

# STATISTICAL MECHANICS

- \* is the study of systems with many degrees-of-freedom
- \* When we have such a system, it is hopeless to try and follow the detailed evolution of each d.o.f. so instead we look at their statistical properties.
- \* This approach is very fundamental and general and can be applied almost in any field of physical sciences.

## 1 THE STATISTICAL BASIS OF THERMODYNAMICS

### Historical Note

- \* Around the middle of 19<sup>th</sup> century, TD = study of macroscopic behavior of physical systems became an established discipline of physics. with the first and second laws.
- \* Around the same time, the kinetic theory of gases which aims to understand the properties of gases based on the motion of molecules.
- \* These two disciplines were connected by Ludwig BOLTZMANN, who showed that the thermodynamic entropy can be related to the microscopic d.o.f. (1872)  
The birth of STAT MECH.

2 / It was shown for the first time that:

TD, the bulk properties of matter are consequences of the statistics of the mechanics of microscopic dof

Hence the term STATISTICAL MECHANICS

### 1.1 The Macroscopic and the Microscopic states

- Consider a system with  $N$  d.o.f in a volume  $V$ .
- The typical  $N$  is huge  $\sim 10^{20}$ .
- Even if we could follow the dynamical equations of each particle, it would not teach us much.

\* So we treat the system statistically:

\* We usually take the thermodynamic limit:

- Let the number of d.o.f approach infinity  $\left\{ \begin{array}{l} N \rightarrow \infty \\ V \rightarrow \infty \end{array} \right\}$   
Such that the ratio  $\frac{N}{V}$ , the density of particles remains constant.

- In this limit the EXTENSIVE properties of the system become proportional to its size  $N \sim V$ .

- INTENSIVE properties become independent.

For example, particle density  $n \equiv \frac{N}{V} \rightarrow \text{const.}$

\* Consider the energy.

If particles are non-interacting with

$$E = \sum_i n_i \epsilon_i$$
$$N = \sum_i n_i$$

3/ - QM teaches us that the possible energies are discrete and depend on system size.

- However for large  $V$  the spectrum becomes a continuum  $\epsilon_i \rightarrow \epsilon$  and  $E$  is continuous

\* The triplet  $(N, V, E)$  defines a macrostate

\* At the molecular level, there is a huge number of possibilities to realize a given macrostate

Each such realization, the distribution of  $E$  among the possible states.

Example  $N = 10, E = 10, V = V_0$  is macrostate

$\epsilon_i = \{0, 1, 2\}$

Now imagine  $N \sim 10^{23}$

The number of combinations grows roughly like  $N! \sim e^{N \ln N}$  (faster than exponent)

$n_i \backslash \epsilon_i$	0	1	2
1	5	-	5
2	4	2	4
3	3	4	3
4	2	8	2
5	1	8	1
6	0	10	0

\* You see that there is no use to deal with each microstate but better do some statistics.

\* In principle, each microstate corresponds to a solution of Schrödinger's equation  $\psi(r_1, r_2, \dots, r_N)$  with eigenvalue  $E$  of  $\hat{H}$ .

## 4/ Postulate of equal a priori probabilities

If we have no further knowledge (constraints), we assume that all microstates are equally likely for a given macrostate.

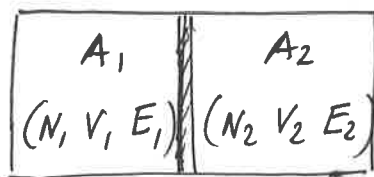
We denote the actual number of microstates as  $\Omega(N, V, E)$ .

The dependence on  $V$  is through  $\epsilon_i(V)$

\* This simple quantity  $\Omega(N, V, E)$  is the basis for the derivation of the whole TD of the system.

### 1.2) Link between statistics and TD through $\Omega$

- Consider two systems  $A_1$  and  $A_2$



$\Omega_1(N_1, V_1, E_1) = \#$  of microstates of  $A_1$

$\Omega_2(N_2, V_2, E_2) = \#$  of microstates of  $A_2$

- We bring the systems into thermal contact

For example, there is a heat conducting wall  
(Still  $N_i, V_i$  are kept constant)

- They can exchange energy:  $E^{(0)} = E_1 + E_2 = \text{const.}$

5/ We assume that there is no interaction between  $A_1$  and  $A_2$  (i.e. short range forces)  
 [Is it true for a system of stars or electric charges]

- For the composite system,  $\Omega_1(E_1)$   $\mu$ states of  $A_1$   
 $\Omega_2(E_2)$   $\mu$ states of  $A_2$

The overall  $\Omega$

$$\Omega^{(0)}(E^{(0)}, E_1) = \Omega_1(E_1) \Omega_2(E^{(0)} - E_1)$$

Q: At what value of  $E_1$  the composite system is at equilibrium?

