Impose periodic boundary conditions.

Non-interacting particles

$\therefore$ Energy eigenstates $\phi = \frac{1}{\sqrt{V}} e^{i\underline{k}\cdot\underline{x}}$ where $k_i = \frac{2\pi}{L} n_i$, $n_i \in \mathbb{N}^T$

Non-relativistic particles

$$E_{\underline{n}} = \frac{\hbar^2 k^2}{2m} = \frac{4\pi^2\hbar^2 k^2}{2mL^2}\underline{n}^2$$

A single particle partition function is

$$Z_1 = \sum_{\underline{n}} e^{-\beta E_{\underline{n}}}$$

Exponent $+\beta E_{\underline{n}} = \pi\lambda^2 \underline{n}^2 / L^2$ (recall $\lambda = \sqrt{\frac{2\pi\hbar^2}{m k_B T}}$)

$\lambda \ll L$, finely spaced energy levels

$\therefore$ approximate sum as integral

$$\sum_{\underline{n}} \cancel{e^{-\beta E_{\underline{n}}}} \approx \int d^3\underline{n} = \frac{V}{(2\pi)^3}\int d^3k = \frac{4\pi V}{(2\pi)^3}\int_0^\infty dk\, k^2$$

Change variables to energy

$$E = \frac{\hbar^2 k^2}{2m} \Rightarrow dE = \frac{\hbar^2 k}{m} dk \boxed{= \frac{(2\hbar)^{1/2}}{m^{1/2}} E^{1/2} dk}$$

$$\therefore \int d^3 n = \frac{V}{2\pi^2} \int_0^\infty \frac{m}{\hbar^2} \sqrt{\frac{2mE}{\hbar^2}}\, dE$$

$$= \int_0^\infty g(E)\, dE$$

where $g(E) = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$

is the density of states.

This is the no. of states with energy between E and $E + \Delta E$, when doing $g(E)\Delta E$.

Relativistic systems

In all systems, $\underline{k}$ is quantised in the same way. But $g(E)$ depends on the relation betweeen E and k. (dispersion relation)

For relativistic systems,

$$E = \sqrt{\hbar^2 k^2 c^2 + m^2 c^4}$$

Repeat the same steps as before

$$\therefore g(E) = \frac{VE}{2\pi^2 \hbar^3 c^3} \sqrt{E^2 - m^2 c^4}$$

For massless particles,

$$g(E) = \frac{V}{2\pi^2 \hbar^3 c^3} E^2$$

3.2 Photons

A gas of photons at fixed temperature T is called "black-body radiation". This is the light emitted by an object if we ignore its atomic emission, absorption lines, ... i.e. the light emitted by a black object.

- Photons are massless and have energy $\hbar\omega$, where ω is the frequency. $\lambda = 2\pi c/\omega$ is the wavelength.
- They have two polarisation states

$\Rightarrow$ no. of states of a single photon with energy E to $E+dE$ is

$$g(E)\,dE = \underset{\substack{\uparrow \\ \text{polaris}^{\text{n}}\text{s}}}{2} \cdot \underset{\substack{\uparrow \\ \text{density of states for massless particles}}}{\frac{VE^2}{2\pi^2\hbar^3c^3}}\,dE$$

No. of states with frequency between ω and $\omega+d\omega$ is

$$g(E)\,dE = g(\omega)\,d\omega = \frac{V\omega^2}{\pi^2 c^3}\,d\omega$$

- Photons are <u>not</u> conserved

$\therefore$ no. of photons is not fixed

and photon states with any no. of photons are accessible

$\Rightarrow$ We have to sum over all photon no.s in the partition f$^{\text{n}}$

To begin with, consider photons with fixed frequency ω.

A state with N photons has energy $E = N\hbar\omega$

$$Z_\omega = \sum_{N=0}^{\infty} e^{-N\beta\hbar\omega} = \frac{1}{1-e^{-\beta\hbar\omega}}$$

Including all frequencies:

$$\ln Z = \int_0^\infty d\omega\, g(\omega)\, \ln Z_\omega$$

$$\ln Z = -\frac{V}{\pi^2 c^3}\int_0^\infty d\omega\ \omega^2 \ln\left(1-e^{-\beta\hbar\omega}\right)$$

Total energy stored in gas of photons:

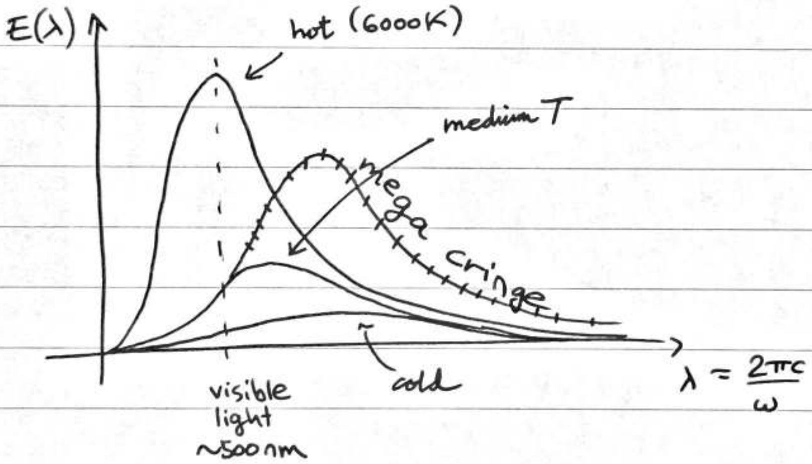
$$E = -\frac{\partial}{\partial\beta}\ln Z$$

$$= \frac{V\hbar}{\pi^2 c^3}\int_0^\infty d\omega \frac{\omega^3}{e^{\beta\hbar\omega}-1}$$

This is the energy of photons with frequencey between ω and $\omega + d\omega$:

$$E(\omega)\,d\omega = \frac{V\hbar}{\pi^2 c^3}\frac{\omega^3}{e^{\beta\hbar\omega}-1}\,d\omega$$

This is the <u>Planck distribution</u>



Maximum at $dE/d\omega = 0$

$$\omega_{max} = \zeta\frac{k_B T}{\hbar} \qquad \underline{\text{Wien's Law}}$$

where $3 - \zeta = 3e^{-\zeta}$, $\zeta \approx 2.822$

This tells you the 'colour' of a hot object.

Total energy:

$$E = \int_0^\infty E(\omega)\,d\omega \qquad [x = \beta\hbar\omega]$$

$$= \frac{V}{\pi^2 c^3}\frac{(k_B T)^4}{\hbar^3}\underbrace{\int_0^\infty x^3/e^x-1 \ dx}_{\text{tricky integral}} = \pi^4/15$$

∴ Energy density

$$\mathcal{E} = \frac{E}{V} = \frac{\pi^2 k_B^4 T^4}{15 \hbar^3 c^3}$$

The is closely related to the Stefan-Boltzmann Law:

$$\text{Energy flux} = \frac{\mathcal{E} c}{4} = \sigma T^4 \qquad \sigma = \frac{\pi^2 k_B^4}{60 \hbar^3 c^2}$$

rate of transfer of energy per unit area

geometric factor

$$\frac{1}{4\pi} \int_0^{2\pi} d\phi \int_0^{\pi/2} d\theta \sin\theta \cdot c\cos\theta = \frac{c}{4}$$

Compute other quantities from

$$F = -k_B T \ln Z = \frac{V k_B T}{\pi^2 c^3} \int_0^\infty d\omega \; \omega^2 \ln\left(1 - e^{-\beta\hbar\omega}\right)$$

$$= -\frac{V \cancel{k_B} \hbar}{3\pi^2 c^3} \int_0^\infty d\omega \; \omega^3 \frac{e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \qquad \text{(by parts}$$

$$= -\frac{V\hbar}{3\pi^2 c^3} \frac{1}{\beta^4 \hbar^4} \underbrace{\int_0^\infty dx \; \frac{x^3}{e^x - 1}}_{= \pi^4/15} \qquad [x = \beta\hbar\omega]$$

$$= -\frac{V\pi^2}{45 \hbar^3 c^3} k_B^4 T^4$$

$$= -\mathcal{E} V/3 = -4\sigma V T^4/3c$$

Radiation pressure is

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{\mathcal{E}}{3} = \frac{E}{3V} = \frac{4\sigma}{3c} T^4$$

Entropy

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{16\sigma V}{3c} T^3$$

Heat capacity

$$c_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{16V\sigma}{c} T^3$$

Most accurate example of blackbody radiation known is cosmic microwave background, at $T \approx 2.7\,K$

Rayleigh - Jeans Law

Compare Planck dist^n with the classical result where there is no minimum energy for a given frequency.

This is effectively $\hbar\omega \ll k_B T$

$$\Rightarrow \frac{1}{e^{\beta\hbar\omega}-1} \approx \frac{1}{\beta\hbar\omega}$$

Planck dist^n becomes

$$E(\omega) = \frac{V\omega^2 k_B T}{\pi^2 c^3}$$

This is the Rayleigh - Jeans law.

If you try to extrapolate to large ω:

$$E = \int E(\omega)\, d\omega \quad \text{diverges}$$

The « ultraviolet catastrophe »

This is another breakdown of classical physics (like heat capacity of diatomic ideal gas).

3.3 – The Debye model of phonons

The vibrations of a crystal (i.e. sound waves) also come in discrete lumps of energy due to quantum mechanics. These are called phonons.

Energy of a phonon is

$$E = \hbar\omega = \hbar|\underline{k}|\,\underset{\nwarrow\ \text{speed of sound}}{c_s}$$

Note : $E = \hbar\omega$ is correct, but $\omega = |\underline{k}|c_s$ is an approximation valid for small $|\underline{k}|$

Actually $\omega \sim \left|\sin\left(\frac{|\underline{k}|a}{2}\right)\right|$

where a is the lattice spacing.

Phonons have 3 polarizations
(2 transverse + 1 longitudinal)

Density of states is

$$g(\omega) = \underset{\nearrow\ 3\ \text{pol}^{\text{n}}\text{s}}{3} \cdot \frac{V}{2\pi^2 c_s^3}\,\omega^2$$

N.B. phonons cannot have arbitrarily high frequency ω.
Minimum wavelength set by atomic spacing (nothing to vibrate on smaller distances)

High $\omega \Rightarrow$ small wavelength $\lambda = \frac{2\pi c_s}{\omega}$

$\Rightarrow$ maximum frequency ω_d (Debye frequency)

Argument to determine ω_d:

Consider no. of single-phonon states.

$$\int_0^{\omega_d} d\omega\, g(\omega) = \frac{V\omega_D^3}{2\pi^2 c_3^3}$$

Identity with the no. of degrees of freedom = 3N

$$3N = \frac{V\omega_D^3}{2\pi^2 c_s^3}$$

$$\Rightarrow \omega_D = \left(\frac{6\pi^2 N}{V} \right)^{1/3} c_s$$

$$\Rightarrow \text{Debye temperature } T_D = \frac{\hbar\omega_D}{k_B}$$

By the time you (me?) reach T_D, you can excite phonons of all allowed frequencies.

$T_D \sim 100\,\text{K}$ for lead

$T_D \sim 2000\,\text{K}$ for diamod

Heat capacity

Like photons, phonons are not conserved. For a single frequency,

$$Z_\omega = 1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + \cdots = \frac{1}{1 - e^{-\beta\hbar\omega}}$$

(just like for photons)

$$\ln Z_{\text{phonon}} = \int_0^{\omega_D} d\omega\, g(\omega)\, \ln Z_\omega$$

Total energy in vibrations (sound waves) is

$$\langle E \rangle = -\frac{\partial}{\partial\beta} \ln Z_{\text{phonon}} = \int_0^{\omega_D} d\omega\, \frac{g(\omega)\hbar\omega}{e^{\beta\hbar\omega} \underset{-}{\cancel{+}} 1}$$

$$\langle E \rangle = \frac{3V\hbar}{2\pi^2 c_s^3} \int_0^{\omega_D} d\omega\, \frac{\omega^3}{e^{\beta\hbar\omega} - 1}.$$

Subst $x = \beta\hbar\omega$, upper limit $x_D = T_D/T$

$$\langle E \rangle = \frac{3V}{2\pi^2 c_s^3 \hbar^3} (k_B T)^4 \int_0^{T_D/T} dx\, \frac{x^3}{e^x - 1}$$

Same integral as for photons, but upper limit is not ∞.

