

μ -canonical ensemble:

- Determine $\Omega(E, V, N)$ for given E , then derive T, D .

Problems:

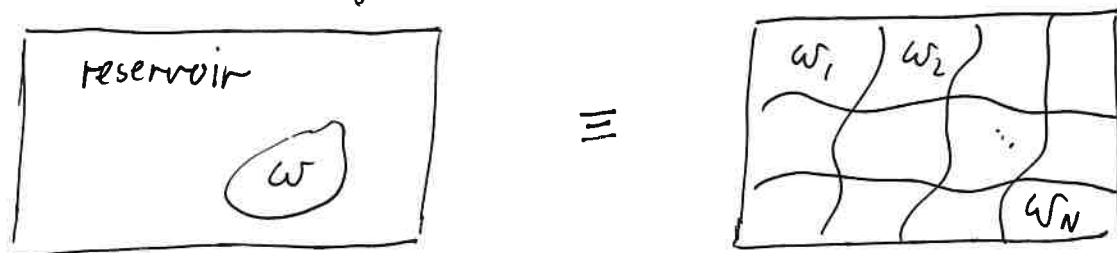
- * Usually it's hard to determine Ω because we count under "stiff" constraint (hyper-sphere)
- * Practically, isolated systems with constant energy are not very realistic.

→ Instead, one can keep the temperature T .

This is much easier to monitor with a thermometer. and to keep by putting the system in a heat reservoir.

We don't have to know much about the reservoir, just that it has "infinite" heat capacity,
so $T = \text{const.}$

In fact, we can build a reservoir from many copies of the same system

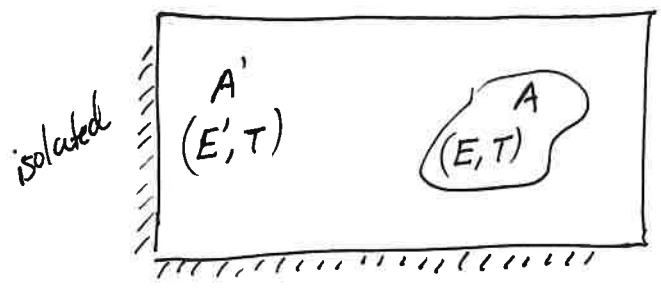


- * This is the canonical ensemble = many systems with the same (T, V, N)
- * The energy of the system can now vary and we will look for $P_f(E_f)$

We can calculate P_r using two methods:

- (A) The reservoir with $T = \text{const.}$
- (B) The ensemble, where we divide E between N systems

3.1 The heat reservoir



$E^{(0)} = E_r + E_r'$ conserved

The reservoir is big

$\frac{E_r}{E^{(0)}} \ll 1$

The probability that A' (reservoir) is in state with E_r' is proportional to number of states

$P_r \propto \Omega'(E_r') = \Omega'(E^{(0)} - E_r)$

state of A
is specified!
(μ -state)

As usual we take the logarithm

$$\begin{aligned} \ln P_r &\propto \ln \Omega'(E_r') = \ln \Omega'(E^{(0)}) + \frac{\partial \ln \Omega'}{\partial E_r'} (E_r' - E^{(0)}) \\ &= \text{const.} + \beta' E_r' = \text{const.} + \beta' E_r \end{aligned}$$

Where we used the definition from the equilibrium condition

$\beta' \equiv \frac{\partial \ln \Omega}{\partial E} = \frac{1}{T} = \beta$

Therefore

$P_r \propto \exp(-\beta E_r)$

To normalize we sum (over μ -states!)

$$P_r = \frac{\exp(-\beta E_r)}{\sum_s \exp(-\beta E_s)}$$

The canonical ensemble

N identical systems

$$\sum_r n_r = N$$

E is total energy

$$\sum_r n_r E_r = N U = E$$

$\{n_r\}$ = distribution of E between systems.

($U \equiv$ average energy per system)

Any combination $\{n_0, \dots, n_N\}$ can be realized in many ways

$$W\{n_r\} = \frac{N!}{n_0! n_1! n_2! \dots}$$

(This is like assigning colors.)

* All distributions $\{n_r\}$ which conserve E are equally likely.

Therefore Prob. $\{n_r\} \propto W\{n_r\}$

And if we want to calculate any average of $F\{n_r\}$

$$\text{It will be } \langle F\{n_r\} \rangle = \frac{\sum F\{n_r\} W\{n_r\}}{\sum W\{n_r\}}$$

* We will see that in the limit of many systems $N \rightarrow \infty$ there is one probable dist. $\{n_r^*\}$ and the rest are not likely.

The method of most probable values (max W ?)

Always easier to work with $\ln W$ (max $\ln W$?)

$$\ln W = \ln(N!) - \sum_r \ln(n_r!)$$

Use Stirling's formula

$$\ln W = N \ln N - N - \sum_r n_r \ln n_r + \sum_r n_r$$

$$\ln W = N \ln N - \sum_r n_r \ln n_r$$

Now if n_r change around maximal $\ln W$ the variation must vanish. We use Lagrang's multipliers

$$K = \ln W - \alpha \sum_r n_r - \beta \sum_r n_r E_r$$

$$\frac{\partial K}{\partial n_r} = -\ln n_r - 1 - \alpha - \beta E_r = 0$$

$$\ln n_r^* = -(1 + \alpha) - \beta E_r$$

$$n_r^* = C e^{-\beta E_r}$$

$$\sum_r n_r^* = N = C \sum_r e^{-\beta E_r}$$

$$n_r^* = N \frac{e^{-\beta E_r}}{\sum_s e^{-\beta E_s}}$$

constraints

$$\sum_r n_r = N$$

$$\sum_r n_r E_r = \mathcal{E}$$

This way we found α

To find β use the second constraint

$$\sum_r n_r^* E_r = \mathcal{E} = \text{---} N U$$

$$\rightarrow U = \frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

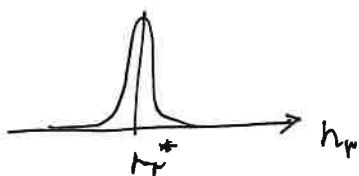
from which we can solve for β .

[This must be the TD β we get from reservoir!]

Method of mean values

A more rigorous method is by evaluating the mean of all possible $W\{n_r\}$ and showing that the deviations are minimizing drastically W

(ch. 3 - 44-49)



3.3 Using the canonical ensemble

Connect SM to TD

Canonical distribution

$$P_r = \frac{\langle n_r \rangle}{\mathcal{N}} = \frac{e^{-\beta E_r}}{\sum_s e^{-\beta E_s}}$$

Define a very useful quantity, the partition function

$$Q_N(V, T) = \sum_r e^{-\beta E_r}$$

Let's see why it is so useful:

$$\langle E_r \rangle = U = \frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = \frac{1}{Q_N} \left(- \frac{\partial}{\partial \beta} Q_N \right)$$

$$\boxed{U = - \frac{\partial}{\partial \beta} \ln Q_N} \quad \equiv \quad + \frac{\partial(A/T)}{\partial(1/T)} = - T^2 \frac{\partial}{\partial T} \left(\frac{A}{T} \right)$$

later ↑

Let's remind ourselves some TD

$$dU = Tds - pdV + \mu dN$$

$A = U - TS$ the Helmholtz free energy

$$\begin{aligned} dA &= dU - d(TS) = dU - Tds - SdT \\ &= -SdT - pdV + \mu dN \end{aligned}$$

$$S = - \left(\frac{\partial A}{\partial T} \right)_{V, N} ; P = - \left(\frac{\partial A}{\partial V} \right)_{T, N} ; \mu = \left(\frac{\partial A}{\partial N} \right)_{T, V}$$

$$\rightarrow U = A + TS = A - T \left(\frac{\partial A}{\partial T} \right)_{V, N} = - T^2 \frac{\partial}{\partial T} \left(\frac{A}{T} \right)$$

$$\boxed{U = \left[\frac{\partial(A/T)}{\partial(1/T)} \right]_{N, V}} = \frac{\partial(A/T)}{\partial T} \cdot \frac{\partial T}{\partial(1/T)} \dots \uparrow$$

By comparing

$$U = - \frac{\partial}{\partial \beta} \ln Q_N \quad \text{and} \quad U = \frac{\partial(A/T)}{\partial(1/T)}$$

knowing $\beta = \frac{1}{T}$

We find

$$A = - T \ln Q_N(V, T)$$

* Now we can derive all TD.