- We assert that this is the macrostate with the maximum  $\Omega^{(0)}(E^{(0)}, E_1)$ .

Statistically, we assume that the macrostate with larger  $\Omega$  is more probable.



We identify equilibrium with this most probable macrostate  $\Omega^{(0)}(\bar{E}^{(0)}, \bar{E}_1)$

Maximize  $\Omega^{(0)}$

$$\left(\frac{\partial \Omega_1}{\partial E_1}\right)_{E_1=\bar{E}_1} \Omega_2(\bar{E}_2) + \Omega_1(\bar{E}_1) \left(\frac{\partial \Omega_2}{\partial E_2}\right)_{E_2=\bar{E}_2} \frac{\partial E_2}{\partial E_1} = 0$$

Since  $\partial E_2 / \partial E_1 = -1$  we get

$$\beta_1 \equiv \left(\frac{\partial \ln \Omega_1(E_1)}{\partial E_1}\right)_{E_1=\bar{E}_1} = \left(\frac{\partial \ln \Omega_2(E_2)}{\partial E_2}\right)_{E_2=\bar{E}_2} \equiv \beta_2$$

\* Equilibrium implies  $\boxed{\beta_1 = \beta_2}$

6  
In the TD limit ( $N \rightarrow \infty$ ), when two systems are brought into thermal contact they reach equilibrium at  $\{\bar{E}_1, \bar{E}_2\}$  when  $\beta_1 = \beta_2$ .

[In finite systems, there are fluctuations around the equilibrium]

This may remind us that in TD temperature is defined as

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

By comparing the two conditions Boltzmann found

$$\frac{\partial S}{\partial \ln \Omega} = \frac{1}{\beta T} = \text{const.}$$

which leads to

$$S = k_B \ln \Omega$$

This is a fundamental formula of physics that connects the microstates to a macrostate.

\*  $S = 0$  means that  $\Omega = 1$  (unique microstate)

\* Relation to 2<sup>nd</sup> law of TD:  $\Delta S \geq 0$

Growing disorder means  $\left. \begin{array}{l} \text{more choice of } \mu\text{-states} \\ \text{less certainty in the system} \end{array} \right\}$

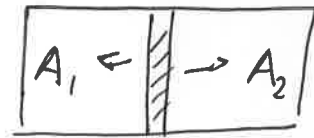
Total order implies  $S = 0 \leftrightarrow \Omega = 1$ .

[Why is  $S$  logarithmic  $S \propto \ln \Omega$  ?]

7/ (1.3) Further contact between statistics and TD

Going back to systems  $A_1, A_2$ . Assume that the separating wall is movable

Now  $V^{(0)} = V_1 + V_2 = \text{const.}$



By exactly the same argument

$$\Omega^{(0)} = \Omega_1 \Omega_2$$

$$\frac{\partial \Omega^{(0)}}{\partial E_1} = 0 \quad \wedge \quad \frac{\partial \Omega^{(0)}}{\partial V_1} = 0$$

$$\Rightarrow \left( \frac{\partial \ln \Omega_1}{\partial E_1} \right)_{N_1, V_1, E_1 = \bar{E}_1} = \left( \frac{\partial \ln \Omega_2}{\partial E_2} \right)_{N_2, V_2, E_2 = \bar{E}_2}$$

$$\text{and } \eta_1 = \left( \frac{\partial \ln \Omega_1}{\partial V_1} \right)_{N_1, E_1, V_1 = \bar{V}_1} = \left( \frac{\partial \ln \Omega_2}{\partial V_2} \right)_{N_2, E_2, V_2 = \bar{V}_2} = \eta_2$$