Two limits :

$T \gg T_D$ Taylor expand :

$$\int_0^{T_D/T} dx \frac{x^3}{e^x - 1} \simeq \int_0^{T_D/T} dx \left(x^2 + \cdots\right)$$

$$= \frac{1}{3}\left(\frac{T_D}{T}\right)^3$$

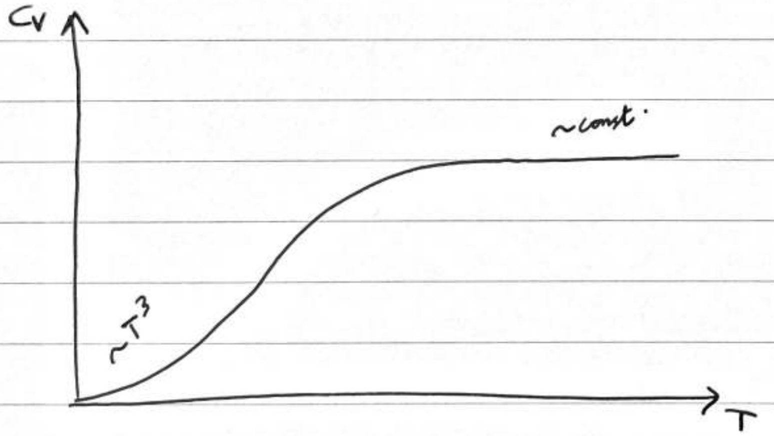
$$c_V = \frac{\partial E}{\partial T} = \frac{V k_B^4 T_D^3}{2\pi^2 \hbar^3 c_s^3} = 3N k_B$$

Dulong - Petit Law

$T \ll T_D$ Use

$$\int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{15}$$

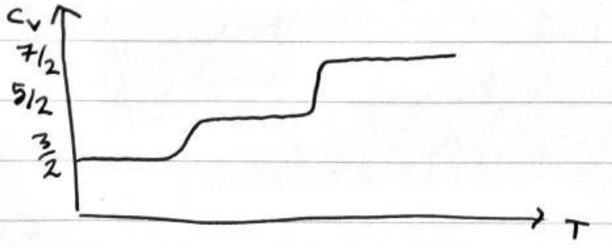
$$\therefore c_V = \frac{2\pi^2 V k_B^4 T^3}{5\hbar^3 c_s^3} = N k_B \frac{12\pi^4}{5}\left(\frac{T}{T_D}\right)^3$$



This agrees with experimetal data, unlike the Einstein model.

3.4 Diatomic gas revisited

Recall the disagreement between classical physics prediction $c_V = \frac{7}{2} N k_B$, and experiment.



This freezing out is a quantum effect.

Rotation

Energy levels: $E = \frac{\hbar^2}{2I} J(J+1)$, $J = 0, 1, 2, 3, \ldots$

degeneracy $= 2J+1$

$$Z_{rot} = \sum_{J=0}^{\infty} (2J+1)\, e^{-\beta \hbar^2 J(J+1)/2I}$$

$T \gg \frac{\hbar^2}{2Ik_B}$ ⇒ approximate by integral

$$Z_{rot} = \int_0^{\infty} dx\, (2x+1)\, e^{-\beta\hbar^2 x(x+1)/2I}$$

$$= \frac{2I}{\beta\hbar^2}$$

This agrees with classical result

$T \ll \frac{\hbar^2}{2Ik_B}$ ⇒ all states except $J=0$ are unimportant

$\Rightarrow Z_{rot} \approx 1$

Vibration

$E = \hbar\omega\left(n+\frac{1}{2}\right)$, $n = 0, 1, \ldots$

$$Z_{vib} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+\frac{1}{2})}$$

$$= e^{-\beta\hbar\omega/2} \cdot \frac{1}{1-e^{-\beta\hbar\omega}}$$

High Temp: $\beta\hbar\omega \ll 1 \Rightarrow Z_{vib} \approx \frac{1}{\beta\hbar\omega}$

in agreement with classical result

Low Temp: $\beta\hbar\omega \gg 1 \Rightarrow Z_{vib} \approx 1 \approx e^{-\beta\hbar\omega/2}$

$E_{vib} \approx \hbar\omega/2$

$c_{vib} \approx 0$

Quantum mechanics ⇒ modes frozen at low T

3.5 Bosons

Classical treatment of an ideal gas is valid if

$$\underbrace{\lambda = \sqrt{\frac{2\pi\hbar^2}{mk_BT}}}_{\text{thermal de Broglie wavelength}} \ll \underbrace{\left(\frac{V}{N}\right)^{1/3}}_{\text{interparticle separation}}$$

For low temperatures, quantum effects become more important (when $\lambda \sim \left(\frac{V}{N}\right)^{1/3}$)

If there are no interactions, we only need to consider quantum statistics.

Recall: quantum particles are indistinguishable and there are two types: ① Bosons: Integer spin particles. Wavefunction symmetric under the interchange of identical bosons.

$$\psi(\underline{r}_1, \underline{r}_2) = \psi(\underline{r}_2, \underline{r}_1)$$

② Fermions: Half-integer spin particles. Anti-symmetric under interchange of two particles

$$\psi(\underline{r}_1, \underline{r}_2) = -\psi(\underline{r}_2, \underline{r}_1)$$

Fermions obey the Pauli exclusion principle: two fermions cannot occupy the same state.

Electrons, quarks and neutrinos are fermions.

Photons, gluons, W, Z, Higgs are bosons.

Protons and neutrons contain 3 quarks => fermions.

An atom with N fermions is effectively a:

- Boson if N is even
- Fermion if N is odd

Bose-Einstein Distribution

Label single-particle energy states $|r\rangle$ with energy E_r.
No. of particles in state $|r\rangle$ is n_r.

In canonical ensemble:

$$Z = \sum_{\{n_r\}} e^{-\beta n_r E_r}$$

$\nwarrow$ set specifies the state
sum over all sets $\{n_r\}$
s.t. $\sum n_r = N$

- Constraint makes this an awkward problem.
- Easier to work in grand canonical ensemble, where N can fluctuate and we don't have to impose this constraint.

Since there is no constraint, the occupation no. n_r of each state is independent

For state $|r\rangle$, the grand partition f^n is

$$\mathcal{Z}_r = \sum_{n_r} e^{-\beta n_r (E_r - \mu)} = \frac{1}{1 - e^{-\beta (E_r - \mu)}}$$

For convergence of the sum, $(E_r - \mu) > 0$ $\forall$ states $|r\rangle$

Picking $E_0 = 0$ as ground state,

$$\Rightarrow \boxed{\mu < 0}$$

Because states are independent, the full grand partition f^n is

$$\mathcal{Z} = \prod_{r=0}^{\infty} \frac{1}{1 - e^{-\beta (E_r - \mu)}}.$$

Average no. of particles

$$N = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \mathcal{Z}$$

$$= \sum_r \frac{1}{e^{\beta (E_r - \mu)} - 1} \equiv \sum_r \langle n_r \rangle$$

with $\langle n_r \rangle$ the average number of particles in state $|r\rangle$

This is the Bose-Einstein distribution,

$$\langle n_r \rangle = \frac{1}{e^{\beta (E_r - \mu)} - 1}.$$

We'll write n_r for $\langle n_r \rangle$.

We've already seen this expression for photons and phonons with $\mu = 0$; it arises because we sum over all particle numbers.

Def <u>fugacity</u> $z = e^{\beta\mu}$

$0 < z < 1$ since $\mu < 0$

Ideal Bose Gas

Non-relativistic particles : $E = \frac{\hbar^2 k^2}{2m}$

Density of states :

$$g(E) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E^{1/2}$$

Total no. of particles :

$$N(\mu, T, V) = \int dE \, \frac{g(E)}{z^{-1} e^{\beta E} - 1}$$

Energy :

$$E(\mu, T, V) = \int dE \, \frac{E\, g(E)}{z^{-1} e^{\beta E} - 1}$$

Pressure :

$$pV = \frac{1}{\beta} \ln \mathcal{Z}$$

$$= -\frac{1}{\beta} \int gE \, dE \, \ln(1 - z e^{-\beta E})$$

Integrate by parts and use $g(E) \sim E^{1/2}$

$$pV = \frac{2}{3} \int dE \, \frac{E\, g(E)}{\cancel{z} \, z^{-1} e^{\beta E} - 1} = \frac{2}{3} E$$

<u>Recall</u> Bose-Einstein dist^{n}

$$\langle n_r \rangle = \frac{1}{e^{\beta(E_r-\mu)}-1}$$

Ideal Bose gas $\frac{N}{V} = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int dE\, \frac{E^{1/2}}{z^{-1}e^{\beta E}-1}$

$$pV = \frac{2}{3}E \qquad (z = e^{\beta\mu})$$

<u>High temperature expansion</u>

Try to expand in limit $z = e^{\beta\mu} \ll 1$

$$\frac{N}{V} = (\text{qqch})\int dE\, \frac{z e^{-\beta E} E^{1/2}}{1 - z e^{-\beta E}}$$

$$= \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} z/\beta^{3/2} \int_0^\infty dx\, \sqrt{x}\, e^{-x}\left(1 + z e^{-x} + \cdots\right)$$

⌜subst $x = \beta E$⌟

Subst $x = u^2 \Rightarrow$ Gaussian integrals (do them yourself)

$$\frac{N}{V} = \frac{z}{\lambda^3}\left(1 + z\frac{1}{2\sqrt{2}} + \cdots\right) \qquad (*)$$

Since $z \ll 1$, expansion is only consistent if $\lambda^3 N/V \ll 1$

$\Rightarrow \lambda^3 \ll V/N$ i.e. classical limit / high temp expansion

Note: $T \to \infty \Rightarrow \beta \to 0$

$\therefore$ might naively expect $z = e^{\beta\mu} \to 1$

But at fixed N, μ depends on T

$\Rightarrow z \sim T^{-3/2}$ as $T \to \infty$

To get the equation of state, compute E:

$$\frac{E}{V} = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^\infty dE\, \frac{E^{3/2}}{z^{-1}e^{\beta E}-1}$$

$$= (\cdots)\frac{z}{\beta^{5/2}}\int_0^\infty dx\, x^{3/2} e^{-x}\left(1 + z e^{-x} + \cdots\right)$$

ℰ> $\frac{E}{V} = \frac{3z}{2\lambda^3\beta}\left(1 + \frac{z}{4\sqrt{2}} + \cdots\right)$

Want this as a function of N, so invert $\frac{N}{V} = \cdots$ to get

$$z = \lambda^3\frac{N}{V}\left(1 - \frac{1}{2\sqrt{2}}\frac{\lambda^3 N}{V} + \cdots\right)$$

$$\Rightarrow E = \frac{3}{2}\frac{N}{\beta}\left(1 - \frac{1}{2\sqrt{2}}\frac{\lambda^3 N}{V} + \cdots\right)\left(1 + \frac{\lambda^3 N}{4\sqrt{2}\,V} + \cdots\right)$$

Know $pV = \frac{2}{3}E$

$$\Rightarrow E \cdot \frac{2}{3} = pV = Nk_BT\Big(\underset{\substack{\uparrow \\ \text{Classical} \\ \text{ideal gas}}}{1} - \underset{\substack{\uparrow \\ \text{2nd virial} \\ \text{coefficient} \\ \text{from quantum} \\ \text{statistics}}}{\frac{1}{4\sqrt{2}}\frac{\lambda^3 N}{V}} + \cdots\Big)$$

High temperature quantum gas
= Classical gas

Bose-Einstein Condensation

What about the low temperature limit of an ideal Bose gas?

Recall $\mu \in (-\infty, 0)$ and $z = e^{\beta\mu}$

High temp. is $z \to 0$

Expect low temp. to be $z \to 1$

Recall
$$\frac{N}{V} = \frac{1}{4\pi^2}\left(\frac{2mk_BT}{\hbar^2}\right)^{3/2}\int dx\, \frac{x^{1/2}}{z^{-1}e^{x} - 1} \qquad (+)$$

$$\equiv \frac{1}{\lambda^3}\, g_{3/2}(z)$$

where
$$g_n(z) = \frac{1}{\Gamma(n)}\int_0^\infty dx\, \frac{x^{n-1}}{z^{-1}e^{x} - 1}$$

$$\lambda = \sqrt{\frac{2\pi\hbar^2}{mk_BT}} \quad \text{and} \quad \Gamma\left(\tfrac{3}{2}\right) = \frac{\sqrt{\pi}}{2}$$

Recall: As $T \to \infty$, $\lambda \sim \frac{1}{\sqrt{T}} \to 0$
But $z \to 0$ and $g_{3/2}(z) \to 0$
to keep $\frac{N}{V}$ fixed.

What about $T \to 0$?