Examples:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{V, N} = \frac{\partial}{\partial T} \left(A - T \frac{\partial A}{\partial T} \right) = \frac{\partial A}{\partial T} - \frac{\partial A}{\partial T} - T \left(\frac{\partial^2 A}{\partial T^2} \right)_{N, V}$$

$$(2) \quad G = A + PV = A - \left(\frac{\partial A}{\partial V} \right) V$$

Now

$$P = - \left(\frac{\partial A}{\partial V} \right)_{N, T} = T \frac{\partial}{\partial V} \ln Q_N(V, T) = T \frac{\sum_r \left(-\beta \frac{\partial E_r}{\partial V} \right) e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

$$P = - \frac{\sum_r \frac{\partial E_r}{\partial V} e^{-\beta E_r}}{Q_N}$$

$$\begin{aligned} \rightarrow P dV &= - \frac{1}{Q_N} \sum_r dE_r e^{-\beta E_r} = - \sum_r P_r dE_r \\ &= - \langle dE_r \rangle = - dU \end{aligned}$$

Note that the energy levels change by the volume

We see that the pressure is the "force" driving the changes in the energy.

We still need to calculate the entropy:

$$S = \frac{1}{T} (U - A) = \beta U - \beta A = \beta \langle E_r \rangle + \ln Q_N$$

$$= \langle -\ln P_r \rangle \leftarrow P_r = \frac{e^{-\beta E_r}}{Q_N}$$

Which we can write as

$$S = -\langle \ln P_r \rangle = -\sum_r P_r \ln P_r$$

* This is a fundamental relation which shows that the entropy of a system is determined by P_r !

* Some conclusions

(i) At $T=0$: If the ground state E_{\min} is unique then $P_r = 1$ and $S = 0$

This is also known by the name "3rd law of TD".

This is also a state of perfect order so S must vanish.

(ii) When there are many accessible states each $p_r \ll 1$ then $-\log p_r \gg 1$ and S is large.

(iii) The equation $S = -\sum p_r \ln p_r$ is the starting point of communication theory developed by Shannon.

(iv) Note that the formula, of course, applies to microcanonical ensemble as well, since

$$P_r = \frac{1}{\Omega} \quad \text{and} \quad S = \langle -\log P_r \rangle = \langle +\log \Omega \rangle = \log \Omega$$

3.4 Alternative expressions for the partition function

- * In most physical cases there is more than one state with the energy E_r , this number g_r is the degeneracy. We can write

$$Q_N(V, T) = \sum_i g_i e^{-\beta E_i}$$

where the summation is over different E_i

The corresponding probability is

$$P_i = g_i P_r(E_r = E_i) = \frac{g_i e^{-\beta E_i}}{\sum_i g_i e^{-\beta E_i}}$$

- * In large systems with many particles the energy levels become very dense and we have a continuous distribution:

$$P(E) dE \propto g(E) e^{-\beta E} dE$$

and normalized

$$P(E) dE = \frac{g(E) e^{-\beta E} dE}{\int g(E) e^{-\beta E} dE} \leftarrow Q_N$$

density of states

basically $\Omega(E)$

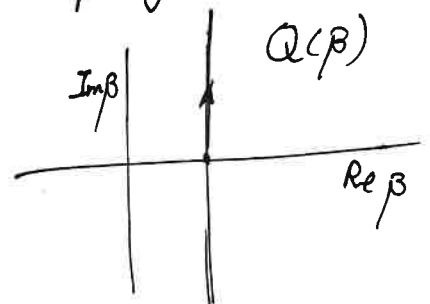
$$Q_N(V, T) = \int g(E) e^{-\beta E} dE$$

This is interesting: Q is just the Laplace transform of $g(E)$

$$Q(\beta) = \int g(E) e^{-\beta E} dE$$

So $g(E)$ is the inverse Laplace transform

$$g(E) = \frac{1}{2\pi i} \int_{\beta' - i\infty}^{\beta' + i\infty} e^{\beta E} Q(\beta) d\beta$$



(35) Classical Systems

The most important point about the canonical ensemble is that it is convenient, much more than the microcanonical ensemble. Let's see that.

Remember that we need to calculate ensemble averages in phase space

$$\langle f \rangle = \frac{\int f(q,p) \rho(q,p) d^{3N}q d^{3N}p}{\int \rho(q,p) d^{3N}q d^{3N}p}$$

$\rho(q,p)$ is the density which tells us the probability to find the system in a small $dqdp$ region of P.S.

In the canonical ensemble

$$\rho(q,p) \sim P(q,p) \sim e^{-\beta \mathcal{H}(q,p)}$$

This simplifies the ensemble average

$$\langle f \rangle = \frac{\int f(q,p) e^{-\beta \mathcal{H}(q,p)} dq dp}{\int e^{-\beta \mathcal{H}(q,p)} dq dp}$$

This is almost the partition function, but we have to remember the correspondence

$$\frac{dw}{N! h^{3N}} = \# \text{ of distinct QM states}$$

So

$$Q_N(V,T) = \frac{1}{N! h^{3N}} \int e^{-\beta \mathcal{H}(q,p)} dw$$

Ideal Gas

Let's go back to the ideal gas:

$$\mathcal{H}(p, q) = \sum_i \frac{p_i^2}{2m} \quad \text{kinetic energy}$$

The partition function is

$$Q_N(V, T) = \frac{1}{N! h^{3N}} \int e^{-\beta \sum_i \frac{p_i^2}{2m}} \underbrace{\pi d^3 q_i d^3 p_i}_{dw}$$

V^N space coordinates

$$= \frac{V^N}{N! h^{3N}} \int e^{-\sum_i \frac{p_i^2}{2mT}} \pi d^3 p_i$$

$$= \frac{V^N}{N! h^{3N}} \int \underbrace{\pi \int e^{-\frac{p_i^2}{2mT}} d^3 p_i}_I = \frac{V^N I^N}{N! h^{3N}}$$

$$\begin{aligned} I &= \int e^{-p_i^2/2mT} d^3 p_i = \\ &= \int e^{-(p_x^2 + p_y^2 + p_z^2)/2mT} dp_x dp_y dp_z \\ &= \left(\int e^{-\frac{p_x^2}{2mT}} dp_x \right) \left(\int \dots dp_y \right) \left(\int dp_z \right) = (2\pi mT)^{3/2} \end{aligned}$$

$$\frac{1}{\sqrt{2\pi\sigma^2}} \int e^{-\frac{x^2}{2\sigma^2}} dx = 1 \quad \nearrow$$

Finally

$$Q_N = \frac{V^N (2\pi mT)^{\frac{3}{2}N}}{N! h^{3N}} = \frac{1}{N!} \left(\frac{V}{\lambda^3} \right)^N$$
$$\lambda = \frac{h}{(2\pi mT)^{1/2}}$$

Notice how fast this is compared to the hypersphere calculation of Ω !

41/ The free energy is simply:

$$\begin{aligned} A(N, V, T) &= -T \ln Q_N = -T \left[N \ln \left(\frac{V}{\lambda^3} \right) - N \ln N + N \right] \\ &= -T \left[N \ln \left(\frac{V}{N \lambda^3} \right) + N \right] \\ &= +NT \left[\ln \left(\frac{N \lambda^3}{V} \right) - 1 \right] \quad \lambda = \frac{h}{\sqrt{2\pi m T}} \end{aligned}$$

We can derive the rest of the TD right away

For example:

$$\mu = \left(\frac{\partial A}{\partial N} \right)_{V, T} = T \ln \left(\frac{N \lambda^3}{V} \right) - 1 + 1 = T \ln \left(\frac{N \lambda^3}{V} \right)$$

$$P = - \left(\frac{\partial A}{\partial V} \right)_{N, T} = - \left(-NT \cdot \frac{1}{V} \right) = \frac{NT}{V}$$

etc. etc.

We further obtain

$$\begin{aligned} U &= - \frac{\partial}{\partial \beta} \ln Q_N(V, T) = - \frac{\partial}{\partial \beta} \left[N \ln \left(\frac{V}{\lambda^3} \right) - N \ln N + N \right] \\ &= - \frac{\partial}{\partial \beta} \left(N \ln \frac{1}{\lambda^3} \right) = \frac{\partial}{\partial \beta} (3N \ln \lambda) = 3N \frac{\partial}{\partial \beta} \ln \lambda \end{aligned}$$

$$\ln \lambda = \ln \left(\frac{h}{\sqrt{2\pi m}} \right) + \ln \frac{1}{\sqrt{T}} = \dots + \frac{1}{2} \ln \beta$$

$$U = 3N \frac{\partial}{\partial \beta} \ln \lambda = \frac{3N}{2\beta} = \frac{3}{2} NT$$

Note what happened in the derivation of Q_N

At some point we wrote

$$\int e^{-\sum \frac{p_i^2}{2m}} \prod_i dp_i = \prod_i \int e^{-\frac{p_i^2}{2m}} dp_i$$

What we get is the decoupling of the partition function into the partition function of single particles

$$Q_N(V, T) = \frac{1}{N!} [Q_1(V, T)]^N$$

This is only because the particles are non-interacting and we can write $\mathcal{H} = \sum \mathcal{H}_i$

(QM particles interact via the wave-function)

In principle we could have used the μ -canonical result

$$g(E) \approx \frac{\partial \Sigma}{\partial E} = \frac{1}{N!} \left(\frac{V}{h^3}\right)^N \frac{(2\pi m)^{3N/2}}{[3N/2 - 1]!} E^{3N/2 - 1}$$

And integrate $\int g(E) e^{-\beta E} dE$ but that would be tedious...