Now for equilibrium  $\{\beta_1, \eta_1\} = \{\beta_2, \eta_2\}$

Similarly if the wall allowed also exchange of particles we would have another parameter

$$\xi = \left( \frac{\partial \ln \Omega}{\partial N} \right)_{V, E, N = \bar{N}}$$

$$\text{and } \{\beta_1, \eta_1, \xi_1\} = \{\beta_2, \eta_2, \xi_2\}$$

To understand what these parameters mean we look at the basic formula of TD

$$dE = T dS - \overset{\text{pressure}}{p} dV + \overset{\text{chemical potential}}{\mu} dN$$

So we can write

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

$$S = k_B \ln \Omega \quad \left( \begin{array}{l} \text{let's take units where } k_B = 1 \\ \text{which means } [T] = [E] \end{array} \right)$$

$$\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{V, N} = \beta \quad ; \quad \frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_{N, E} = \eta$$

$$-\frac{\mu}{T} = \left( \frac{\partial S}{\partial N} \right) = \xi$$

This follows what we know from TD

Equal  $\{\beta, \eta, \xi\} \Leftrightarrow$  Equal  $\{T, P, \mu\}$   
which are the conditions of equilibrium.

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We have a general recipe for deriving TD from statistics.  
For macrostate  $(E, V, N)$  determine  $\Omega(E, V, N)$

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

The intensive fields are

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

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

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



derivation

$z(x, y)$



$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

Take a direction  $dx, dy$  where  $z = \text{const.}$

$$dx, dy = \left(\frac{\partial y}{\partial x}\right)_z dx, dz = 0$$

$$dz = \left(\frac{\partial z}{\partial y}\right)_x dy + \left(\frac{\partial z}{\partial x}\right)_y dx$$

$$= \left[ \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z + \left(\frac{\partial z}{\partial x}\right)_y \right] dx = 0$$

$$\rightarrow \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z / \left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial x}{\partial z}\right)_y = -1$$

9 / We can use this formula to write

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

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

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

while

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

$$\left[ \begin{array}{l} \text{We use} \\ \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \end{array} \right]$$

We assume that  
we can express  
 $E(N,V,S)$  from  
 $S(N,V,E)$

We could derive these formula directly from

$$dE = -p dV + T ds + \mu dN$$

We can get the usual definitions

$$\boxed{E = -PV + TS + \mu N}$$

by gradually increasing the system  $N, S, V$  grow proportionally while keeping the intensive variables constant.

Now we define the usual TD potentials

$$A = E - TS = -PV + \mu N \quad : \text{ Helmholtz free energy (F)}$$

$$G = A + PV = \mu N \quad : \text{ Gibbs free energy}$$

$$H = E + PV = \mu N + TS = G + TS \quad : \text{ Enthalpy}$$

The specific heats, at constant volume and pressure are

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

$$C_P = T \left( \frac{\partial S}{\partial T} \right)_{N,P} = \left( \frac{\partial (E + PV)}{\partial T} \right)_{N,P} = \left( \frac{\partial H}{\partial T} \right)_{N,P}$$

### 1.4 Classical Ideal Gas

- The simplest and most basic system in SM is the classical ideal gas composed of monoatomic molecules (noble gases He, Ar, Xe).
- In the limit of high  $T$  and low  $\frac{N}{V}$  most systems approach this limit.

Since the particles are non-interacting, the total # of microstate is just the product of # for each particle

$$\Omega(N, E, V) \propto V^N$$

$$S = \ln \Omega = N \ln V$$

$$\frac{P}{T} = \left( \frac{\partial \ln \Omega}{\partial V} \right)_{N,E} = \frac{N}{V}$$

In QM we also demand that the single particle wave functions do not overlap much

from which we get the equation of state:

$$\boxed{PV = NT}$$

if we measure  $T$  in degrees

$$PV = k_B N T$$

Chemists like to measure the number in moles

$$N = n N_A \quad N_A = 6 \cdot 10^{23} \text{ Avogadro number}$$

And they write

$$\boxed{PV = N k_B T = n R T} \quad \text{with } R = k_B N_A$$

Thus, for any classical system of non-interacting particles the ideal-gas law holds.