We need to understand $g_n(z)$.

$$g_n(z) = \frac{1}{\Gamma(n)} \int_0^\infty dx \; \frac{z x^{n-1} e^{-x}}{1 - z e^{-x}}$$

$$= \frac{z}{\Gamma(n)} \int_0^\infty dx \; x^{n-1} e^{-x} \sum_{m=0}^{\infty} z^m e^{-mx}$$

$$= \frac{1}{\Gamma(n)} \sum_{m=1}^{\infty} z^m \int_0^\infty dx \; x^{n-1} e^{-mx}$$

subst $u = mx$

$$= \frac{1}{\Gamma(n)} \sum_{m=1}^{\infty} z^m \underbrace{\int_0^\infty \frac{du}{m^n} u^{n-1} e^{-u}}_{\frac{1}{m^n}\Gamma(n)}$$

$$\therefore \; g_n(z) = \sum_{m=1}^{\infty} \frac{z^m}{m^n}$$

$\therefore$ at $z=1$, $g_n(z) = \zeta(n)$ ↖ Riemann zeta function

and $\zeta(\frac{3}{2}) \approx 2.612$

So as T decreases, $z \to 1$ and $g_{3/2}(z)$ increases so $\frac{N}{V}$ fixed

But at some temperature T_c, $z = 1$

$$\Rightarrow \frac{N}{V} = \left(\frac{m k_B T}{2\pi\hbar^2} \right)^{3/2} \zeta\left(\frac{3}{2}\right)$$

$$\Rightarrow T_c = \frac{2\pi\hbar^2}{m k_B} \left(\frac{N}{V} \frac{1}{\zeta(\frac{3}{2})} \right)^{2/3}$$

If we lower $T < T_c$, then at face value ~~(*)~~ (+) tells us that $\frac{N}{V}$ goes down. But that seems non-sensical!

Actually, we missed something when we replaced the sum over states with an integral against $g(E)dE$.

$$\sum_{\underline{k}} \approx \frac{V (2m)^{3/2}}{4\pi^2\hbar^3} \int dE \; E^{1/2}$$

Because of $\sqrt{E}$ there is no density of states for $E=0$

$\Rightarrow$ the ground state is missing.

How many particles in the ground state ?

From Bose-Einstein distb, when $E_0 = 0$,

$$n_0 = \frac{1}{z^{-1} - 1}$$

XD ↙

For most values of $z \in (0,1)$, n_0 is of order a few, so ignoring it doesn't matter.

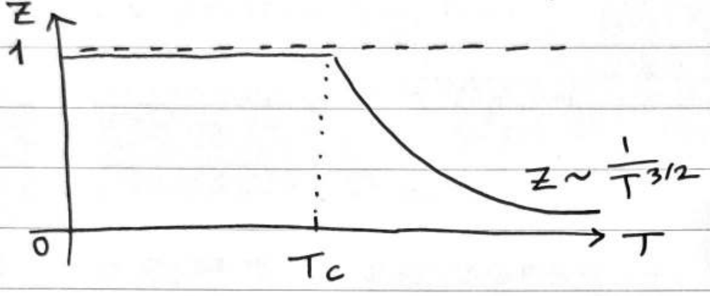
But when $z \approx 1 - \frac{1}{N}$ we get a large fraction in the ground state. This is what we missed.

We can redo the calculation:

$$N = \frac{V}{\lambda^3} g_{3/2}(z) + \frac{z}{1-z}$$

Now no problem keeping N fixed as $T \to 0$

For finite N we can never get to $z=1$ and instead z must level out at $z \approx 1 - \frac{1}{N}$



The fraction of particles in the ground state for $T < T_c$ is

$$\frac{n_0}{N} \approx 1 - \frac{V}{N\lambda^3}\zeta\left(\frac{3}{2}\right) = 1 - \left(\frac{T}{T_c}\right)^{3/2}$$

We have a macroscopic no. of particles in a single quantum state.

This is the <u>Bose-Einstein</u> <u>condensate</u> (BEC).

Equation of state:

$$p = \frac{2}{3}\frac{E}{V} = \frac{k_B T}{\lambda^3} g_{5/2}(z)$$

For $T < T_c$, $z \approx 1$ and

$$p \approx \frac{k_B T}{\lambda^3}\zeta(5/2) \quad , \quad p \sim T^{5/2} \ \left(\text{indep of } \frac{N}{V}\right)$$

<u>The phase transition</u>

A <u>phase transition</u> is a discontinuity in a physical observable. The formation of a BEC is an example.

To see this, look at the heat capacity.

$$\frac{E}{V} = \frac{3}{2} k_B T/\lambda^3 \cdot g_{5/2}(z)$$

$$\Rightarrow \frac{C_V}{V} = \frac{1}{V}\frac{dE}{dT} = \underset{\substack{\uparrow \\ \text{contributes} \\ \text{for all } T}}{\frac{15}{4}\frac{k_B}{\lambda^3} g_{5/2}(z)} + \frac{3}{2}\frac{k_B T}{\lambda^3} \underset{\substack{\uparrow \\ \text{only important} \\ \text{for } T > T_c}}{\frac{dg_{5/2}(z)}{dz}} \frac{dz}{dT}$$

For $T < T_c$:

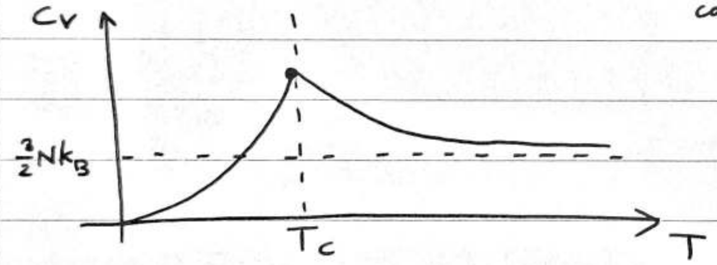
$$\frac{c_V}{V} \approx \frac{15}{4}\frac{k_B}{\lambda^3}\zeta\left(\tfrac{5}{2}\right) \sim T^{3/2}$$

Note: $g_{5/2}(z) < g_{5/2}(1)$
and $\frac{dz}{dT} < 0$

$\Rightarrow$ c_V decreases as $T > T_c$
$\Rightarrow$ c_V has a max at $T = T_c$

A long-ish calculation gives, for $T > T_c$:

$$c_V = \frac{15 k_B V}{4\lambda^3} g_{5/2}(z) - \underset{\substack{\uparrow \\ \text{const.}}}{b}\left(\frac{T-T_c}{T_c}\right)$$

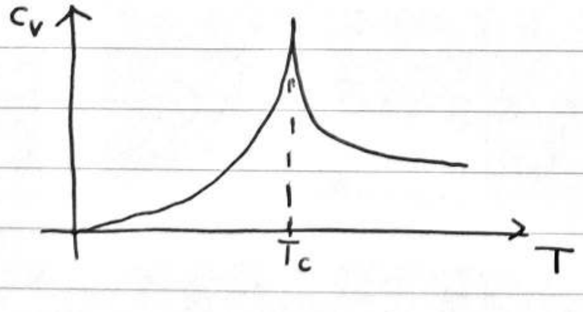


Note: discontinuity in derivative of c_V is because

$$\frac{dz}{dT} \sim \begin{cases} -b(T-T_c), & T > T_c \\ O\left(\frac{1}{N}\right), & T < T_c \end{cases}$$

Discontinuous only in $N \to \infty$ limit.

E.g. superfluid Helium 4
- a Bose condensation of strongly interacting atoms



3.6 Fermions

Pauli exclusion principle says two fermions cannot occupy the same state.

Work in grand canonical ensemble.

The grand partition f^n for state $|r\rangle$ is:

$$\mathcal{Z}_r = \sum_{n=0,1} e^{-\beta n(E_r-\mu)}$$
$$= 1 + e^{-\beta(E_r-\mu)}$$

No restriction on μ; it can be positive or negative

$$\mathcal{Z} = \prod_r \mathcal{Z}_r$$

$$\langle N\rangle = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln\mathcal{Z}$$
$$= \sum_r \frac{1}{e^{\beta(E_r-\mu)}+1}$$
$$= \sum_r \langle n_r\rangle$$

We'll write $n_r = \langle n_r\rangle$ = avg no. of particles in state $|r\rangle$

$$n_r = \frac{1}{e^{\beta(E_r-\mu)}+1}$$

This is the Fermi-Dirac distribution.

Recall: Fermi-Dirac distribution

$$n_r = \frac{1}{e^{\beta(E_r - \mu)} + 1}$$

Ideal Fermi gas

Non-relativistic: $E = \hbar^2 k^2 / 2m$

Fermions have $\frac{1}{2}$ integer spin s

$\Rightarrow$ degeneracy is $g_s = 2s+1$

$\therefore$ density of states is

$$g(E) = \frac{g_s V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} E^{1/2}$$

$$N = \int dE \, \frac{g(E)}{z^{-1} e^{\beta E} + 1} \qquad (z = e^{\beta\mu} \text{ fugacity})$$

$$E = \int dE \, \frac{E \, g(E)}{z^{-1} e^{\beta E} + 1}$$

$pV = k_B T \ln \mathcal{Z}$

$pV = \frac{2}{3} E$ (integrating by parts, like with bosons)

High Temperature

Expand for $z \ll 1$ (examples sheet 3)

$$\Rightarrow \quad pV = N k_B T \Big(\underset{\substack{\nearrow \\ \text{classical} \\ \text{ideal gas}}}{1} + \underset{\substack{\uparrow \\ \text{correction has} \\ \text{opposite sign c.f.} \\ \text{bosons (increases} \\ \text{pressure)}}}{\frac{\lambda^3 N}{4\sqrt{2}\, g_s V}} + \dots \Big)$$

Zero Temperature

At $T=0$, the Fermi-Dirac distribution is very simple:

$$\frac{1}{e^{\beta(E-\mu)} + 1} \rightarrow \begin{cases} 1 & \text{for } E < \mu, \\ 0 & \text{for } E > \mu, \end{cases}$$

"degenerate Fermi gas"

Define the Fermi energy

$$E_F = \mu(T=0)$$

for fixed N.

At $T=0$,

$$N = V\int_0^{E_F} g(E)\,dE$$

$$= \frac{g_s V}{6\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E_F^{3/2}$$

$$\Rightarrow \quad E_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2 N}{g_s V}\right)^{2/3}$$

This is characteristic energy scale of the problem.
Associated temperature scale is $T_F = \frac{E_F}{K_B}$.

$T_F \sim 10^4\,K$ for electrons in metal

$T_F \sim 10^7\,K$ for white dwarf

(Note: high temperature means $T \gg T_F$)
Define Fermi momentum k_F:

$$\hbar k_F = (2mE_F)^{1/2}$$

All states with momentum $|\underline{k}| < k_F$ are fielled and form the Fermi sea.

Those states with $|\underline{k}| = k_F$ form the Fermi surface.
At $T=0$ the equation of state is

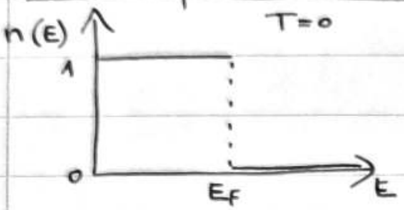
$$pV = \frac{2}{3}E = \frac{2}{3}\int_0^{E_F} E\,g(E)\,dE$$

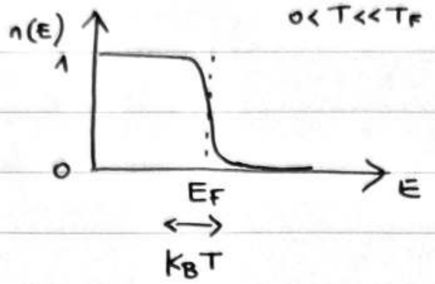
$$= \frac{2}{5}NE_F$$

$\Rightarrow p \neq 0$ at $T=0$

This is "degeneracy" pressure.
It is important for supporting white dwarfs and neutron stars.

Low temperature Fermi gas $(T \ll T_F)$





At low temperatures

$$\frac{\mu}{k_B T} \approx \frac{E_F}{k_B T} \gg 1$$

$$\Rightarrow z \gg 1$$

$$\frac{N}{V} = \frac{g_s}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty dE \, \frac{E^{1/2}}{z^{-1}e^{\beta E}+1}$$

$$\frac{E}{V} = \quad '' \quad \int_0^\infty dE \, \frac{E^{3/2}}{z^{-1}e^{\beta E}+1}$$

We want to expand E at low T keeping N fixed. Rigorous way is tricky (Sommerfeld Expansion). We'll sketch out the result.