From $Q_N(\beta)$ we can get $g(E)$ which is just the inverse Laplace transform

$$g(E) = \frac{1}{2\pi i} \int_{\beta' - i\infty}^{\beta' + i\infty} Q(\beta) e^{\beta E} d\beta = \frac{V^N}{N! (h^3/2\pi m)^{3N}} \underbrace{\left[\frac{1}{2\pi i} \int_{\beta' - i\infty}^{\beta' + i\infty} \frac{e^{\beta E}}{\beta^{3N/2}} d\beta \right]}_{\mathcal{L}^{-1}(\beta^{3N/2})}$$

We have the result

$$\mathcal{L}^{-1}\left(\frac{1}{s^{n+1}}\right) = \frac{1}{2\pi i} \int_{s' - i\infty}^{s' + i\infty} \frac{e^{sx}}{s^{n+1}} ds = \begin{cases} \frac{x^n}{n!} & x \geq 0 \\ 0 & x \leq 0 \end{cases}$$

From which we get

$$g(E) = \frac{V^N}{N!} \left(\frac{2\pi m}{h^2} \right)^{3N/2} \frac{E^{(3N/2)-1}}{(3N/2-1)!}$$

The surface of the hypersphere!

This procedure can be very helpful when it's hard to calculate the density of states

(3.6) Energy fluctuations in the canonical Ensemble

In the canonical ensemble E can be anywhere in $[0, \infty]$

In the μ -canonical ensemble E is very accurate $\sim E$.
How come both ensembles give the same result?

The answer, of course is in the probability dist.

To look at the distribution:

$$U = \langle E_T \rangle = \frac{1}{Q_N} \sum_T E_T e^{-\beta E_T} = \frac{1}{Q_N} \left(-\frac{\partial}{\partial \beta} Q_N \right) = -\frac{\partial}{\partial \beta} \ln Q_N$$

$$\frac{\partial U}{\partial \beta} = -\frac{\partial}{\partial \beta^2} \ln Q_N = -\frac{\partial}{\partial \beta} \left(\frac{1}{Q_N} \frac{\partial Q_N}{\partial \beta} \right) = -\frac{1}{Q_N^2} \left(\frac{\partial Q_N}{\partial \beta} \right) \left(\frac{\partial Q_N}{\partial \beta} \right) - \frac{1}{Q_N} \frac{\partial^2 Q_N}{\partial \beta^2}$$

$$= \left(\frac{\partial \ln Q_N}{\partial \beta} \right)^2 - \frac{1}{Q_N} \sum_T E_T^2 e^{-\beta E_T} = \langle E \rangle^2 - \langle E^2 \rangle$$

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

From which we find

$$\langle \Delta E^2 \rangle = -\frac{\partial U}{\partial \beta} = -\frac{\partial U}{\partial T} \cdot \frac{\partial T}{\partial \beta} = -\frac{\partial U}{\partial T} / \frac{\partial \beta}{\partial T} = T^2 \frac{\partial U}{\partial T} = \underline{\underline{T^2 C_V}}$$

The relative r.m.s fluctuation

$$\frac{\sqrt{\langle (\Delta E)^2 \rangle}}{\langle E \rangle} = \frac{\sqrt{T^2 C_V}}{E} \sim \frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}}$$

← extensive $\propto N$

← Extensive $\propto N$

For large N the fluctuations are quite negligible.

We find that the energy is always very close to U

This explains why the two ensembles are similar

Let's look at the distribution

$$P(E) dE \propto e^{-\beta E} g(E) dE$$

$$\left. \frac{\partial}{\partial E} (e^{-\beta E} g(E)) \right|_{E=E^*} = 0$$

$$-\beta e^{-\beta E} g(E) + e^{-\beta E} \frac{\partial g}{\partial E} = 0$$

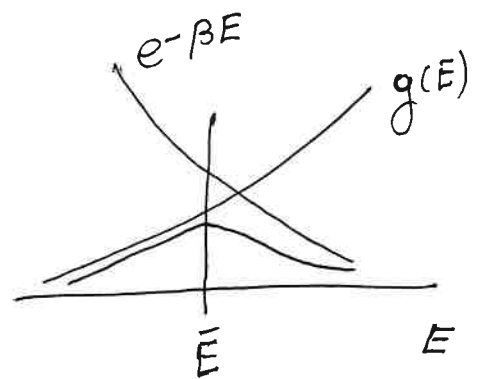
$$e^{-\beta E} \left(\frac{\partial g}{\partial E} - \beta g(E) \right) = 0$$

$$\boxed{\left(\frac{\partial \ln g}{\partial E} \right)_{E=E^*} = \beta}$$

Recall that $S(E) = \ln g$ so $\left(\frac{\partial S}{\partial E} \right)_{E=U} = \beta = \frac{1}{T}$

This implies that $E^* = U$

* In other words the most probable energy is the average.



We expand the distribution around the maximum

$$\ln P(r) = \ln [g(E) e^{-\beta E}]$$

$$\approx \ln [g(E^*) e^{-\beta E^*}] + \frac{1}{2} \frac{\partial^2}{\partial E^2} \left[\ln [g(E) e^{-\beta E}] \right] (E-U)^2$$

$$\ln g - \beta E^* = S - \frac{U}{T}$$

$$\frac{\partial^2}{\partial E^2} [\ln g(E) - \beta E] = \frac{\partial^2 \ln g}{\partial E^2} = \frac{\partial}{\partial E} \left(\frac{\partial \ln g}{\partial E} \right) = \frac{\partial^2 S}{\partial E^2}$$

$$\frac{\partial^2 S}{\partial E^2} = \frac{\partial}{\partial E} \left(\frac{\partial S}{\partial E} \right) = \frac{\partial}{\partial E} \left(\frac{1}{T} \right) = -\frac{1}{T^2} \left(\frac{\partial T}{\partial E} \right) = -\frac{1}{T^2 C_V}$$

So we get Gaussian

$$\ln P(r) = \text{const} - \frac{1}{2T^2 C_V} (E-U)^2$$

$$P(r) \approx \frac{1}{\sqrt{2\pi T^2 C_V}} e^{-\frac{(E-U)^2}{2T^2 C_V}} \cdot e^{(S - \frac{U}{T})}$$

Ideal gas $g(E) \sim E^{\left(\frac{3N}{2}-1\right)}$

$$\frac{\partial \ln g}{\partial E} = \left(\frac{3N}{2} - 1 \right) \frac{\partial \ln E}{\partial E} = \frac{3N}{2E} = \beta = \frac{1}{T}$$

$$E^* = \frac{3}{2} N T$$

$$C_V = \frac{\partial E}{\partial T} = \frac{3}{2} N$$

$$\frac{\sqrt{\langle \Delta E^2 \rangle}}{E} = \frac{\sqrt{\frac{3}{2} N \cdot T^2}}{\frac{3}{2} N T} = \sqrt{\frac{1}{\frac{3}{2} N}}$$

Finally expand Q_N itself with

$$Q_N(V, T) = e^{(S - \frac{U}{T})} \int_{-\infty}^{\infty} e^{-\frac{\Delta E^2}{2\sigma^2}} d(\Delta E)$$

$$= e^{(S - \frac{U}{T})} \cdot \sqrt{2\pi\sigma^2} \quad \sigma^2 = T^2 C_V$$

$$-T \ln Q_N \equiv A = -T(S - \frac{U}{T}) - T \ln \sqrt{2\pi T^2 C_V}$$

$$\equiv U - TS - \underbrace{\frac{1}{2} T \ln(2\pi T^2 C_V)}_{\sim \ln N}$$

In TD limit $A = U - TS$

Again we see that the difference between the ensembles vanishes like $\frac{\ln N}{N} \rightarrow 0$.

$$\frac{\ln 10^{24}}{10^{24}} = \frac{56}{10^{24}}$$

Summary

* Canonical ensemble

$$P(r) = \frac{1}{Q_N} e^{-\beta E_r}$$

* Average energy

$$U = \langle E_r \rangle = -\frac{1}{Q_N} \frac{\partial}{\partial \beta} Q_N = -\frac{\partial}{\partial \beta} \ln Q_N$$