To derive the full TD we need to know how  $\Omega$  depends on  $E$ . In other words, how many ways we have to distribute the energy

$$\sum_{k=1}^N \epsilon_k = E$$

From the solution of Schrödinger equation in a box, the energy levels are quantized as

$$E(n_x, n_y, n_z) = \frac{h^2}{8mL^2} (n_x^2 + n_y^2 + n_z^2) \quad L - \text{size of box}$$

Therefore, the number of distinct eigenfunctions i.e. the # of  $\mu$ -states is # solutions to

$$\cancel{\epsilon} n_x^2 + n_y^2 + n_z^2 = \frac{8mL^2}{h^2} \cdot \epsilon \quad \text{where } n_x, n_y, n_z \text{ are natural numbers}$$
$$n_x^2 + n_y^2 + n_z^2 = \frac{8mV^{2/3}}{h^2} \epsilon \quad \text{call it } \Omega(1, \epsilon, V)$$

Similarly

$$\sum_{r=1}^{3N} n_r^2 = \frac{8mV^{2/3}}{h^2} E$$

$$\Omega(N, V, E) = \# \text{ solutions to}$$

Even before we solve this equation, we see that  $E$  and  $V$  enter via a combination  $V^{2/3}E$  (in general dimension  $V^{2/d}E$ )

So 
$$S(N, V, E) = S(N, V^{2/3}E)$$

Hence, for constant  $S, N$  which defines reversible adiabatic process  $V^{2/3}E = \text{const.}$

Then,

$$P = - \left( \frac{\partial E}{\partial V} \right)_{S, N} = \frac{2}{3} \cdot \frac{E}{V}$$

$$E = c V^{-2/3} \quad \frac{\partial E}{\partial V} = -\frac{2}{3} c V^{-5/3} = -\frac{2}{3} \frac{E}{V}$$

That is, the pressure of non-relativistic, non-interacting particles is  $\left(\frac{2}{d}\right)$  times the energy density

This holds for both quantum and classical systems.

Similarly  $PV^{5/3} = \text{const.}$  in adiabatic process.

Together with the ideal gas law

$$\left. \begin{array}{l} PV = NT \\ PV = \frac{2}{3}E \end{array} \right\} \rightarrow \boxed{E = \frac{3}{2}NT} \quad \frac{1}{2}T \text{ per d.o.f.}$$

Now we finally calculate  $\Omega(N, V, E) = \Omega_N(E^*)$

$$E^* = \frac{8mL^2}{h^2} E$$

What we actually look for is

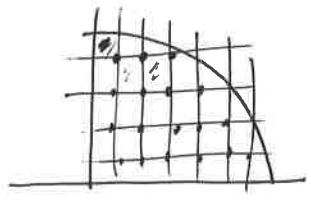
# of integral lattice points on hypersphere of radius  $\sqrt{E^*}$

To avoid jumps in  $\Omega_N(E^*)$  due to discreteness, we look at  $\Sigma_N(E^*) = \#$  of integral points in the sphere.

$$\Sigma(N, V, E) = \sum_{E' \leq E} \Omega(N, V, E')$$

or

$$\Sigma_N(E^*) = \sum_{E^{*'} \leq E^*} \Omega_N(E^{*'})$$



Asymptotically,  $\Sigma_1(E^*) = \frac{1}{8}$  Sphere ( $R = \sqrt{E^*}$ )

$$\lim_{E^* \rightarrow \infty} \Sigma_1(E^*) \approx \frac{\pi}{6} E^{*3/2}$$

For the hypersphere  $\Sigma_N(E^*) = \left(\frac{1}{2}\right)^{3N} \left[ \frac{\pi^{3N/2}}{(3N/2)!} E^{*3N/2} \right]$

which for  $E^* = \frac{8mL^2}{h^2} E = \frac{8mV^{2/3}}{h^2} E$   $V_{sp}(3N)$

$$\Sigma_N(E) = \frac{V^{3N/2}}{(3N/2)!} \left(\frac{V}{h^3}\right)^{3N} (2\pi mE)^{3N/2}$$

Taking log and applying Stirling's formula  $\log n! \approx n \log n - n$

$$\begin{aligned} \log \Sigma_N(E) &= N \cdot \log \left[ \frac{V}{h^3} (2\pi mE)^{3/2} \right] - \underbrace{\frac{3N}{2} \log \frac{3N}{2} + \frac{3N}{2}}_{N \log \left(\frac{3N}{2}\right)^{3/2} + \frac{3}{2}N} \\ &= N \log \left[ \frac{V}{h^3} \left(\frac{2\pi mE}{3N}\right)^{3/2} \right] + \frac{3}{2}N \end{aligned}$$