Claim $\quad \frac{dN}{dT} = 0$ at $T=0$ if $\frac{d\mu}{dT} = 0$ at $T=0$

Pf $\quad \frac{dN}{dT} = \frac{d}{dt}\left(\int_0^\infty dE \, \frac{g(E)}{e^{\beta(E-\mu)}+1} \right)$

$$= \int_0^\infty dE \, g(E) \underbrace{\frac{\partial}{\partial T}\left(\frac{1}{e^{\beta(E-\mu)}+1}\right)}_{\text{varies only near } E_F}$$

$\downarrow$ use $\left.\frac{d\mu}{dT}\right|_{T=0} = 0$

$$\approx g(E_F) \int_0^\infty dE \, \frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta}\left(\frac{1}{e^{\beta(E-\mu)}+1}\right)$$

$$\approx g(E_F) \int_0^\infty dE \left(\frac{E-E_F}{k_B T^2}\right) \frac{e^{\beta(E-E_F)}}{\left(e^{\beta(E-E_F)}+1\right)^2}$$

$$= g(E_F) \int_0^\infty dE \underset{\substack{\uparrow \\ \text{odd about } E_F}}{\left(\frac{E-E_F}{k_B T^2}\right)} \underset{\substack{\uparrow \\ \text{even}}}{\frac{1}{4\cosh^2\left(\beta(E-E_F)/2\right)}} \approx 0 .$$

□

The heat capacity is

$$c_V = \left(\frac{\partial E}{\partial T}\right)_{N,V} = \int_0^\infty dE\; E g(E)\, \frac{\partial}{\partial T}\left(\frac{1}{e^{\beta(E-\mu)}+1}\right)$$

$$\approx \int_0^\infty dE\, \Big[E_F g(E_F) + \underset{\substack{\uparrow \\ \text{Taylor exp}^n \\ \text{of } g(E)E \\ \text{about } E=E_F}}{\tfrac{3}{2}} g(E_F)(E-E_F)\Big]\, \frac{\partial}{\partial T}\left(\frac{1}{e^{\beta(E-E_F)}+1}\right)$$

- First term vanishes by the odd/even f^n argument
- Second term survives

Define $x = \beta(E-E_F)$

$$\Rightarrow \; c_V \approx \frac{3}{2} g(E_F)\, T k_B^2 \underset{\substack{\uparrow \\ \text{only region near } E_F \\ \text{contributes anyway} \\ \text{i.e. near } x=0}}{\int_{-\infty}^{\infty}} dx\, \frac{x^2}{4\cosh^2\left(\frac{x}{2}\right)}$$

So $c_V \sim T g(E_F)$

Can we understand this result ?

- At low T, only fermions with energy within $\sim k_B T$ of the Fermi energy 'participate in physics'.
- No. of particles $\sim g(E_F) k_B T$
- Each of these gets energy $\sim k_B T$ (above E_F)
- Total energy $\sim g(E_F)(k_B T)^2$

$\Rightarrow c_V \sim g(E_F)\, T$ as above

Since $N \sim E_F^{3/2}$, we can write $c_V \sim N k_B \left(\frac{T}{T_F}\right)$

Metals Despite strong interactions b/w electrons, the free Fermi gas describes conduction electrons in metals very well.
(Landau explained this in the 1950s – Landau's Fermi liquid theory)

$$c_V = \underset{\substack{\uparrow \\ \text{electrons}}}{\gamma T} + \underset{\substack{\uparrow \\ \text{phonons}}}{\alpha T^3}$$

$\Rightarrow$ phonons dominate at high T

$T_D \sim 10^2\,K$, $T_F \sim 10^4\,K$

$\Rightarrow$ comparable contributions where $T \sim 1K$

Pauli Paramagnetism

A magnetic field affects electrons in two ways:

- They move in circles (Landau Levels)
- Their spins are polarised

$$E_{\text{spin}} = \underset{\substack{\uparrow \\ \text{Bohr magneton} \\ \frac{|e|\hbar}{2mc}}}{\mu_B} B s \qquad s = \begin{cases} +1 & \text{"up"} \uparrow \\ -1 & \text{"down"} \downarrow \end{cases}$$

Spin up and down have different energies
$\Rightarrow$ different occupation no.s

$$\frac{N_\uparrow}{V} = \frac{1}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty dE \, \frac{E^{1/2}}{e^{\beta(E+\mu_B B-\mu)}+1}$$

$$\frac{N_\downarrow}{V} = \text{''} \int_0^\infty dE \, \frac{E^{1/2}}{e^{\beta(E-\mu_B B-\mu)}+1}$$

The magnetisation is $M = -\frac{\partial E}{\partial B}$

$$E = E_0 + \mu_B B N_\uparrow - \mu_B B N_\downarrow$$

$$M = -\mu_B (N_\uparrow - N_\downarrow)$$

High temperature

Integrals $\rightarrow \frac{z}{\lambda^3} e^{\mp \beta \mu_B B}$ as $z \rightarrow 0$

$$\therefore M \approx 2\frac{\mu_B V z}{\lambda^3} \sinh(\beta \mu_B B)$$

Particle no. $N = N_\uparrow + N_\downarrow$

$$N \approx \frac{2Vz}{\lambda^3} \cosh(\beta \mu_B B)$$

$$\therefore M \approx \mu_B N \tanh(\beta \mu_B B)$$

The magnetic susceptibility

$$\chi = \frac{\partial M}{\partial B} \qquad \chi\Big|_{B=0} = \frac{N\mu_B^2}{k_B T} \sim \frac{1}{T}$$

Curie's Law

Low temperature

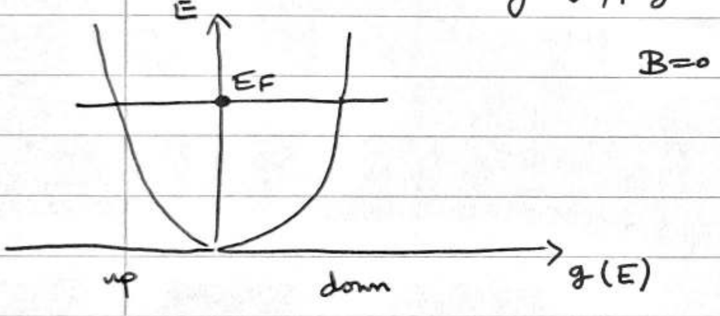
Using low temp approx to the integrals,

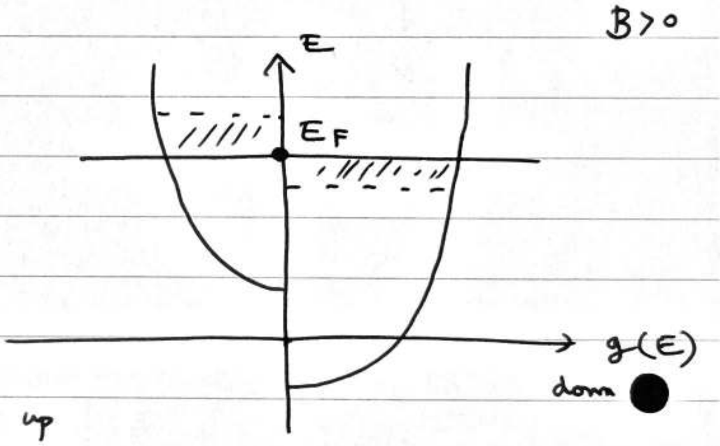
$$M \approx \frac{\mu_B V}{6\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \times \left[(E_F + \mu_B B)^{3/2} - (E_F - \mu_B B)^{3/2} \right]$$

$$M \approx \frac{\mu_B^2 V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} E_F^{1/2} B \qquad \text{using } \frac{\mu_B B}{E_F} \ll 1$$

$$M \approx \mu_B^2 g(E_F) B$$

$$\chi = \frac{\partial M}{\partial B} = \underset{\substack{\uparrow \\ \text{only states at Fermi surface can participate by flipping their spins}}}{\mu_B^2 g(E_F)}$$





4. Classical Thermodynamics ·ω·

4.1 – Temperature and the zeroth law of

Some definitions :

- A system that is isolated from all outside influences is contained within <u>adiabatic walls</u>. Refer to such systems as <u>insulated</u>.
- Walls that are not adiabatic are called <u>diathermal walls</u>. Systems separated by diathermal walls are in <u>thermal contact</u>.

- An isolated system will relax to <u>equilibrium</u> where no further change is noticeable.
- We've avoided using "energy" or "heat" or "temperature" etc. because these are yet to be defined.

The state of a system in equilibrium is described using macroscopic variables.

E.g. for a gas, p and V will specify the state.

<u>0^{th} Law</u>: If two systems, A and B, are in equilibrium with C then they are also in equilibrium with each other.

(i.e. equilibrium is transitive)

The Zeroth Law allows us to define temperature.

Consider gases:

$A\ (p_1, V_1)$

$C\ (p_3, V_3)$

For generic $(p_1, V_1), (p_3, V_3)$ there will be a change when systems are placed in thermal contact

If in equilibrium $\Rightarrow$ no change

$\Rightarrow$ some relationship $F_{AC}(p_1, V_1; p_3, V_3) = 0$

or $V_3 = f_{AC}(p_1, V_1; p_3)$

But if another gas $B\ (p_2, V_2)$ is also in equilibrium with C we have $F_{BC}(p_2, V_2; p_3, V_3) = 0$

or $V_3 = f_{BC}(p_2, V_2; p_3)$

$\therefore f_{AC}(p_1, V_1; p_3) = f_{BC}(p_2, V_2; p_3) \qquad (*)$

But, by the 0th Law,

$F_{AB}(p_1, V_1; p_2, V_2) = 0 \qquad (+)$

But (+) doesn't depend on p_3, so it must be possible to cancel p_3 on both sides of (*)

$\Rightarrow \theta_A(p_1, V_1) = \theta_B(p_2, V_2)$

This function θ_A refers only to the properties of A. It's a function of state. It's value we call the <u>temperature</u>.

$T = \theta(p, V)$ is the equation of states

<u>Note</u>: The above argument says that there exists a property called temperature.

Need a reference system.

We choose the ideal gas thermomether, $T = \frac{pV}{Nk_B}$.

4.2 The First Law

<u>1st Law</u> The amount of work required to change an isolated system from state ① to state ② is independent of how the work is performed.

This allows us to define another function of state: the energy $E(p, V)$

Do some work W on a system in any way you choose.

The change in energy $\Delta E = W$.

For systems that are not isolated, the state can change without doing work. (E.g. place a system in thermal contact with another system at a different temperature).

We call this other way to transfer energy <u>heat</u> Q:

$$\Delta E = W + Q$$

<u>Note</u>: we can't write $E = Q + W$

Once the system has the energy, it doesn't matter how it got it

Heat is not a type of energy, it's a mode of transferring energy.

<u>Definition</u> A <u>quasi-static process</u> is effectively in equilibrium and can be described by p, V at each stage

<u>Infinitesimal version of 1st Law:</u>

$$dE = \text{đ}Q + \text{đ}W$$

OMEGA CRINGE

no such expressions for $\text{đ}Q$, $\text{đ}W$

E is a function of state $E(p, V)$

$$dE = \frac{\partial E}{\partial p} dp + \frac{\partial E}{\partial V} dV$$

We'll restrict to one type of work: compressing

work done = force × distance

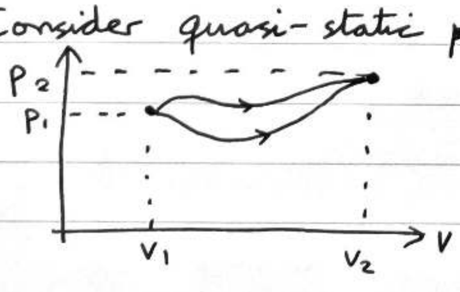
$$\text{đ}W = -p\,dV$$

Note sign: $\text{đ}W$ is work done <u>on</u> the system

There is no function $W(p, V)$ which has $dW = -p\,dV$

Not an exact differential.

Consider quasi-static paths

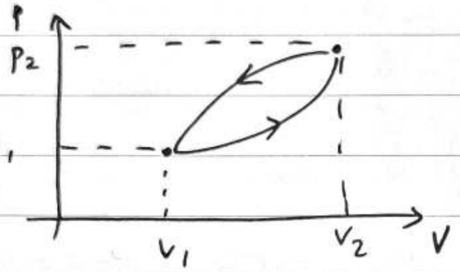


- $\int dE = E(p_2, V_2) - E(p_1, V_1)$ is independent of the path

- $\int \text{đ}W = -\int_{V_1}^{V_2} p\,dV$ depends on the path taken

4.3 The Second Law

Definition A reversible process is a quasi-static process that can be run in reverse (no friction)



Then $\oint dE = 0$

Heat absorbed/emitted

But $\oint p\,dV \neq 0$ and so $\oint \text{đ}Q \neq 0$

$= \oint p\,dV$ Work done by/on

∴ Going around reversible cycles transfers heat ⟷ work

The 2nd Law is the statement that there is an 'arrow of time' in the universe.

~~The~~ TWO equivalent statements:

Kelvin : No process is possible whoose sole effect is to convert heat entirely into work

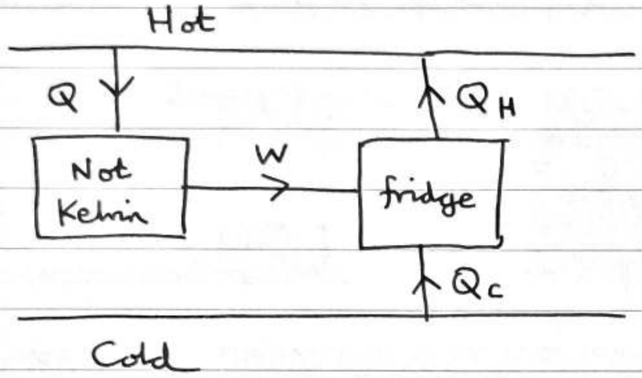
Clausius : No process is possible whose sole effect is transfer of heat from a colder to a hotter body

Claim: Kelvin not true

$\Rightarrow$ Clausius not true

Build a "not-Kelvin" machine that violates Kelvin's statement, and use it to power a fridge.