* Helmholtz

$$A = -T \ln Q_N$$

* Entropy

$$S = \langle -\ln P(r) \rangle = -\sum P_r \ln P_r$$

* Density of states

$$Q_N(V, T) = \int g(E) e^{-\beta E} dE$$

* Classical systems

$$Q_N(V, T) = \frac{1}{N! h^{3N}} \int e^{-\beta \mathcal{H}} d\omega$$

* Energy fluctuations

$$\langle \Delta E^2 \rangle = -\frac{\partial U}{\partial \beta} = T^2 C_V \sim N$$

$$\frac{\sqrt{\langle \Delta E^2 \rangle}}{\langle E \rangle} = \frac{1}{\sqrt{N}}$$

3.7) Two Important Theorems

That are related to each other: equipartition & virial

These theorems deal with the average $\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \rangle$

$\mathcal{H}(p, q)$ classical Hamiltonian $x_i, x_j \in \{q, p\}$

$$\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \rangle = \frac{\int x_i \frac{\partial \mathcal{H}}{\partial x_j} e^{-\beta \mathcal{H}} d\omega}{\int e^{-\beta \mathcal{H}} d\omega}$$

by parts $\rightarrow = \int x_i \left(\frac{\partial \mathcal{H}}{\partial x_j} e^{-\beta \mathcal{H}} \right) dx_j d\omega_{\neq j} = \int \dots = d\omega$ deriv w.r.t x_j

$$= \int \left[-x_i \frac{e^{-\beta \mathcal{H}}}{\beta} \Big|_{x_{j, \min}}^{x_{j, \max}} + \left(\frac{\partial x_i}{\partial x_j} \right) \frac{1}{\beta} e^{-\beta \mathcal{H}} dx_j d\omega_{\neq j} \right] = \frac{1}{\beta} \delta_{ij} \int e^{-\beta \mathcal{H}} d\omega$$

vanishes at extrem x_j $\rightarrow \delta_{ij}$

* Finally $\langle x_i \frac{\partial \mathcal{H}}{\partial x_j} \rangle = \frac{\delta_{ij}}{\beta} = T \delta_{ij}$

* In the special case $x_i = x_j = p_i$

$$\langle p_i \frac{\partial \mathcal{H}}{\partial p_i} \rangle = \langle + p_i \dot{q}_i \rangle = T \delta_{ij}$$

and for $x_i = x_j = q_i$

$$\langle q_i \frac{\partial \mathcal{H}}{\partial q_i} \rangle = \langle -q_i \dot{p}_i \rangle = T \delta_{ij}$$

For all $3N$ momenta $\langle \sum_{i=1}^{3N} p_i \frac{\partial \mathcal{H}}{\partial p_i} \rangle = 3N \cdot T$

48
and for the coordinates

$$\left\langle \sum_{i=1}^{3N} q_i \frac{\partial \mathcal{H}}{\partial q_i} \right\rangle = - \left\langle \sum_{i=1}^{3N} q_i \dot{p}_i \right\rangle = 3NT$$

* If the Hamiltonian is a quadratic function of the coordinates, a canonical transformation can make it

$$\mathcal{H} = \sum_j A_j p_j^2 + \sum_j B_j q_j^2$$

For this case

$$\sum_j p_j \frac{\partial \mathcal{H}}{\partial p_j} + \sum_j q_j \frac{\partial \mathcal{H}}{\partial q_j} = 2\mathcal{H}$$

So we find

$$\left\langle \sum_j + \sum_j \right\rangle = \boxed{\langle 2\mathcal{H} \rangle = fT}$$

where f is the number of non-zero A_j and B_j .

In other words:

Each harmonic degree-of-freedom contributes $\frac{1}{2}T$ to the internal energy

Equipartition theorem (Boltzmann 1871)

$$C_v = \frac{\partial U}{\partial T} = \frac{1}{2} N T \quad \frac{1}{2} \text{ per each d.o.f.}$$

* Equip. Th. is not valid if the d.o.f. cannot be excited, as we will see in certain QM systems

49 / The virial theorem

The virial is the quantity

$$\mathcal{V} = \left\langle \sum_i q_i \dot{p}_i \right\rangle = -3NT$$

Why the virial is an interesting quantity?

Consider ideal gas (non-interacting particles)

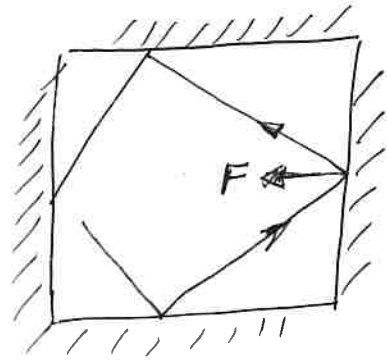
\mathcal{V} is the product of coordinates and forces acting on them. In an ideal gas forces are only from the walls.

The force on unit area is

$$-P ds \quad (\text{because } ds \text{ is outwards})$$

$$\mathcal{V}_0 = \sum_i q_i F_i = -P \oint \mathbf{F} \cdot d\mathbf{S}$$

$$= -P \underbrace{\int \text{div}(\mathbf{F}) dV}_{=3} = -3PV$$



From which we get $\mathcal{V}_0 = -3PV = -3NT \Rightarrow \boxed{PV = NT}$

The internal energy of an ideal gas is

just kinetic $K = \mathcal{H} = \sum_{i=1}^N \frac{p_i^2}{2m}$ with $3N$ d.o.f

$$\langle \mathcal{H} \rangle = U = \frac{1}{2} (3N) T \quad \text{and} \quad \boxed{\mathcal{V} = -2K}$$

If the particles interact we have (2-body)

$$\mathcal{V} = \left\langle \sum_i q_i f_i \right\rangle = \underbrace{-3PV}_{\text{ideal}} \neq \left\langle \sum_{\langle ij \rangle} r_{ij} \frac{\partial u(r_{ij})}{\partial r_{ij}} \right\rangle = -3NT$$

$$f_{ij} = - \frac{\partial u(r_{ij})}{\partial r_{ij}}$$

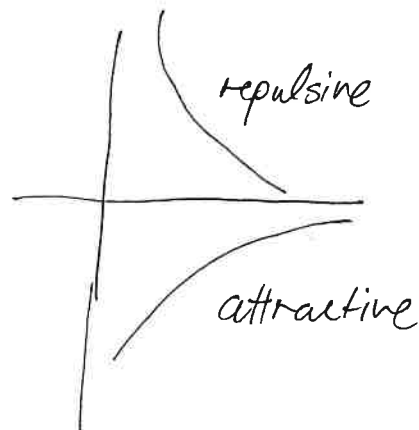
50 / From which we get

$$\frac{PV}{NT} = 1 - \frac{1}{3NT} \left\langle \sum_{i < j} r_{ij} \frac{\partial u(r_{ij})}{\partial r_{ij}} \right\rangle$$

The virial equation of state

Attractive $PV < NT$

Repulsive $PV > NT$



(3.8) Harmonic Oscillators

N independent oscillators 

For each oscillator $\mathcal{H}(q_i, p_i) = \frac{1}{2} \frac{m\omega^2}{K} q_i^2 + \frac{1}{2m} p_i^2$

A single oscillator partition function

$$Q_1(\beta) = \frac{1}{h} \int dp dq e^{-\frac{\beta}{2} m\omega^2 q^2 - \frac{\beta}{2m} p^2} \quad \boxed{\text{CLASSICAL}}$$

$$\sqrt{2\pi\sigma^2} \rightarrow = \frac{1}{h} \left(\frac{2\pi}{\beta m \omega^2} \right)^{1/2} \left(\frac{2\pi m}{\beta} \right)^{1/2} = \frac{2\pi}{h} \frac{1}{\beta \omega} = \frac{1}{\beta \hbar \omega} = \frac{T}{\hbar \omega}$$

$$Q_N(\beta) = [Q_1(\beta)]^N = (\beta \hbar \omega)^{-N}$$

Note that we assumed distinguishable oscillators

This is because the oscillators represent energy levels and real particles like phonons and photons.

$$A = -T \ln Q_N = NT \ln \left(\frac{\hbar \omega}{T} \right)$$

51 / - $\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V} = T \ln\left(\frac{h\omega}{T}\right)$ ← Same TD

- $P = \left(\frac{\partial A}{\partial V}\right) = 0$

- $S = \frac{1}{T} (U - A) = \beta \left[-\frac{\partial \ln Q}{\partial \beta} + \frac{1}{\beta} \ln Q \right]$
 $= N + (-N) \log(h\omega\beta) = N \left[1 - \log(\beta h\omega) \right]$

- $U = NT$

- $C_V = \frac{\partial U}{\partial T} = N$

↪ The mean energy per oscillator is $\frac{1}{2}T$ for kinetic and $\frac{1}{2}T$ for potential