# Hyper sphere volume

Integrate hyper-Gaussian

$$I = \int e^{-\frac{1}{2} \sum x_i^2} \prod_i dx_i = \prod_i \int e^{-\frac{1}{2} x_i^2} dx_i = (2\pi)^{N/2}$$

Now in spherical coordinates

$$I = \int_0^{\infty} \left[ \int_{S_{N-1}(r)} e^{-\frac{1}{2} r^2} dS_{N-1}(r) \right] dr$$

Now  $S_{N-1}(r) = S_{N-1}(1) r^{N-1}$  so

$$I = S_{N-1}(1) \cdot \int_0^{\infty} e^{-\frac{1}{2} r^2} r^{N-1} dr$$

$$\left. \begin{aligned} t &= \frac{r^2}{2} \rightarrow \\ r &= (2t)^{1/2} \\ dr &= 2^{-1/2} t^{-1/2} dt \end{aligned} \right\} = S_{N-1}(1) 2^{\frac{N}{2}-1} \underbrace{\int_0^{\infty} e^{-t} t^{\frac{N}{2}-1} dt}_{\Gamma(\frac{N}{2}) \approx (\frac{N}{2}-1)!}$$

$$S_{N-1}(1) 2^{\frac{N}{2}-1} \Gamma(\frac{N}{2}) = (2\pi)^{N/2}$$

$$S_{N-1}(1) = \frac{2\pi^{N/2}}{\Gamma(\frac{N}{2})}$$

$$S_{N-1}(R) = \frac{2\pi^{N/2}}{\Gamma(\frac{N}{2})} R^{N-1} \rightarrow S_N(R) = R^N$$

$$V_N(R) = \int_0^R S_{N-1}(r) dr = \frac{2\pi^{N/2}}{N \Gamma(\frac{N}{2})} \cdot R^N = \frac{\pi^{N/2}}{\Gamma(\frac{N}{2}+1)} R^N$$

$$\frac{N}{2} \Gamma(\frac{N}{2}) = \Gamma(\frac{N}{2}+1)$$

$$\approx \left(\frac{N}{2}\right)!$$



14 / To derive the value of  $\Omega_N(E)$  let's calculate the volume of a thin shell between  $E - \frac{1}{2}\Delta$  and  $E + \frac{1}{2}\Delta$

$$\Gamma = \Delta \cdot \frac{\partial \Sigma(N, V, E)}{\partial E} = \Delta \cdot \frac{3N}{2E} \Sigma(N, V, E)$$

$$\ln \Gamma = \ln \Sigma + \underbrace{\left\{ \ln \frac{3N}{2} + \ln \frac{\Delta}{E} \right\}}_{\text{negligible}} \approx \ln \Sigma$$

We see that the width of  $\Delta$  does not really matter since in high dimension "all" the volume is at the surface of hyper-sphere...

From all this,

$$\Omega(N, V, E) = N \ln \left[ \frac{V}{h^3} \left( \frac{4\pi m E}{3N} \right)^{3/2} \right] + \frac{3}{2} N$$

We can invert this and get

$$\frac{V}{h^3} \left( \frac{4\pi m E}{3N} \right)^{3/2} = \exp \left( \frac{S}{N} - \frac{3}{2} \right)$$

$$E = \frac{3N h^2 N}{4\pi m V^{2/3}} \exp \left( \frac{2}{3} \frac{S}{N} - 1 \right) \quad (\text{keep})$$

$$T = \left( \frac{\partial E}{\partial S} \right)_{V, N} = \frac{2E}{3N} \rightarrow E = \frac{3}{2} N T$$