The whole system violates Clausius' statement.



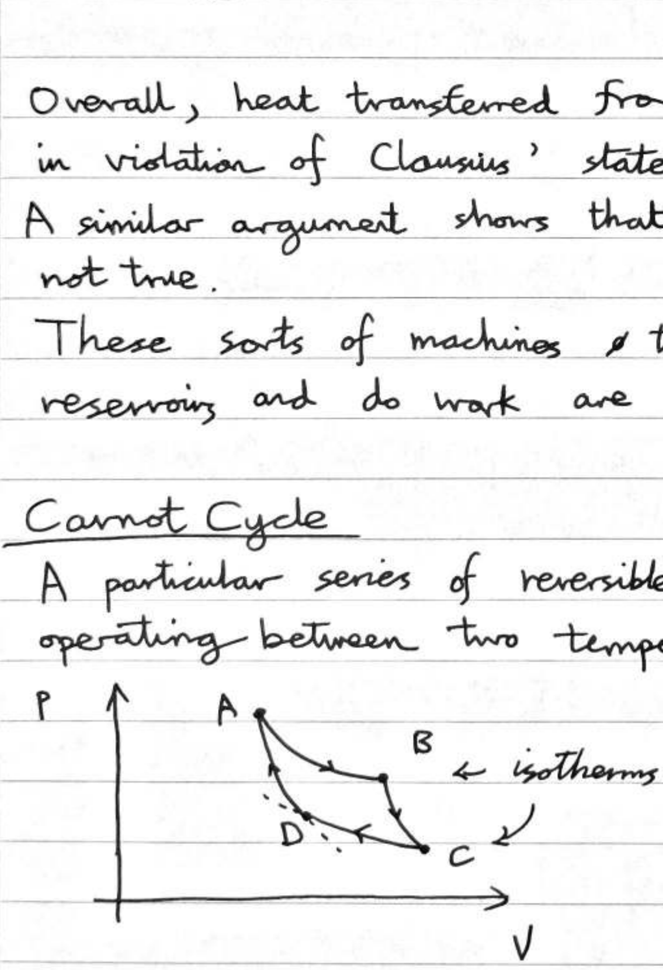
Overall, heat transferred from cold → hot is $Q_H - Q = Q_C$. in violation of Clausius' statement

A similar argument shows that Clausius not true $\Rightarrow$ Kelvin not true.

These sorts of machines that extract / deposit heat to reservoirs and do work are called "heat engines".

Carnot Cycle

A particular series of reversible processes run in a cycle, operating between two temperatures T_H and $T_C < T_H$.



heat Q_H absorbed

AB: Isothermal expansion at T_H

BC: Adiabatic expansion

System is isolated and so no heat transfer

T decreases to T_C

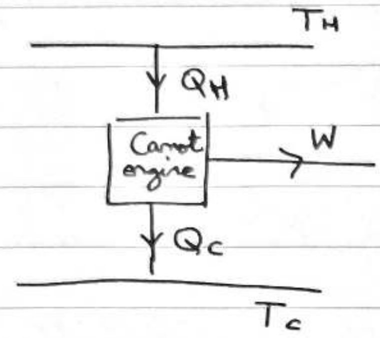
CD: Isothermal compression at T_C)

heat Q_C dumped into reservoir

DA: Adiabatic compression,

T increases to T_H

Because we're now back at the starting point, work done by the system $= W = Q_H - Q_C$



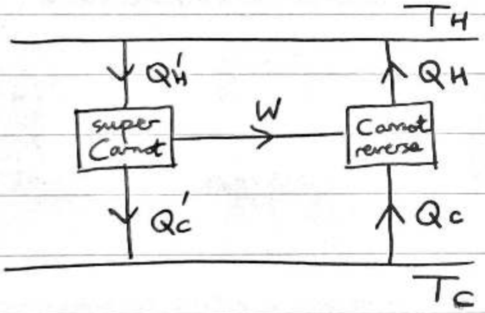
Define efficiency

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

Carnot's Theorem : of all the engines operating between two heat reservoirs, a reversible engine is the most efficient

$\Rightarrow$ all reversible engines have the same efficiency $\eta(T_H, T_C)$

Proof Consider another "super - Carnot" engine and a Carnot engine in reverse.



Heat $Q_H' - Q_H$ extracted from T_H $= Q_C' - Q_C$ heat deposited to T_C.

Clausius $\Rightarrow Q_H' \geq Q_H$

$$\therefore \eta_{sc} = \frac{W}{Q_H'} \leq \frac{W}{Q_H} = \eta_{Carnot}$$

i.e. $\eta_{Carnot} \geq \eta_{sc}$

Is SC reversive? Yes iff $Q_H = Q_H'$ i.e. $\eta_{sc} = \eta_{carnot}$ iff SC is reversible.

Thermodynamic Temperature Scale

We use a Carnot cycle to define a temperature.
Consider two Carnot engines: one operating between T_1 and $T_2 < T_1$; another between T_2 and $T_3 < T_2$

Efficiency only depends on the temperature.

If 1st extracts Q_1 at T_1 and emits Q_2 at T_2,

then $Q_2 = Q_1(1-\eta(T_1,T_2))$

2nd extracts Q_2 at T_2 and emits Q_3 at T_3,

so $$Q_3 = Q_2(1-\eta(T_2,T_3))$$
$$= Q_1(1-\eta(T_1,T_2))(1-\eta(T_2,T_3))$$

But we can think of the whole system as a Carnot engine operating between T_1 and T_3

$$Q_3 = Q_1(1-\eta(T_1,T_3))$$

Equating these, the dependence on T_2 must cancel

$$\Rightarrow \quad 1-\eta(T_1,T_3) = \frac{f(T_3)}{f(T_1)}$$

for some f^n $f(T)$.

We can pick a f^n to define a thermodynamic temperature

$$f(T) = T \quad \Rightarrow \quad \eta = 1 - \frac{T_3}{T_1}$$

An example of a Carnot engine: ideal classical gas

All Carnot cycles have the same efficiency. We'll use an ideal classical gas (monoatomic)

Ideal gas: $pV = Nk_BT$, $\quad E = \frac{3}{2}Nk_BT$,
$$C_V = \frac{3}{2}Nk_B$$

- Isothermal $(dT=0) \Rightarrow dE = 0$

$\therefore$ Along AB: $$Q_H = \int_A^B đQ = -\int_A^B đW = \int_A^B p\,dV$$
$$= \int_A^B \frac{Nk_BT_H}{V}dV = Nk_BT_H \ln\left(\frac{V_B}{V_A}\right)$$

Similarly, along CD: $$Q_C = -Nk_BT_C\ln\left(\frac{V_D}{V_C}\right)$$

- adiabatic $đQ = 0 \Rightarrow dE = -p\,dV$

$$\therefore \; dE = c_V\,dT = -\frac{Nk_BT}{V}\,dV$$

$$\frac{dT}{T} = -\frac{Nk_B}{c_V}\,\frac{dV}{V}$$

$$\therefore \; \ln\left(\frac{T_f}{T_i}\right) = -\left(\frac{Nk_B}{c_V}\right)\ln\left(\frac{V_f}{V_i}\right)$$

$$= -\frac{2}{3}\ln\left(\frac{V_f}{V_i}\right)$$

$$\therefore \; TV^{2/3} = \text{const.}$$

$$\therefore \; T_H V_B^{2/3} = T_C V_C^{2/3},$$

$$T_C V_D^{2/3} = T_H V_A^{2/3},$$

$$\therefore \; \frac{V_A}{V_B} = \frac{V_D}{V_C}$$

$$\therefore \; \frac{Q_H}{Q_C} = \frac{T_H}{T_C}$$

$\therefore$ efficiency of the Carnot cycle:

$$\eta_{\text{carnot}} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$$

This is true for all Carnot cycles of any system

Last time: Carnot's Theorem

"Reversible engine is most efficient"

$$\eta_{carnot} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$$

Entropy

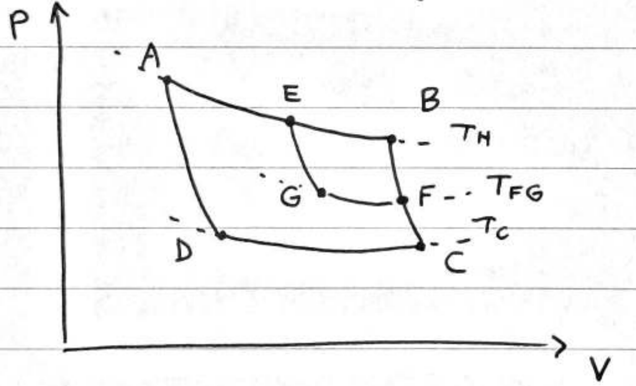
For a Carnot cycle: $\frac{Q_H}{Q_C} = \frac{T_H}{T_C}$

Q_H absorbed Q_C given out

or, writing: $Q_1 = Q_H$, $T_1 = T_H$,
$Q_2 = -Q_C$, $T_2 = T_C$

$$\sum_{i=1}^{2} \frac{Q_i}{T_i} = 0$$

Consider reversible cycle:



Carnot ABCD: $\frac{Q_{AB}}{T_H} + \frac{Q_{CD}}{T_C} = 0$

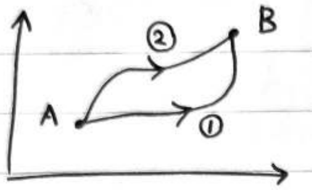
cycle

Carnot EBFG: $\frac{Q_{EB}}{T_H} + \frac{Q_{FG}}{T_{FG}} = 0$

For AEGFCD: $\frac{Q_{AE}}{T_H} + \frac{Q_{GF}}{T_{FG}} + \frac{Q_{CD}}{T_C} = 0$

Breaking up further:

$\Rightarrow \oint \frac{\text{đ}Q}{T} = 0$ for reversible processes



(Both paths are reversible)

$\therefore \int_A^B \frac{đQ}{T}$ indep of path (reversible)

Hence, there is a function of state, denoted <u>entropy</u>

$$S(A) = \int_0^A \frac{đQ}{T} \qquad S = S(p,V) \text{ is a function of state}$$

some reference state

Note: $dE = TdS - pdV$

$\Rightarrow$ this is the same entropy as we introduced when counting microstates.

For an <u>irreversible</u> engine extracting Q_H' at T_H and emitting heat Q_c' at T_c, doing the same work W as a Carnot engine extracting Q_H at T_H and emitting Q_c at T_c.

$$W = Q_H' - Q_c' = Q_H - Q_c$$

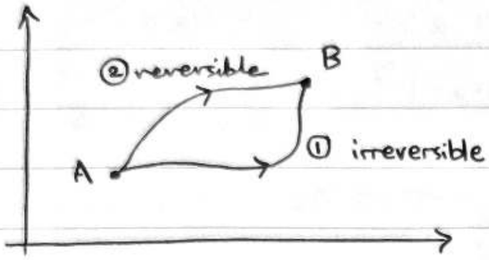
$$\Rightarrow \frac{Q_H'}{T_H} - \frac{Q_c'}{T_C} = \underbrace{\cancel{\frac{Q_H}{T_H} - \frac{Q_c}{T_c}}}_{\text{zero; Carnot}} + \underbrace{(Q_H' - Q_H)}_{\geq 0}\underbrace{\left(\frac{1}{T_H} - \frac{1}{T_c}\right)}_{\leq 0}$$

$\Big[\ \eta' < \eta_{\text{Carnot}} \Rightarrow Q_H' > Q_H$

$\eta' = \frac{W}{Q_H'}$ $\Big]$

Thus $\frac{Q_H'}{T_H} - \frac{Q_c'}{T_c} \leq 0$.

Considering lots of small processes, using the same method as above, $\oint \frac{đQ}{T} \leq 0$



$$\oint \frac{đQ}{T} = \int_{①} \frac{đQ}{T} - \int_{②} \frac{đQ}{T} \leqslant 0$$

$$\therefore \int_{①} \frac{đQ}{T} - \left(S(B) - S(A)\right) \leqslant 0$$

$$\therefore \int_{①} \frac{đQ}{T} \leqslant S(B) - S(A)$$

Suppose that path 1 is adiabatic (i.e. isolated)

$\Rightarrow đQ = 0$ on path 1

$\Rightarrow S(B) \geqslant S(A)$

i.e. entropy never decreases in an isolated system

4.4 Thermodynamic Potentials

- We now have several fns of state : T, E, S
- We can choose almost any 2 of p, V, E, T, S to specify the state of a system.