- We can find the density of states

(A) from the entropy

$$S = N \left[1 + \log \frac{T}{h\omega} \right] = N \left[1 + \log \frac{E}{N h\omega} \right] = \ln g(E)$$

$$= \underbrace{N - N \log N}_{- \ln N!} + N \log \left(\frac{E}{h\omega} \right)$$

$$g(E) \approx \frac{1}{N!} \left(\frac{E}{h\omega} \right)^N$$

(B) By actual inverse Laplace

$$g(E) = \mathcal{L}^{-1} [Q(\beta)] = \frac{1}{(h\omega)^N} \frac{1}{2\pi i} \int_{\beta'-i\infty}^{\beta+i\infty} \frac{e^{\beta E}}{\beta^{N/2}} d\beta$$

$$= \frac{1}{(h\omega)^N} \begin{cases} \frac{E^{N-1}}{(N-1)!} & ; E \geq 0 \\ 0 & ; E \leq 0 \end{cases}$$

QM oscillator

$$E_n = (n + \frac{1}{2}) \hbar \omega$$

For a single oscillator

$$Q_1(\beta) = \sum_n e^{-\beta(n + \frac{1}{2}) \hbar \omega} = \frac{e^{-\frac{1}{2} \beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}}$$

$$= [e^{\frac{1}{2} \beta \hbar \omega} - e^{-\frac{1}{2} \beta \hbar \omega}]^{-1} = [2 \sinh(\frac{1}{2} \beta \hbar \omega)]^{-1}$$

$$Q_N(\beta) = [Q_1(\beta)]^N = [2 \sinh(\frac{1}{2} \beta \hbar \omega)]^{-N}$$

Free energy

$$A = -T \ln Q = NT \log [2 \sinh(\frac{1}{2} \beta \hbar \omega)]$$

$$\mu = \frac{\partial A}{\partial N} = \frac{A}{N}$$

$$p = \frac{\partial A}{\partial V} = 0$$

$$U = -\frac{1}{\beta} \frac{\partial \ln Q}{\partial \beta} = \frac{N}{\beta} \frac{\beta \hbar \omega \cosh(\frac{1}{2} \beta \hbar \omega)}{2 \sinh(\frac{1}{2} \beta \hbar \omega)}$$

$$= \frac{1}{2} N \hbar \omega \coth(\frac{1}{2} \beta \hbar \omega)$$

$$S = \beta(U - A) = -N \log [2 \sinh(\frac{1}{2} \beta \hbar \omega)] + \frac{1}{2} N \beta \hbar \omega \coth(\frac{1}{2} \beta \hbar \omega)$$

→ The QM oscillators do not obey equipartition

$$U = \langle \mathcal{H} \rangle = \frac{1}{2} NT$$

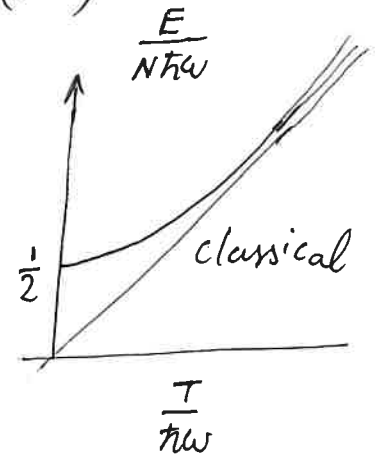
Only at high T (small β) $\coth(x) \approx \frac{1}{x}$ $U = \frac{1}{2} NT$

53

$$\frac{E}{N\hbar\omega} = \frac{1}{2} \coth\left(\frac{1}{2}\beta\hbar\omega\right) \approx \frac{1}{2} \coth\left(\frac{\hbar\omega}{2T}\right)$$

At $T \rightarrow 0$ $E = \frac{1}{2} N \hbar\omega$

At $T \rightarrow \infty$ $E = NT$



Next, let's calculate the density of states

$$g(E) = \Omega(E)$$

One way described in the book is the

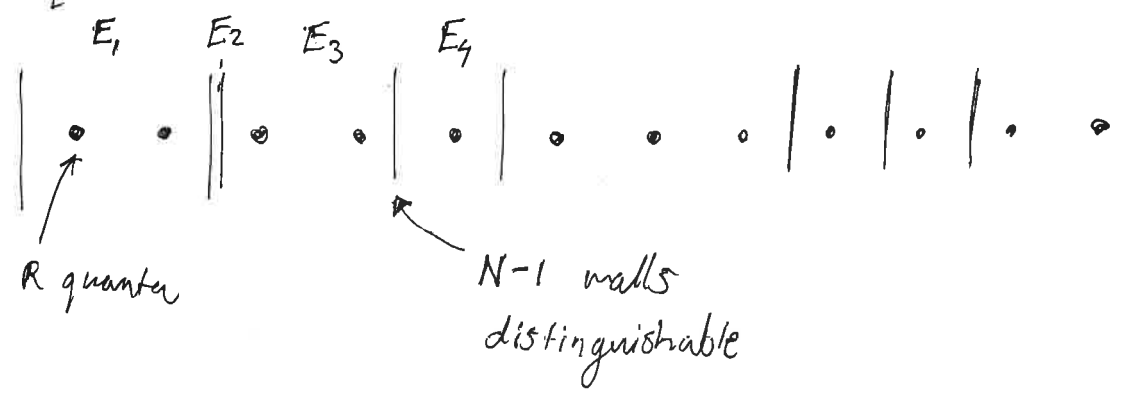
inverse Laplace transform $\Omega(E) = \mathcal{L}^{-1}[\mathcal{Q}_N(\beta)]$

- Another way is to consider the microcanonical ensemble:

We have a total energy E that we have to divide into N oscillators; each oscillator has at least $\frac{1}{2}\hbar\omega$

So we are left with $R = (E - \frac{1}{2}N\hbar\omega)/\hbar\omega \in \mathbb{N}$

$$\Omega = \left[\# \text{ of ways to divide } R \text{ quanta to } N \text{ oscillators} \right]$$



$$\Omega(E) = \frac{(R + N - 1)!}{R! (N - 1)!}$$

51 9

$$S = \ln(R+N)! - \ln R! - \ln N!$$

$$S = (R+N) \ln(R+N) - R \ln R - N \ln N$$

$\leftarrow N-1 \approx N$

Using $R = \frac{E}{\hbar\omega} - \frac{1}{2}N$ we can find S (exercise)

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \ln(R+N) \frac{\partial R}{\partial E} + \frac{\partial R}{\partial E} - \ln R \cdot \frac{\partial R}{\partial E} - \frac{\partial R}{\partial E}$$

$$= \frac{\partial R}{\partial E} \ln \frac{R+N}{R} = \frac{1}{\hbar\omega} \ln \frac{E/\hbar\omega + \frac{1}{2}N}{E/\hbar\omega - \frac{1}{2}N}$$

$$e^{\frac{1}{\hbar\omega T}} = \frac{E/\hbar\omega + \frac{1}{2}}{E/\hbar\omega - \frac{1}{2}} \rightarrow \frac{E}{N\hbar\omega} (e^{\frac{\hbar\omega}{T}} - 1) = \frac{1}{2} (1 + e^{\frac{\hbar\omega}{T}})$$

$$\boxed{\frac{E}{N\hbar\omega} = \frac{1}{2} \coth\left(\frac{\hbar\omega}{2T}\right)}$$

as in the canonical ens.

Classical limit $E \gg N\hbar\omega \rightarrow R \gg N$

$$S = (R+N) \ln(R+N) - R \ln R - N \ln N = R \ln\left(1 + \frac{N}{R}\right) + N \ln\left(\frac{R+N}{N}\right)$$

$$\approx R \cdot \frac{N}{R} + N \ln\left(\frac{R}{N} \cdot \left(1 + \frac{N}{R}\right)\right) = N + N \ln\left(\frac{R}{N}\right) + \frac{N^2}{R}$$

$$\approx N \left(1 + \ln \frac{R}{N}\right) = \cancel{N \left(1 + \ln \frac{N\hbar\omega}{E - \frac{1}{2}N\hbar\omega}\right)} \approx N \left(1 + \ln \frac{E}{N\hbar\omega}\right)$$

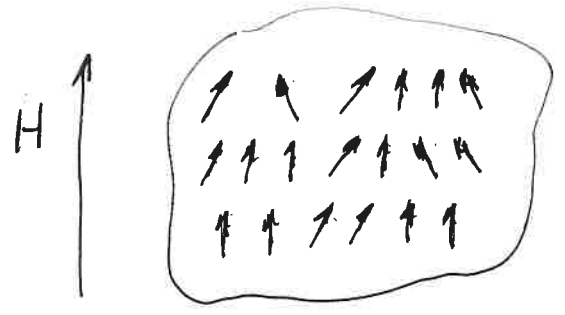
~~$$= N \left(1 + \ln \frac{E}{N\hbar\omega} - \ln \frac{1}{2} \right) = N \left(1 + \ln \frac{E}{N\hbar\omega} - \ln \frac{1}{2} \left(\coth\left(\frac{\hbar\omega}{2T}\right) - 1\right)\right)$$~~