The specific heat at constant volume

$$C_V = \left( \frac{\partial E}{\partial T} \right)_{N, V} = \frac{3}{2} N \quad \left( \text{almost the number of} \right. \\ \left. \text{d.o.f.} \dots \right)$$

$$P = - \left( \frac{\partial E}{\partial V} \right)_{N,S} = - \left( - \frac{2}{3} \frac{E}{V} \right) = \frac{2}{3} \frac{E}{V}$$

with  $E = \frac{3}{2} NT$  this gives  $PV = NT$

$$H = E + PV = \frac{5}{3} E = \frac{5}{3} \cdot \frac{3}{2} PV = \frac{5}{2} PV$$

$$C_p = \left( \frac{\partial H}{\partial T} \right)_{P,N} = \frac{5}{3} \left( \frac{\partial E}{\partial T} \right)_{P,N} \quad \cancel{P, N, T}$$

$$= \frac{5}{2} P \left( \frac{\partial V}{\partial T} \right)_{P,N} = \frac{5}{2} P \cdot \frac{N}{P} = \frac{5}{2} N \quad \left| \quad V = \frac{NT}{P} \right.$$

\* Isothermal change: Now if we follow an isotherm  $T = \text{const.}$   $N = \text{const.}$  then the total energy of the gas  $E = \frac{3}{2} NT = \text{const.}$   
 $PV = NT = \text{const.}$

Then the entropy change is

$$\Delta S = S_f - S_i = N \ln \frac{V_f}{V_i}$$

\* Adiabatic change (isolated system,  $TdS = 0$ )

$$S = \text{const.} \quad N = \text{const.} \quad \Rightarrow \quad V E^{3/2} = \text{const.}$$

$$E \propto V^{-2/3} \quad T = \frac{2}{3} \frac{E}{N} \propto V^{-2/3}$$

$$P = \frac{NT}{V} \propto V^{-5/3}$$

In the adiabatic process  $dE = -P dV = -\frac{2E}{3V} dV$

This was our first demonstration of how to derive TD from S

# 15 The Entropy of Mixing and the Gibbs Paradox

There is one serious problem with our expression for entropy

$$S = \ln Z = N \ln \left[ \frac{V}{h^3} \left( \frac{4\pi m E}{3N} \right)^{3/2} \right] + \frac{3}{2} N$$

It's not extensive!

We have a term  $-\frac{3}{2} N \ln N$

This means that if we increase the system by a factor  $\alpha$  the entropy does not increase by  $\alpha$

$$V \rightarrow \alpha V ; N \rightarrow \alpha N ; E \rightarrow \alpha E$$

$$S \rightarrow \alpha S + \underbrace{N \alpha \log \alpha}$$

This means that the entropy is not additive!

Another look at this problem is the Gibbs paradox

$N_2$	$T$	$T$	$N_1$
$V_2$			$V_1$

→  
mixing

$N = N_1 + N_2$
$V = V_1 + V_2$
$T$

Used  
 $E = \frac{3}{2} NT$

$$S_i = N_i \ln V_i + \frac{3}{2} N_i \left[ 1 + \ln \left( \frac{2\pi m_i T}{h^2} \right) \right] \quad i = 1, 2$$

after mixing

$$S_T = \sum_{i=1}^2 \left\{ N_i \ln V + \frac{3}{2} N_i \left[ 1 + \ln \left( \frac{2\pi m_i T}{h^2} \right) \right] \right\}$$

$$S_i = N_i \log \left( \frac{V}{\lambda_i^3} \right) + \frac{3}{2} N_i$$

$$\lambda_i = \frac{h}{\sqrt{2\pi m_i T}}$$

17/ The entropy of mixing is

$$\Delta S = S_T - \sum_{i=1}^2 S_i = N_1 \log \frac{V}{V_1} + N_2 \ln \frac{V}{V_2} \geq 0 \quad (\text{more disorder})$$

For the case where the initial densities are equal

$$\frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N}{V}$$

$$\Delta S = N_1 \ln \frac{N}{N_1} + N_2 \ln \frac{N}{N_2}$$

Now take molecules of the same gas:

$$m_1 = m_2 \quad \text{and}$$

$$S_T = N \ln V + \frac{3}{2} N \left\{ 1 + \ln \left( \frac{2\pi m T}{h^2} \right) \right\}$$

So again

$$\Delta S = N_1 \ln \frac{N}{N_1} + N_2 \ln \frac{N}{N_2}$$

However this is unacceptable!

This mixing process is definitely reversible:

One has just to re-insert the partition

(Note that this is true only if the molecules are similar)

We see that

$$\Delta S = \ln(N_1 + N_2)! - \ln N_1! - \ln N_2!$$

If we divide  $\Omega$  by  $N!$  we avoid this problem

Then we would get  $S \rightarrow S - N \log N + N$

$$S = N \log \left( \frac{V}{N} \right) + \frac{3}{2} N \left\{ \frac{5}{2} + \ln \left( \frac{2\pi m T}{h^2} \right) \right\}$$

That was exactly what Gibbs suggested.