It's pest to think of $E = E(S, V)$, cf $dE = TdS - pdV$

Taking mixed partial derivatives, get interesting rel^n

$$\frac{\partial^2 E}{\partial S \partial V} = \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$$

This is a Maxwell relation.

It holds for all systems.

We can also define Helmoltz free energy $F = E - TS$

$\Rightarrow dF = -SdT - pdV$,

and Gibbs free energy $G = E + pV - TS$

$\Rightarrow dG = -SdT + Vdp$,

and enthalpy $H = E + pV$

$\Rightarrow dH = TdS + Vdp$.

Each of these thermodynamic potentials gives a Maxwell relation. We can also get results by taking further derivatives.

e.g. $$\underset{\underset{T\left(\frac{\partial S}{\partial T}\right)_V}{\nearrow}}{c_V} - \underset{\underset{T\left(\frac{\partial S}{\partial T}\right)_p}{\nwarrow}}{c_p} = T\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial p}{\partial T}\right)_V$$

Note on the Gibbs free energy:

Recall that it also depends on N: $G(T,p,N)$

$$dG = -S\,dT + V\,dp + \mu\,dN$$

Extensive $\Rightarrow$ $G(T,p,\lambda N) = \lambda G(T,p,N)$

$$\Rightarrow G(T,p,N) = \mu(T,p)N$$

4.5 The Third Law

$$\frac{S}{N} \longrightarrow 0 \quad \text{as } T \to 0 \text{ and } N \to \infty$$

No new function of state.

$$S(B) - S(A) = \int_A^B dT \, \frac{C_V}{T}$$

$\Rightarrow C_V \to T^n$ for $n \geq 1$ or faster as $T \to 0$ (bruh, $T^{1/2}$ is fine)
(otherwise integral doesn't converge)
Heat capacity of classical ideal gas is constant and would violate this. Including quantum effects → heat capacities satisfy this.
Low temperature needs quantum description.

5 – Phase Transitions

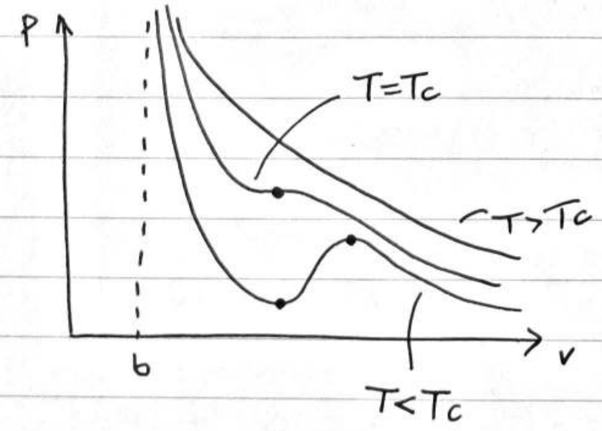
A phase transition is an abrupt, discontinuous change in the properties of a system.

5.1 – Liquid - Gas Transition

Recall the Van der Waals eq^n.

$$p = \frac{k_B T}{v - b} - \frac{a}{v^2} \quad , \quad v = \frac{V}{N} \text{, density } \rho = \frac{1}{v}$$

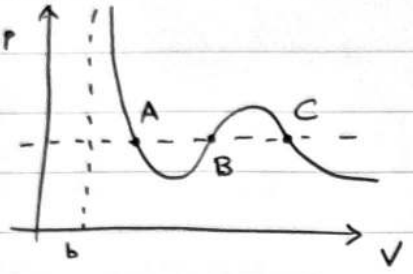
Plot isotherms (curves of const. T)



$T > T_c$: monotonically dec^n
$T < T_c$: two turning points
Determine T_c from $\frac{\partial p}{\partial V} = 0$,
and $\frac{\partial^2 p}{\partial V^2} = 0$,

$$k_B T_c = \frac{8a}{27b}$$ (holy shit!)

Consider $T < T_c$:



For fixed p there are 3 possible densities.

Solution B: $\left(\frac{\partial p}{\partial V}\right)_T > 0$

$\Rightarrow$ squeeze and pressure decreases, expand and it pushes back harder

$\Rightarrow$ unstable.

Solution A: $v \gtrsim b \Rightarrow$ atoms closely packed

$\left|\frac{\partial p}{\partial V}\right|$ large $\Rightarrow$ hard to compress

This is a <u>liquid</u>

Solution C: $v \gg b$, $\left|\frac{\partial p}{\partial V}\right|$ small $\Rightarrow$ <u>gas</u>

What replaces solution B?

<u>Phase equilibrium</u>

So far we've assumed constant density.

But with two phases (liquid and gas) they can coexist.

Conditions for equilibrium:

same temperature ✓

same pressure ✓

same chemical potential ?

Require $\mu_{liquid} = \mu_{gas}$

How can we check this?

Move along isotherm, consider

$$\mu = \mu(p,T) \quad , \quad d\mu = \left(\frac{\partial \mu}{\partial p}\right)_T dp$$

Since $G(p,T,N) = \mu(p,T)\,N$,

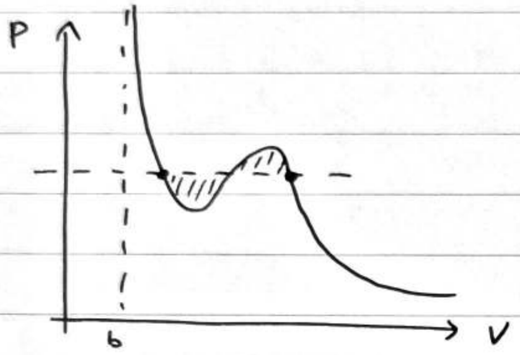
and $dG = -S\,dT + V\,dp + \mu\,dN$,

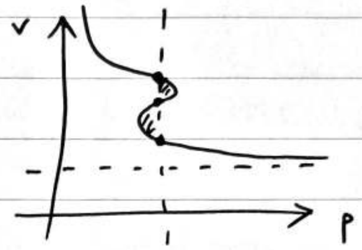
$$\Rightarrow \left(\frac{\partial G}{\partial p}\right)_{N,T} = \left(\frac{\partial \mu}{\partial p}\right)_T N = V$$

Integrate along isotherm

$$\mu(p,T) = \mu_{\text{Liquid}} + \int_{p_{\text{liq}}}^{p} dp' \; V(p',T)/N$$

↑ "Area under curve"

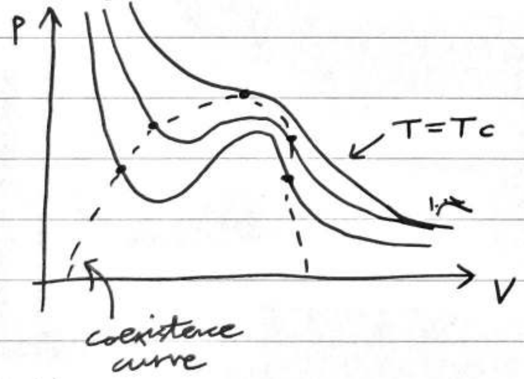


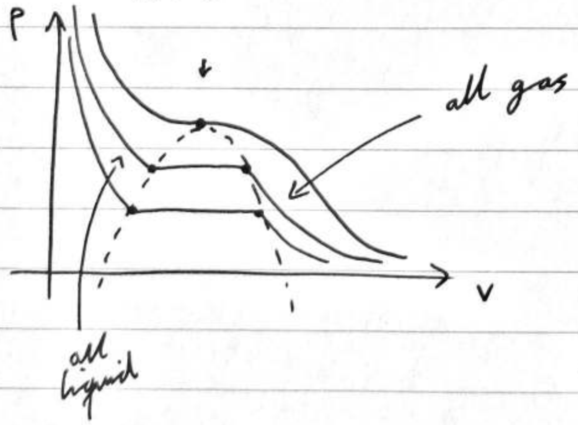


$\mu_{gas} = \mu_{liquid}$ ⇒ area of shaded regions must be equal (Maxwell construction)

For fixed T, there is a unique pressure at which the liquid and gas phases coexist.

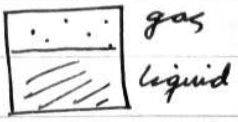
The defines the coexistence curve



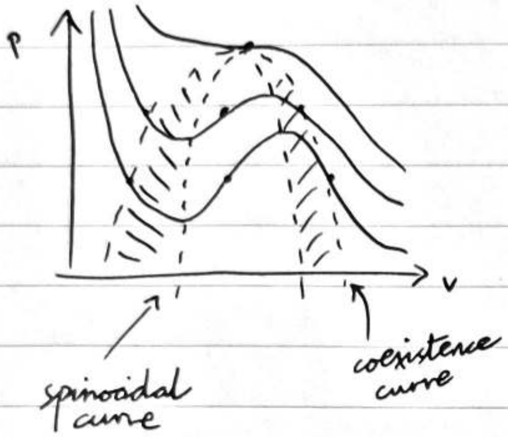


'Inside' the coexistence curve, liquid and gas can both exist, ⇒ average density can vary at fixed pressure

e.g. start at T > Tc and cool
⇒ phase separation



Meta-stable states



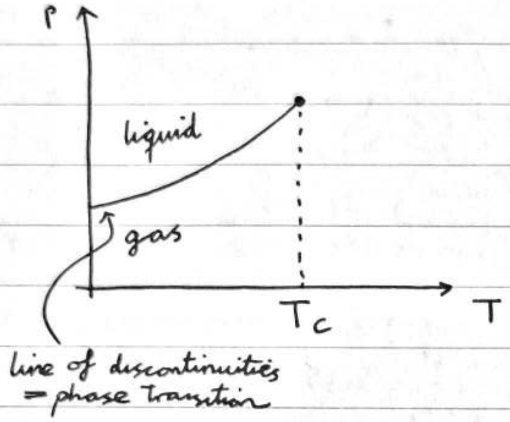
unstable region $\frac{\partial p}{\partial v} > 0$

phase equilibrium removes this, but also removed other points shown as shaded region.

These are <u>meta-stable</u>; they exist but any small disturbance ⇒ separation (e.g. supercooled vapour, superheated liquid)

Clausius – Clapeyron Equation

Consider the p – T plane:



Note: for $T > T_c$ there is no distinction between liquid and gas

On each side of the line, all particles are either in gas or liquid phase.

$$\frac{G_{liquid}}{N_{liquid}} = \frac{G_{gas}}{N_{gas}}$$

$$\Rightarrow g_L = g_g \quad \left(g = \frac{G}{N}\right)$$

How does G change as we move along this line?

$$dg_L = -s_L\,dT + v_L\,dp$$
$$= dg_g = -s_g\,dT + v_g\,dp \qquad \left(\begin{matrix} s = \frac{S}{N}, \\ v = \frac{V}{N} \end{matrix}\right)$$

$$\Rightarrow \underset{\substack{\uparrow \\ \text{slope of the line}}}{\frac{dp}{dT}} = \frac{s_g - s_L}{v_g - v_L} = \frac{L}{T(v_g - v_L)} \quad \Leftarrow \text{Clausius – Clapeyron equation}$$

where $L = T(s_g - s_L)$ = latent heat

A phase transition is <u>nth order</u> if the n^{th} derivative of the free energy is discontinuous (but not the lower derivatives).

For $T < T_c$:

$$\left.\begin{matrix} S = -\left(\frac{\partial F}{\partial T}\right)_V \\ \\ V = \left(\frac{\partial G}{\partial p}\right)_T \end{matrix}\right\} \text{both discontinuous}$$

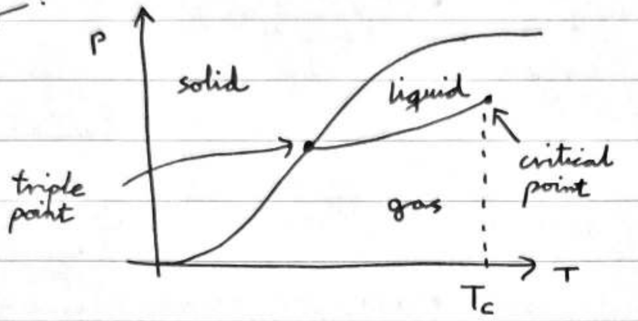
$\Rightarrow$ 1st order

At $T \to T_c$, $s_{liquid} \to s_{gas}$

$\Rightarrow$ 2nd order

For most simple materials, this liquid - gas phase transition is part of a larger phase diagram which includes solids.