In the classical limit

$$\frac{E}{N\hbar\omega} = \frac{1}{2} \coth \frac{\hbar\omega}{2T} \approx \frac{1}{2} \frac{2T}{\hbar\omega} = \frac{T}{\hbar\omega} \rightarrow \boxed{E = NT \text{ equipartition}}$$

3.9 Paramagnetism

- N magnetic dipoles
- μ - magnetic dipole
- H - external field



High $T \rightarrow \infty$ disorder, no magnetization

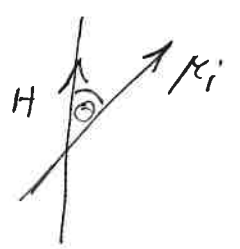
$T \rightarrow 0$ order, dipoles are aligned - magnetization

* magnets are localized and therefore distinguishable

Assume non-interacting magnets:

CLASSICAL

$$E = \sum_{i=1}^N E_i = - \sum_{i=1}^N \mu_i \cdot H = -\mu H \sum_{i=1}^N \cos \theta_i$$



Thanks to decoupling

$$Q_N = \int e^{-\beta H \sum \mu_i \cos \theta_i} \prod d\theta_i = \pi \left[\int e^{-\beta \mu H \cos \theta} d\theta \right]^N = Q_1^N$$

$$Q_1 = \int_0^{2\pi} \int_0^\pi e^{\beta \mu H \cos \theta} (\sin \theta d\theta) d\phi = \int_{-1}^1 e^{\beta \mu H z} dz \cdot 2\pi$$

$$= \frac{2\pi}{\beta \mu H} (e^{\beta \mu H} - e^{-\beta \mu H}) = 4\pi \frac{\sinh(\beta \mu H)}{\beta \mu H}$$

The average magnetization

$$M_z = N\mu \langle \cos \theta \rangle = \frac{N}{\beta} \frac{\partial \ln Q_1}{\partial H} = \frac{N}{\beta} \frac{1}{Q_1}$$

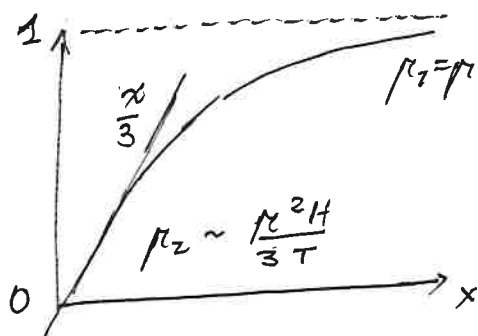
$$\mu_z = \frac{M_z}{N} = \frac{1}{\beta} \frac{\partial \ln Q_1}{\partial H}$$

$$\mu_z = \frac{1}{\beta} \frac{\partial \ln Q_1}{\partial H} = \frac{1}{\beta} \frac{\partial}{\partial H} \left[\ln [\sinh(\beta \mu H)] - \ln \beta \mu H \right]$$

$$= \frac{1}{\beta} \left[\mu \beta \frac{\cosh(\beta \mu H)}{\sinh(\beta \mu H)} - \frac{1}{H} \right] = \mu \left[\coth(\beta \mu H) - \frac{1}{\beta \mu H} \right]$$

This is Langevin's function $L(x) = \coth(x) - \frac{1}{x}$
 $x = \beta \mu H = \frac{\mu H}{T}$

$$\frac{\mu_z}{\mu} = L(x)$$



$x \ll 1 \quad L(x) \approx \frac{x}{3} \quad \text{high } T$
 $x \gg 1 \quad L(x) \approx 1 \quad \text{low } T$

$$M_z \equiv N \mu_z = \frac{N \mu^2}{3T} H \quad \text{high } T \text{ limit}$$

Susceptibility at high T

$$\frac{\partial M_z}{\partial H} = \frac{N \mu^2}{3T}$$

Curie's law

Quantum Mechanical treatment

The magnetic dipole $\underline{\mu}$ and its projection $\underline{\mu}_z$ are both quantized

gyromagnetic ratio

$$\underline{\mu} = \left(g \frac{e}{2mc} \right) \underline{l}$$

← angular momentum

$$l^2 = j(j+1) \hbar^2 \quad j = \frac{1}{2}, \frac{3}{2}, \frac{5}{2} \quad \text{on } 0, 1, 2$$

fermions

boson

g is Landé's g -factor

$g = 2$ if angular momentum is from electron spin ($J = S$)

$g = 1$ if from orbital motion ($J = L$)

mixed $g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$

↗ orbital

↖ angular

We can write

$$\mu^2 = g^2 \mu_B^2 J(J+1)$$

with $\mu_B = \frac{e\hbar}{2mc}$ Bohr's magneton

The projection on the z -axis is quantized as

$$\mu_z = g \mu_B m$$

$$m = -J, -J+1, \dots, 0, J-1, J$$

$2J+1$ orientations

Now the single particle partition is

$$Q_1(\beta) = \sum_{m=-J}^J \exp(\beta g \mu_B m H)$$

Define parameter $x = \beta(g \mu_B J) H$

$$Q_1(\beta) = \sum_{m=-J}^J e^{\frac{x}{J} \cdot m} = e^{-x} \left(\frac{e^{\frac{x}{J}(2J+1)} - 1}{e^{\frac{x}{J}} - 1} \right)$$

$$Q_1(\beta) = \frac{\sinh \left[\left(1 + \frac{1}{2J}\right) x \right]}{\sinh \left[\frac{1}{2J} x \right]}$$

5b / The mean magnetic moment is

$$M_z = N \langle \mu_z \rangle = \frac{N}{\beta} \frac{\partial}{\partial H} \ln Q_{\pm}(\beta)$$

$$= \frac{N}{\beta} \frac{\partial \ln Q_{\pm}}{\partial x} \frac{\partial x}{\partial H}$$

$$x = \beta (g \mu_B J) H$$

$$= N \frac{\beta g \mu_B J}{\beta} \left[\left(1 + \frac{1}{2J}\right) \frac{\cosh\left[\left(1 + \frac{1}{2J}\right)x\right]}{\sinh\left[\left(1 + \frac{1}{2J}\right)x\right]} - \frac{1}{2J} \frac{\cosh\left(\frac{1}{2J}x\right)}{\sinh\left(\frac{1}{2J}x\right)} \right]$$

$$= N (g \mu_B J) \left[\left(1 + \frac{1}{2J}\right) \coth\left[\left(1 + \frac{1}{2J}\right)x\right] - \frac{1}{2J} \coth\left(\frac{1}{2J}x\right) \right]$$

$B_J(x)$ Brillouin's function

$$\boxed{\bar{\mu}_z = (g \mu_B J) B_J(x)}$$

$$\coth x \approx \frac{1}{x} + \frac{x}{3}$$

low - T $x \gg 1$ $B_J(x) \approx 1$ for all J

high - T $x \ll 1$ $B_J(x) \approx \frac{1}{3} \left(1 + \frac{1}{J}\right) x$

- At high T:

$$\bar{\mu}_z = (g \mu_B J) \frac{1}{3} \left(1 + \frac{1}{J}\right) \beta (g \mu_B J) H = \frac{g^2 \mu_B^2}{3 T} J(J+1) H$$

$$\chi = \frac{\partial M_z}{\partial H} = N \frac{\partial \bar{\mu}_z}{\partial H} = \frac{N g^2 \mu_B^2 J(J+1)}{3 T} = \boxed{\frac{N \mu^2}{3 T}}$$

QM Curie's law and note that the coefficient relates directly to the QM eigenvalues of μ^2
We see QM in the classical limit ...

54/* Dependence on quantum number J :

$J \rightarrow \infty$ together with $g \rightarrow 0$ such that $\mu = \text{const.}$

$$B_J(x) \approx \coth x - \frac{1}{2J} \cdot \frac{2J}{x} = \coth x - \frac{1}{x} = L(x)$$

This corresponds to the classical limit of infinite # of orientations.