Now we see that  $S \rightarrow \alpha S$  is additive

And  $\Delta S = 0$  for mixing

Note that the expression for  $E(S, V, N)$  is modified a bit

$$E = \frac{3h^2}{4\pi m} \cdot \frac{N^{5/3}}{V^{2/3}} \exp\left(\frac{2}{3} \frac{S}{N} - \frac{5}{3}\right)$$

← factor of N
← was 1

Now  $E$  is also extensive,  $E \rightarrow \alpha E$

All other results remain the same.

The only potential that changes is w.r.t.  $N$ ...

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{V, S} = \frac{5}{3N} E \left[ \frac{5}{3N} - \frac{2S}{3N^2} \right]$$

To express in  $N, V, T$  we write

$$\begin{aligned} \mu &= \frac{5}{3} \cdot \frac{3}{2} T - \frac{2}{3} \cdot \frac{3}{2} T \cdot \left\{ \log\left(\frac{V}{N}\right) + \frac{5}{2} + \frac{3}{2} \ln\left(\frac{2\pi m T}{h^2}\right) \right\} \\ &= -T \log\left[ \frac{V}{N} \left(\frac{2\pi m T}{h^2}\right)^{3/2} \right] \end{aligned}$$

$$\boxed{\mu = T \log\left[ \frac{N h^3}{V (2\pi m T)^{3/2}} \right]} \equiv \frac{G}{N} \quad \text{intensive!}$$

Another quantity of interest is the Helmholtz energy

$$A = F = E - TS = G + PV = NT \left\{ \log\left[ \frac{N h^3}{V (2\pi m T)^{3/2}} \right] + 1 \right\}$$

1.6 What is the correct enumeration of microstates?

The reason for the ad-hoc factor  $N!$  is that the particles are not only identical but also indistinguishable:

All we can say is the number of particles in each energy state  $n_1$  in  $E_1$ ,  $n_2$  in  $E_2$  and so on.

The correct way to define a  $\mu$ -state is by this distribution  $\{n_j\}$  and not through assigning  $E$  to a particle indexed  $i$ .

If we exchange particles between two energies, then in the old counting method there are two  $\mu$ -states, but now there is only one!

The total # of permutations if one distributes  $N$  particles is  $\frac{N!}{n_1! n_2! \dots}$  with  $\sum_j n_j E_j = E$  and  $\sum_j n_j = N$

If our particles were distinguishable all these permutations were different  $\mu$ -states, but they are not!

So in principle we should correct every distribution separately.

Gibbs recipe ignores that and divides by  $N!$

This is true if  $n_j$  are either 0 or 1 (classical limit),  $\bar{n}_i \ll 1$

## Summary - Ch. (1)

- $\Omega(E, V, N) = \# \mu\text{-states that exhibit macrostate } (E, V, N)$
- Postulate of equal probabilities
- $\left\{ \begin{array}{l} S = \ln \Omega \\ \Omega(E, V, N) \end{array} \right\}$  links stat-mech to TD
- Equilibrium  $\rightarrow \max \Omega^{(o)} = \Omega_1 \Omega_2$   
 $\{P, T, \mu\}$  are equal

- TD potentials:

$$dE = -pdV + TdS + \mu dN$$

$$\left\{ \begin{array}{l} E = -PV + TS + \mu N \\ A = E - TS = -PV + \mu N \\ G = A + PV = \mu N \\ H = E + PV = TS + \mu N = G + TS \end{array} \right.$$

- Ideal gas:  $PV = NT$   
 $E = \frac{3}{2}NT$

$$S = N \log\left(\frac{V}{N}\right) + \frac{3}{2}N \left\{ \frac{5}{2} + \ln\left(\frac{2\pi m T}{h^2}\right) \right\}$$

$$= \frac{5}{2}N + N \log\left[\left(\frac{2\pi m T}{h^2}\right)^{3/2} V\right] = \frac{5}{2}N + N \log\left(\frac{V}{\lambda^3}\right)$$

$$\lambda = \frac{h}{\sqrt{2\pi m T}}$$

# ② Theory of Ensembles

A macrostate  $\{E, V, N\}$  corresponds to a huge set of  $\mu$ -states of number  $\Omega(E, V, N)$ .