Generically:

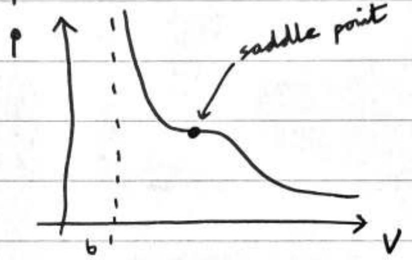


For water: $T_c \approx 647K$, $p_c \approx 218$ atm

The critical point

Let's look at the critical point in more detail.

$$p = \frac{k_B T}{v-b} - \frac{a}{v^2}$$



$$\Rightarrow pv^3 - (pb + k_B T)v^2 + a(v-b) = 0,$$

$$p_c(v - v_c)^3 = 0 \quad (\text{at } T = T_c)$$

$$\Rightarrow k_B T_c = \frac{8a}{27b}, \quad v_c = 3b, \quad p_c = \frac{a}{27b^2}$$

Define reduced variables

$$\bar{T} = \frac{T}{T_c}, \quad \bar{v} = \frac{v}{v_c}, \quad \bar{p} = \frac{p}{p_c}$$

The van der Waals equation is then the same for all gases.

$$\bar{p} = \frac{8}{3}\frac{\bar{T}}{\bar{v} - \frac{1}{3}} - \frac{3}{\bar{v}^2}$$

"law of corresponding states"

It predicts a universal ratio: $\frac{p_c v_c}{k_B T_c} = \frac{3}{8} = 0.375$

Actual values $\sim 0.28 - 0.3$

Plot coexistence curve $\bar{T}$ vs $\bar{V}$

$\Rightarrow$ all gases sit on the some curve

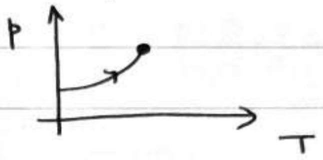
$\Rightarrow$ universality

$\Rightarrow$ explore this more

Critical exponents

Look at the behaviour as we approach the critical point :

① How does $v_{gas} - v_{liquid}$ vary as we approach the c.p. along the coexistence curve?



$$\bar{p} = \frac{8\bar{T}}{3\bar{v}_L - 1} - \frac{3}{\bar{v}_L^2} = \frac{8\bar{T}}{3\bar{v}_g - 1} - \frac{3}{\bar{v}_g^2}$$

$$\Rightarrow \quad \bar{T} = \frac{(3\bar{v}_L - 1)(3\bar{v}_g - 1)(\bar{v}_L + \bar{v}_g)}{8\,\bar{v}_g^2\,\bar{v}_L^2}$$

Expand for small $\bar{v}_g - \bar{v}_L$

$$\bar{T} \approx 1 - \frac{1}{16}(\bar{v}_g - \bar{v}_L)^2$$

$$\bar{v}_g - \bar{v}_L \sim (T_c - T)^{1/2}$$

② How does the pressure vary with volume on the critical isotherm?

At $T = T_c$, there's a unique pressure $p(V, T_c)$, and

$$\frac{\partial p}{\partial V} = \frac{\partial^2 p}{\partial V^2} = 0 \quad \text{at critical point}$$

$$\Rightarrow \quad (p - p_c) \sim (V - V_c)^3$$

③ How does the compressibility $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$

change as we approach $T \to T_c$ from above?

At $T = T_c$, $\left(\frac{\partial p}{\partial V}\right)_T = 0$

$\therefore$ expect $\left(\frac{\partial p}{\partial V}\right)_T = -a(T - T_c)$ at $V = V_c$

$$\Rightarrow \kappa \sim (T - T_c)^{-1}$$

<u>Note</u>: answers in ② and ③ only needed assumption of analytic behaviour near the c.p.

Experimental results

$$v_g - v_L \sim (T_c - T)^{\beta}, \quad \beta \approx 0.32$$
$$p - p_c \sim (v - v_c)^{\delta}, \quad \delta \approx 4.8$$
$$\kappa \sim (T - T_c)^{-\gamma}, \quad \gamma \approx 1.2$$

↑

These are examples of critical exponents.

What are we missing?

The van der Waals equation is missing <u>fluctuations</u>.

Work in grand canonical ensemble.

Usually, $\frac{\Delta N}{N} \sim \frac{1}{\sqrt{N}}$

$\Delta N \Rightarrow$ density fluctuations ; $\rho = N/V$

Recall $\ln \mathcal{Z} = \beta V p(T,\mu)$

$$\langle N \rangle = V \left(\frac{\partial p}{\partial \mu}\right)_{T,V}$$

$$(\Delta N)^2 = \frac{1}{\beta}\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{T,V}$$

$$\frac{(\Delta N)^2}{\langle N \rangle} = \frac{1}{V\beta}\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{T,V}\left(\frac{\partial \mu}{\partial p}\right)_{T,V} = \frac{1}{V\beta}\left(\frac{\partial \langle N \rangle}{\partial p}\right)_{T,V}$$

$\downarrow$ cyclic rel^{r}

$$= -\frac{1}{\beta}\left(\frac{\partial \langle N \rangle}{\partial V}\right)_{p,T} \underbrace{\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{\langle N \rangle, T}}_{-\kappa}$$

But $\kappa \to \infty$ at critical point

$\Rightarrow$ fluctuations are large

Understanding how to correctly understand (!) behaviour is the subject of 'critical phenomena'.

5.2 The Ising Model

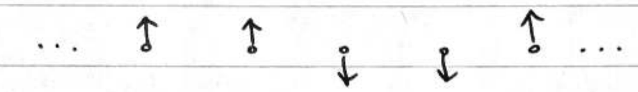
The Ising model consists of N sites in a d-dimensional lattice. There is a spin variable on each site:

$$s_i = \begin{cases} \pm 1 & \text{"spin up"} \\ \mp 1 & \text{"spin down"} \end{cases}$$

$$E = -\underset{\text{interactions}}{J} \sum_{\langle ij \rangle} s_i s_j - \underset{\text{magnetic field}}{B} \sum_i s_i$$

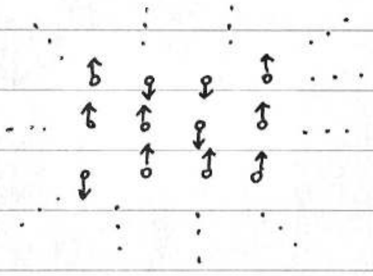
$\langle ij \rangle$ runs over neighbouring pairs i, j

e.g. $d=1$



$d = 2$

square lattice



Let q = no. of nearest neighbours

e.g. $q=2$ for $d=1$

$q=4$ for $d=2$ square lattice

$J>0 \Rightarrow$ spins want to be aligned with each other ↑↑ or ↓↓

$\Rightarrow$ ferromagnet

$J<0 \Rightarrow$ spins want to be anti-aligned ↑↓ or ↓↑

$\Rightarrow$ anti-ferromagnet

We'll consider $J>0$.

In canonical ensemble,

$$Z = \sum_{\{s_i\}} e^{-\beta E[s_i]}$$

Define the average magnetisation

$$m = \frac{1}{N} \sum_i \langle s_i \rangle = \frac{1}{N\beta} \frac{\partial \ln Z}{\partial \cancel{\beta} B}$$

Mean Field Theory

- We'll make an approx: fluctuations about average are small.

Write $s_i s_j = [(s_i - m) + m][(s_j - m) + m]$

$$\simeq m^2 + 2m\left(\frac{s_i + s_j}{2} - m\right)$$ to first order in fluctuations ← SUBTLE, ignoring fluctuations that go against alignment

$$\Rightarrow E_{mf} = -J \sum_{\langle ij \rangle} \left[m(s_i + s_j) - m^2 \right] - B \sum_i s_i$$

$$= +Jm^2 \underset{\underset{\sum_{\langle ij\rangle} \rightsquigarrow \frac{1}{2}Nq}{\uparrow}}{\tfrac{1}{2}} Nq - (Jqm + B)\sum_i s_i$$

This is now similar to problem we've seen before with $B_{eff} = B + Jqm$

$$\Rightarrow Z = e^{-\frac{1}{2}\beta J N q m^2} \left(e^{-\beta B_{eff}} + e^{+\beta B_{eff}} \right)^N$$

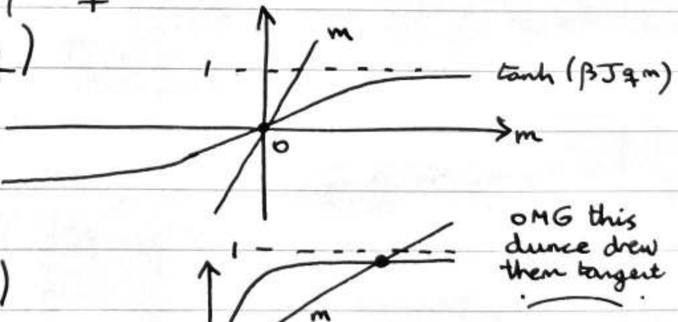
$$= e^{-\frac{1}{2}\beta J N q m^2}\, 2^N \cosh^N(\beta B_{eff})$$

But this still depends on m which we don't yet know! Determine self-consistently:

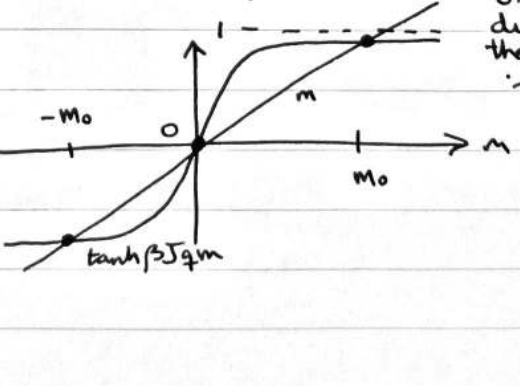
$$m = \frac{1}{N\beta} \frac{\partial \ln Z}{\partial B} = \tanh(\beta B + \beta J q m)$$ [something something perturbation]

Solutions for $B = 0$ $\quad m = \tanh \beta J q m$

If
- $\beta J q < 1$ $(k_B T > Jq)$ then $m = 0$



- $\beta J q > 1$ $(k_B T < Jq)$ then $m = 0$ (unstable) or $m = \pm m_0$ (true solutions)

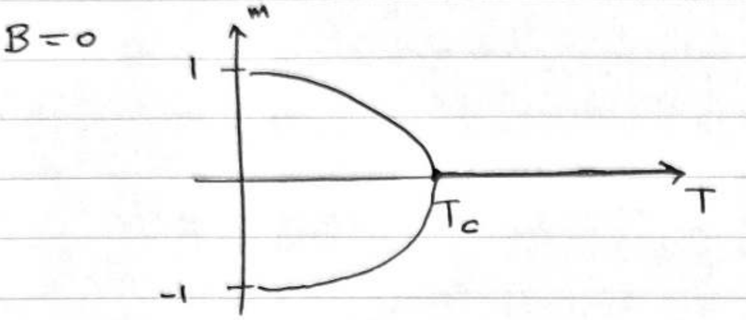


OMG this dunce drew them tangent

As $T \to 0$, expect $m \to \pm 1$ (all up or all down) ✓

- critical temperature:

$$k_B T_C = Jq$$



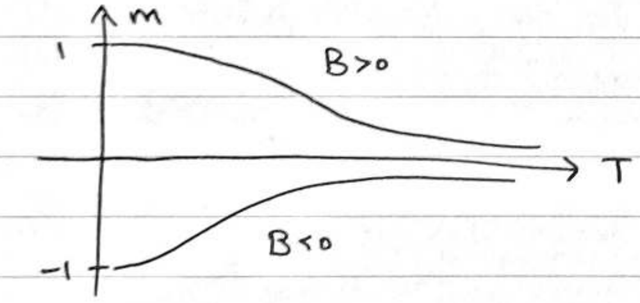
Abrupt change as T passes through Tc.
2nd order phase transition

Solution for $B \neq 0$

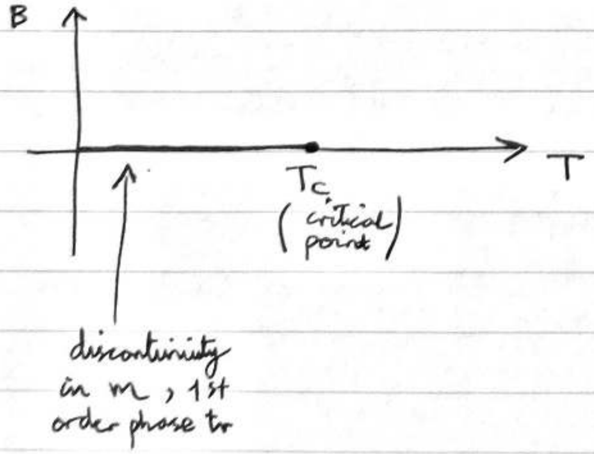
Taylor expand (small βB, m)

$$m \to \frac{B}{k_B T} \quad \text{as } T \to \infty$$

Goes smoothly to zero.
Also no ambiguity whether $+m_0$ or $-m_0$ at low temperature.
B picks out one of them.