$J = \frac{1}{2}$ only two allowed orientations $m = -1, +1$

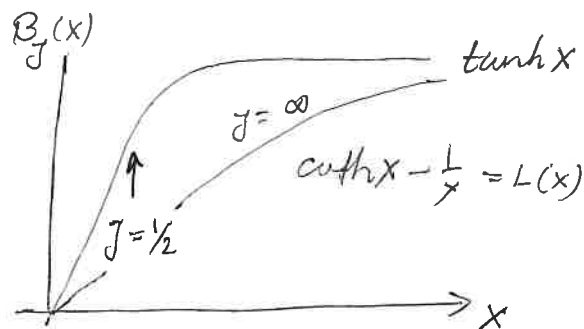
$$J = \frac{1}{2} \quad B_J(x) = 2 \coth 2x - \coth x = \tanh x$$

$$= \frac{2 \cosh^2 x - 1}{2 \sinh x \cosh x} - \frac{\cosh x}{\sinh x} = \frac{\cosh^2 x - 1}{\sinh x \cosh x} = \frac{\sinh^2 x}{\sinh x \cosh x} = \tanh x$$

If $g = 2$ we get

$$\mu_z = \mu_B \tanh x$$

The case $J = \frac{1}{2}$ is one of the simplest models that we will use all over the course



(3.10) Negative Temperature

Let's look at TD of a $J = \frac{1}{2}$ system

In fact we don't need all the elaborate calculations
 Just to remember that we have two states with
 dipoles $\mu_z = \pm \mu_B$ and energies $E = \mp \mu_B H$

60

$$Q_N(\beta) = (e^{\beta\epsilon} + e^{-\beta\epsilon})^N \quad \epsilon = \mu_B H$$

$$= [2 \cosh(\beta\epsilon)]^N$$

$$A = -T \ln Q = -NT \ln [2 \cosh(\beta\epsilon)] = -NT \ln \left[2 \cosh\left(\frac{\epsilon}{T}\right) \right]$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_H = N \ln \left[2 \cosh\left(\frac{\epsilon}{T}\right) \right] + NT \frac{\sinh(\epsilon/T)}{\cosh(\epsilon/T)} \left(-\frac{\epsilon}{T^2}\right)$$

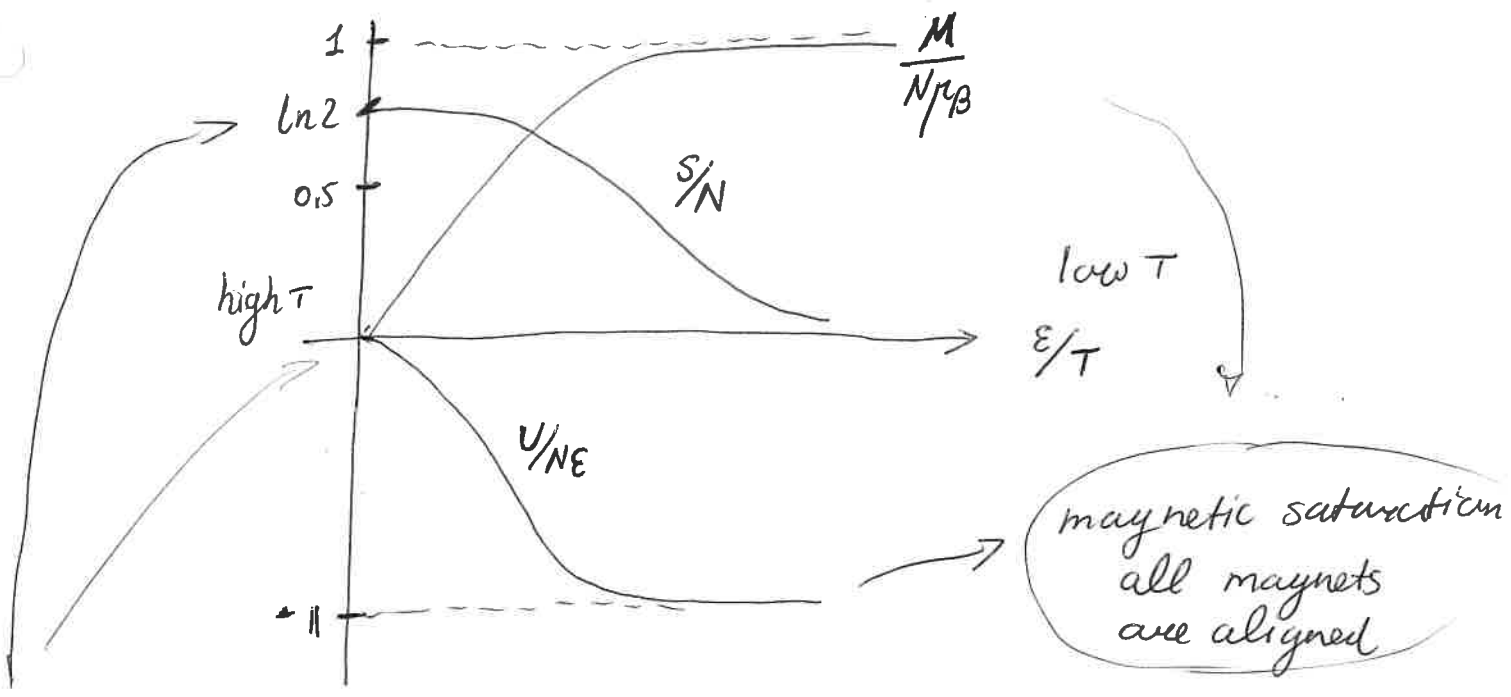
$$= N \left[\ln \left(2 \cosh\left(\frac{\epsilon}{T}\right) \right) - \frac{\epsilon}{T} \tanh\left(\frac{\epsilon}{T}\right) \right]$$

$$U = A + TS = -N\epsilon \tanh\left(\frac{\epsilon}{T}\right)$$

$$M = -\left(\frac{\partial A}{\partial H}\right)_T = +NT \frac{\sinh(\epsilon/T)}{\cosh(\epsilon/T)} \cdot \left(+\frac{\mu_B}{T}\right) = N\mu_B \tanh\left(\frac{\epsilon}{T}\right)$$

Finally, specific heat

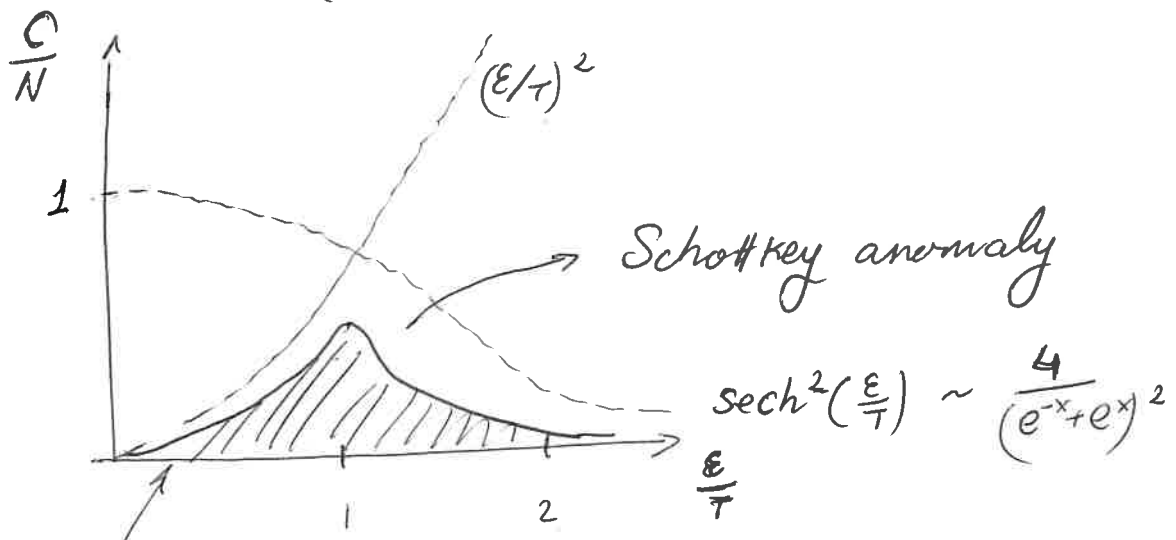
$$C = \left(\frac{\partial U}{\partial T}\right)_H = -N\epsilon \operatorname{sech}^2\left(\frac{\epsilon}{T}\right) \left(-\frac{\epsilon}{T^2}\right) = N\left(\frac{\epsilon}{T}\right)^2 \operatorname{sech}^2\left(\frac{\epsilon}{T}\right)$$



* At high T both states $\pm\epsilon$ are equally likely so $\frac{S}{N} = \ln 2$
 Random state

61 / Specific heat is of special interest

$$C = N \left(\frac{\epsilon}{T}\right)^2 \operatorname{sech}^2\left(\frac{\epsilon}{T}\right)$$



high T : energy is saturated $\frac{\partial U}{\partial T} \rightarrow 0$

What is the temperature?

Sofar we considered $T \geq 0$. Otherwise $e^{-\epsilon/T} \rightarrow \infty$ as $\epsilon \rightarrow \infty$

However, if the energy states have a maximum there is no problem with $T < 0$.