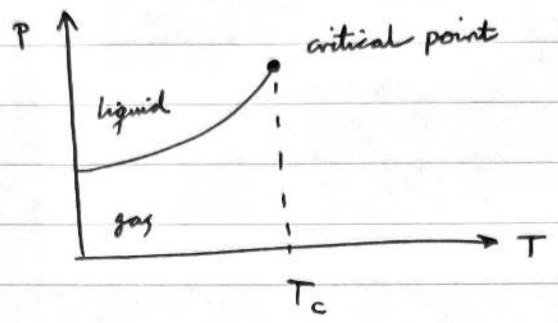


m changes discontinuously if we vary B from B>0 to B<0.



L22.4

compare



Let's compute critical exponents:

① How does m decrease at $B = 0$ as we approach the critical point? ($T \to T_c$ from below)

$$(*) \Rightarrow \quad m \approx \beta J q m - \tfrac{1}{3}(\beta J q m)^3 \qquad (\text{small } m)$$

$$\Rightarrow \quad m_0 \sim (T_c - T)^{1/2}$$

② How does m vary with B at $T = T_c$? $(\beta J q = 1)$

$$(*) \Rightarrow \quad m = \tanh\left(\frac{\beta}{Jq} + m\right)$$

$$m \approx m + \frac{\beta}{Jq} - \frac{1}{3}\left(m + \frac{\beta}{Jq}\right)^3 + \cdots$$

$$m \sim B^{1/3}$$

③ How does the magnetic SUSceptibility $\chi = N\left(\frac{\partial \overset{\text{small!}}{M}}{\partial B}\right)_T$ change as we approach $T \to T_c$ (from above) at $B = 0$?

$$\frac{d}{dB}(*) \Rightarrow \quad \chi = \frac{N\beta}{\cosh^2 \beta J q m}\left(1 + \frac{Jq}{N}\chi\right)$$

$$T > T_c \Rightarrow m = 0 \Rightarrow \chi = \frac{N\beta}{1 - Jq\beta} \sim (T - T_c)^{-1}$$

Ⓐ

Validity of mean-field theory

All 3 critical exponents are the same as for the van der Waals equation (!) But are they correct?

This depends on the number of dimensions.

$d = 1$: completely wrong :-, actually no phase transition exact solution known (and fairly straightforward).

$d \geq 2$: basic phase diagram is correct. There is a phase transition.

$d \geq 4$: MFT's critical exponents are correct.

$d = 2$: Exact solution by Onsager, when $B = 0$.

$m_0 \sim (T_c - T)^{\beta}$ where $\beta = \frac{1}{8}$ $\qquad$ $\chi \sim (T - T_c)^{-\gamma}$ where $\gamma = \frac{7}{4}$

$m \sim B^{1/\delta}$ $\qquad$ " $\delta = 15$

d=3 No exact solution known.

Critical exponents have been computed numerically

$$\beta \approx 0.32 \, , \quad \delta \approx 4.8 \, , \quad \gamma \approx 1.2$$

These are exactly (!) the same as for the liquid-gas transition.

The theory governing the critical point is the same for liquid-gas and the Ising model. This is an example of universality.

5.3 – Landau Theory

Landau Theory is a unified way of looking at phase transitions. It's based on mean field approx and so has limitations. We will illustrate using the Ising model, but it can be applied to all systems.

Recall mean field approx for Ising:

$$Z = e^{-\frac{1}{2}\beta JNqm^2} 2^N \cosh^N \beta B_{eff} \, , \qquad \left(B_{eff} = B + Jqm \right)$$

$$\Rightarrow F = -\frac{1}{\beta} \ln Z = \frac{1}{2} JNqm^2 - \frac{N}{\beta} \ln (2 \cosh \beta B_{eff})$$

To get free energy, we should sub in

$$m = \frac{1}{N\beta} \frac{\partial \ln Z}{\partial \beta}$$

Landau's idea: instead treat $F(T, V; m)$ seriously.

Equilibrium config^n minimise $F(m)$: $\frac{\partial F}{\partial m} = 0$

$$\Rightarrow m = \tanh(\beta B_{eff})$$

The magnetisation m is an example of an order parameter ($m \neq 0$ ordered, $m = 0$ unordered)

General Landau Theory:

- Identify order parameter, m
  (e.g. $V_{gas} - V_{liquid}$ in vicinity of critical point where m small)

- Expand free energy in vicinity of critical point where m is small.

Second order phase transition

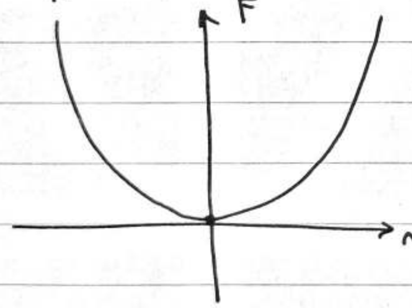
Consider a general system with order parameter m.
Suppose the system has a symmetry $m \to -m$
Then expansion of the free energy must have only even powers of m.

$$F(T;m) = F_0(T) + a(T)m^2 + b(T)m^4 + \ldots$$

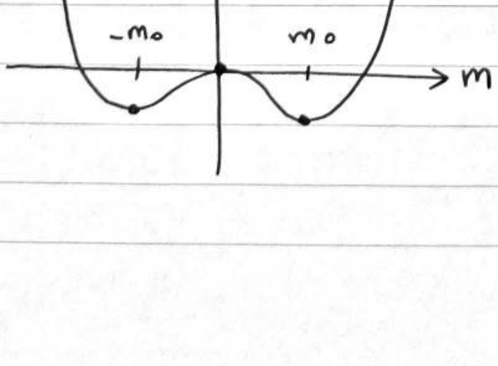
For example, this is what happens in the Ising model with $B=0$.

$$F_{Ising}(T;B) = -Nk_B T \ln 2 + \frac{NJq}{2}(1 - Jq\beta)m^2 + \frac{N\beta^3 J^4 q^4}{24} m^4 + \cdots$$

The condition for equilibrium is $\frac{\partial F}{\partial m} = 0$
The solution depends on the signs of $a(T)$ and $b(T)$.
Suppose $b(T) > 0$.



$a(T) > 0 \Rightarrow$ unique eq value



$a(T) < 0 \Rightarrow$ 3 stationary points

$m=0$ unstable

$m = \pm m_0$ stable

As T decreases, we typically go from $a(T) > 0$ to $a(T) < 0$. A second order phase transition occurs at $T = T_c$ where $a(T_c) = 0$.

Typical behaviour is $b(T_c) = b_0$,

$$a(T) \approx a_0 (T - T_c)$$

$$\Rightarrow \quad m_0 = \sqrt{\frac{a_0}{2b_0}} \, (T_c - T)^{1/2} \qquad (T < T_c)$$

This is the critical exponent we calculated for VdW, Ising

We can check that this is a 2nd order phase transition by computing:

$S = -\frac{\partial F}{\partial T}(T ; m = m_0)$ is continuous at $T = T_c$

$c = T \frac{\partial S}{\partial T}$ is discontinuous at $T = T_c$

The underlying dynamics and free energy are symmetric under $m \to -m$.

But the ground state picks $m = +m_0$ or $m = -m_0$. This spontaneous symmetry breaking is. It's important in many other areas of physics.

Last time:

Landau Theory

$$F(T; m) = F_0(T) + a(T)\, m^2 + b(T)\, m^4 + \cdots$$

Second order phase transition

First order phase transition

Suppose there are also odd powers in expansion of F:

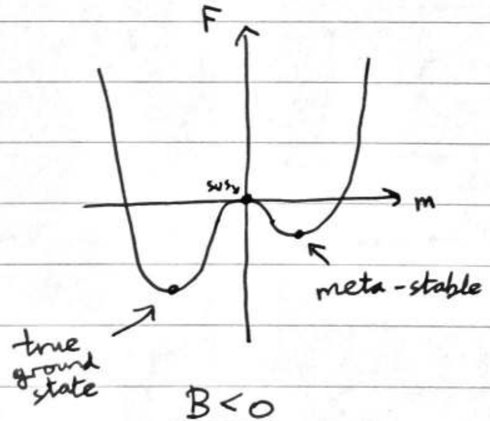
$$F(T; m) = F_0(T) + \alpha(T) m + a(T) m^2 + \gamma(T) m^3 + b(T) m^4 + \cdots$$

e.g. Ising model when $B \neq 0$

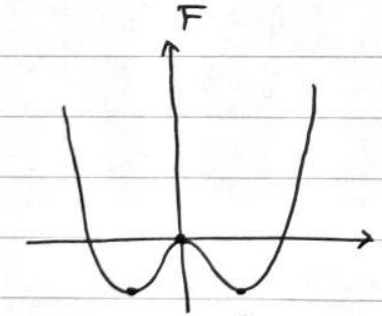
$$F_{\text{Ising}} = -N k_B T \ln 2 + \frac{JNq}{2} m^2 - \frac{N}{2k_B T}(B + Jqm)^2 + \frac{N}{24 (k_B T)^3}(B + Jqm)^4 + \cdots$$

Assume $b(T) > 0 \quad \forall T$

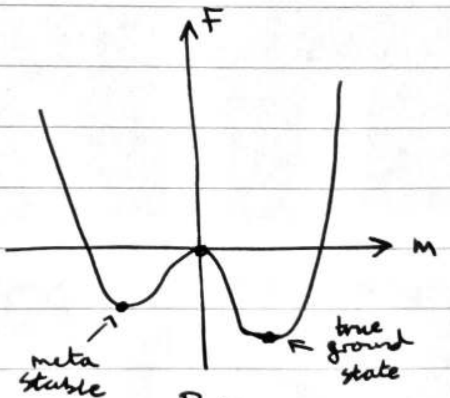
Low T: As B changes from +ve to −ve, then $\alpha(T)$ and $\gamma(T)$ change sign



B<0



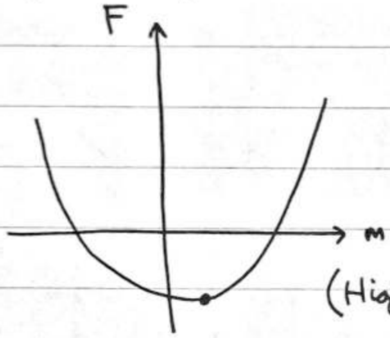
B=0



B>0

Minimise F: m changes discontinuously as B varies through 0
$\Rightarrow$ 1st order phase transition

Eventually, for large enough T, the metastable equilibrium disappears at the spinoidal point.
$\Rightarrow$ Only a single minimum



(High T, B>0)

5.4 Landau - Ginzburg Theory

Landau theory ignores fluctuations in order parameter m.
Landau - Ginzburg Theory allows us to take these fluctuations into account.

$$m \to m(\underline{r}) \quad \text{i.e. depends on position}$$

local order parameter

Assume $m \to -m$ symmetry

$$F[m(\underline{r})] = \int d^d r \left[a(T) m^2 + b(T) m^4 + c(T)(\underline{\nabla} m)^2 + \cdots \right]$$

"stiffness term"

Minimise F. $m(\underline{r}) \mapsto m(\underline{r}) + \delta m(\underline{r})$

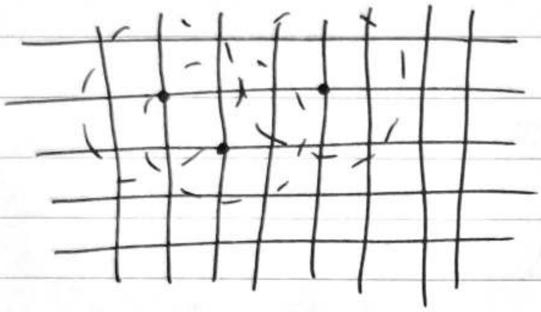
$$\delta F = \int d^d r \left[2am\,\delta m + 4bm^3 \delta m + 2c(\underline{\nabla} m)\cdot \underline{\nabla}\delta m + \cdots \right]$$

$$= \int d^d r \left[2am + 4bm^3 - 2c\nabla^2 m + \cdots \right] \delta m$$

So $c\nabla^2 m = am + 2bm^3$.

To understand how to deal with $F[m(\underline{r})]$, let's see how we could calculate it (in principle).

Each microstate $|n\rangle \Rightarrow$ spatially varying order parameter $m(\underline{r})$



Pick average spin around points

Very fine lattice $\rightarrow$ almost continuous function

But remember $m(\underline{r})$ doesn't change on small distance scales.

Note: many $|n\rangle \Rightarrow$ same $m(\underline{r})$

The true free energy, F_*, is given by

$$Z = e^{-\beta F_*} = \sum_{|n\rangle} e^{-\beta E(n)}$$

To define $F[m(\underline{r})]$ we sum over all those microstates which give $m(\underline{r})$.

$$e^{-\beta F[m(\underline{r})]} = \sum_{|n\rangle \text{ s.t. } m(\underline{r})} e^{-\beta E_n}$$

The full partition function then requires that we sum over all possible $m(\underline{r})$.

But if we're approximating m as a continuous f^n, then

$$Z = \underset{\nwarrow \text{ functional integral}}{\int} Dm(\underline{r})\, e^{-\beta F[m(\underline{r})]}$$