* Take the energy $U = -N\epsilon \tanh\left(\frac{\epsilon}{T}\right)$

If $U < 0 \rightarrow T > 0$

But if $U > 0 \rightarrow \underline{\underline{T < 0}}$!

$$\frac{U}{N\epsilon} = \frac{e^{-x} - e^x}{e^x + e^{-x}} = \frac{1 - e^{2x}}{1 + e^{2x}}$$

$$\frac{1}{T} = -\frac{1}{\epsilon} \tanh^{-1}\left(\frac{U}{N\epsilon}\right) = \frac{1}{2\epsilon} \ln\left(\frac{N\epsilon - U}{N\epsilon + U}\right)$$

To get S use

$$\boxed{\frac{\epsilon}{T} = \frac{1}{2} \ln\left(\frac{N\epsilon - U}{N\epsilon + U}\right)}$$

62

$$\frac{S}{N} = \underbrace{\ln\left(2 \cosh \frac{\epsilon}{T}\right)}_{-A/T} - \underbrace{\frac{\epsilon}{T} \tanh \frac{\epsilon}{T}}_{+U/NT} \quad \left| \quad \begin{array}{l} A = U - TS \\ S = (U - A) T \end{array} \right. \quad 17$$

$$\begin{aligned} &= \ln\left(\sqrt{\frac{N\epsilon - U}{N\epsilon + U}} + \sqrt{\frac{N\epsilon + U}{N\epsilon - U}}\right) - \frac{1}{2} \ln\left(\frac{N\epsilon - U}{N\epsilon + U}\right) \times \frac{\sqrt{\frac{N\epsilon - U}{N\epsilon + U}} - \sqrt{\frac{N\epsilon + U}{N\epsilon - U}}}{\sqrt{\frac{-}{+}} + \sqrt{\frac{+}{-}}} \\ &= \ln\left(\frac{2N\epsilon}{\sqrt{(N\epsilon)^2 - U^2}}\right) - \frac{1}{2} \ln\left(\frac{N\epsilon - U}{N\epsilon + U}\right) \frac{(-2U)}{2N\epsilon} \\ &= \frac{1}{2} \ln \frac{4(N\epsilon)^2}{(N\epsilon)^2 - U^2} + \frac{U}{N\epsilon} \cdot \frac{1}{2} \ln \frac{N\epsilon - U}{N\epsilon + U} \\ &= \frac{2}{2} \ln(2N\epsilon) - \frac{1}{2} \ln(N\epsilon + U) - \frac{1}{2} \ln(N\epsilon - U) \\ &\quad \neq \frac{1}{2} \frac{U}{N\epsilon} \ln(N\epsilon + U) + \frac{1}{2} \frac{U}{N\epsilon} \ln(N\epsilon - U) \end{aligned}$$

$$\rightarrow \boxed{\frac{S}{N} = -\left(\frac{N\epsilon + U}{2N\epsilon}\right) \ln\left(\frac{N\epsilon + U}{2N\epsilon}\right) - \left(\frac{N\epsilon - U}{2N\epsilon}\right) \ln\left(\frac{N\epsilon - U}{2N\epsilon}\right)}$$

- For $U = -N\epsilon$ both $T = 0$ and $S = 0$

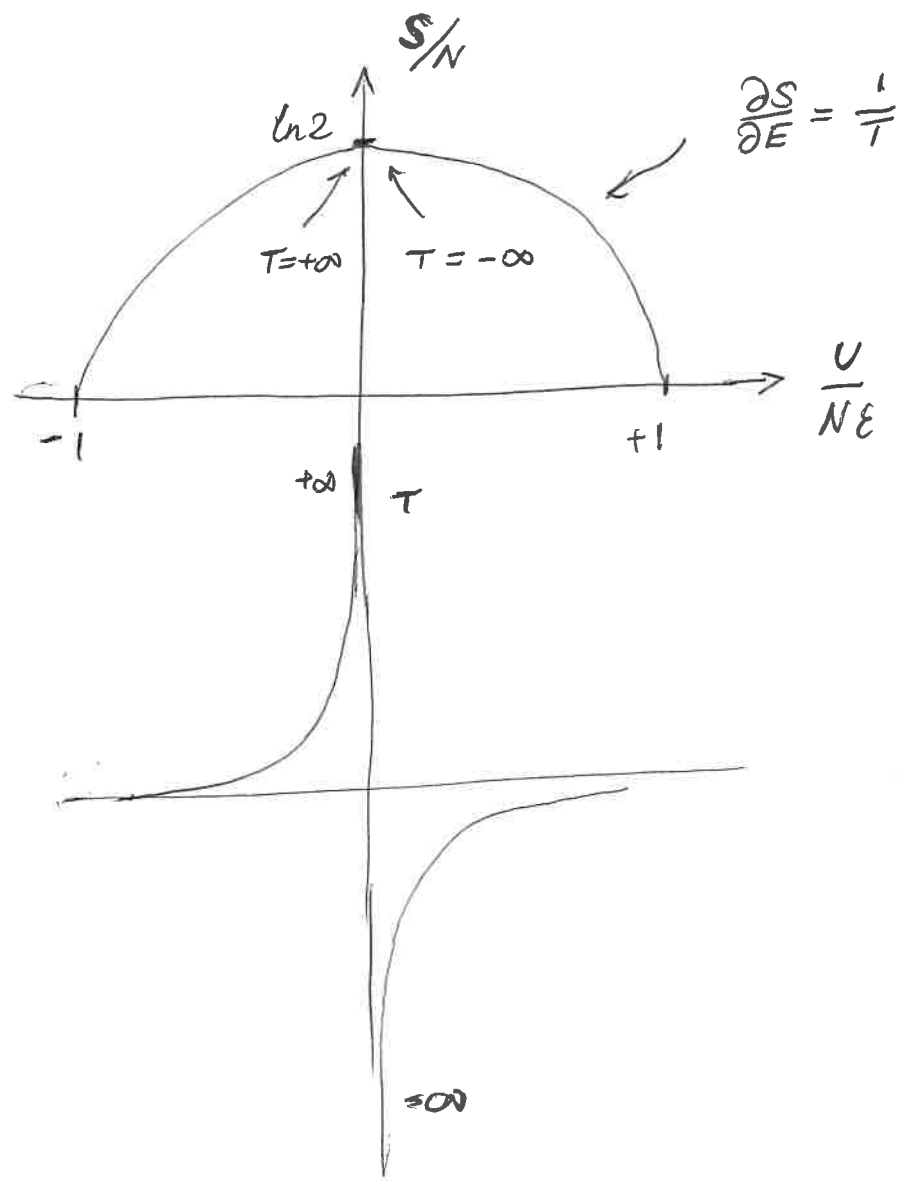
As U increases both T and S increase

Until $U = 0$ at $T = \infty$ where entropy is maximal

$$S_{\max} = N \ln 2 \quad \frac{\epsilon}{T} = \frac{1}{2} \ln \left(\frac{N\epsilon - 0}{N\epsilon + 0}\right)$$

However if we now increase U $U \rightarrow 0+$ the entropy decreases so $\frac{1}{T} = \frac{dS}{dU} \rightarrow 0$ and $T \rightarrow -\infty$!

The temperature continues to be negative.



The region $U > 0$ is abnormal because it is opposite to the magnetic field, but still can be realized.

Negative temperature is a general phenomenon

Take a system with $NT \gg E_n$ any energy

At very high T we can assume non-interacting particles

$$Q_N(\beta) = \left(\sum_n e^{-\beta E_n} \right)^N \quad \text{since } \beta E_n \ll 1$$

$$Q_N(\beta) \approx \left[\sum_n \left(1 - \beta E_n + \frac{1}{2} \beta^2 E_n^2 \right) \right]^N \quad \leftarrow \quad \left(\text{actually } |\beta E_n| \ll 1 \right)$$

64 / Now if there are g states we can write

$$\sum_n (1 - \beta \epsilon_n + \frac{1}{2} \beta^2 \epsilon_n^2) = g [1 - \beta \bar{\epsilon} + \frac{1}{2} \beta^2 \bar{\epsilon}^2]$$

$$\begin{aligned} \text{So } \ln Q_N &\approx N \left[\ln g + \ln \left(1 - \beta \bar{\epsilon} + \frac{1}{2} \beta^2 \bar{\epsilon}^2 \right) \right] \\ &\approx N \left[\ln g - \beta \bar{\epsilon} + \frac{1}{2} \beta^2 (\bar{\epsilon}^2 - \bar{\epsilon}^2) \right] \end{aligned}$$

$$A = -T \ln Q_N$$

$$\approx -\frac{N}{\beta} \ln g + N \bar{\epsilon} - \frac{N}{2} \beta \overline{\Delta \epsilon^2}$$

$$S = -\frac{\partial A}{\partial T} = N \ln g - \frac{N}{2} \beta^2 \overline{\Delta \epsilon^2}$$

$$U = \frac{N \bar{\epsilon}}{\beta} - \beta N \overline{\Delta \epsilon^2} = A + \frac{S}{\beta}$$

$$C = \frac{\partial U}{\partial T} = N \beta^2 \overline{\Delta \epsilon^2}$$

These are good approximations for $|\beta| \ll 1$

We see that S is an even function of β while U is odd which leads to

$\frac{\partial S}{\partial U}$ odd - i.e. positive and negative