These states are equally probable.



After long enough time we can assume that the time average = ensemble average

The Ergodic assumption  $\langle f(t) \rangle = \langle f \rangle_{\text{ensemble}}$ . This why looking at ensembles is so useful to us

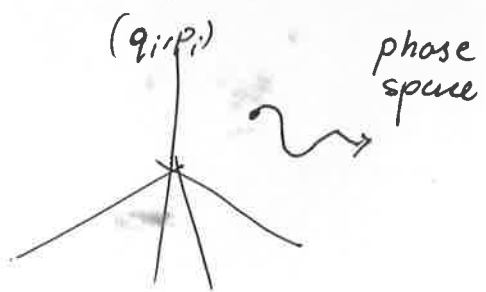
## ②.1 Phase space of a classical system

$\mu$ -state of a classical system is defined by specifying all positions and momenta of the particles:

$$+ \begin{cases} 3N \text{ positions } q_1, q_2, \dots, q_{3N} & (x_i, y_i, z_i) \\ 3N \text{ momenta } p_1, p_2, \dots, p_{3N} & (p_x, p_y, p_z) \end{cases}$$

This set is a point in  $\mathbb{R}^{6N} \equiv$  PHASE SPACE  
 $(q_i, p_i)$

This point evolves in time



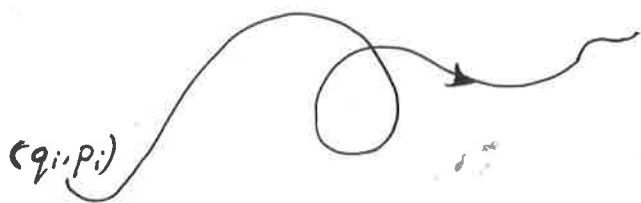


The time evolution is determined by the canonical equations of motion (a.k.a. Hamilton's Eqs.)

$$\left\{ \begin{array}{l} \dot{q}_i = \frac{\partial \mathcal{H}}{\partial p_i} \\ \dot{p}_i = -\frac{\partial \mathcal{H}}{\partial q_i} \end{array} \right\} \quad \begin{array}{l} 6N \text{ equations} \\ i = 1, 2, \dots, 3N \end{array}$$

- The function  $\mathcal{H}(q_i, p_i)$  is the Hamiltonian.

$(\dot{q}_i, \dot{p}_i)$  is the velocity vector in phase space



example: free particle in gravity

$$\mathcal{H} = \frac{p_x^2 + p_y^2 + p_z^2}{2m} + mgz$$

$$\dot{x} = \frac{p_x}{m}; \quad \dot{y} = \frac{p_y}{m}; \quad \dot{z} = \frac{p_z}{m}$$

$$\dot{p}_x = 0; \quad \dot{p}_y = 0; \quad \dot{p}_z = -mg$$

- Usually the trajectory is limited to a finite region in phase space

$$q_i \in V$$

$E$  limits both  $p_i, q_i$  through  $\mathcal{H}(p, q)$

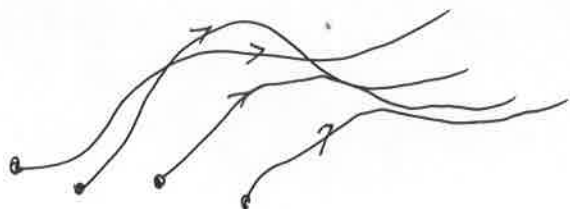
- In particular if total energy is conserved

hypersurface

$$\mathcal{H}(q_i, p_i) = E = \text{const.}$$

If  $E$  is not accurately determined the trajectory is in the hypershell  $(E - \frac{\Delta}{2}, E + \frac{\Delta}{2})$ .

- The movement of an ensemble of  $\mu$ -states:



- We can describe the motion by the density function  $\rho(q, p, t)$

$$q_i \quad p_i \quad i=1, \dots, 3N$$

$\int d^{3N}p d^{3N}q \Rightarrow$  # of systems (points) in  $d^{3N}q d^{3N}p$

- The density function tells the distribution of  $\mu$ -states in phase space, as a function of time.
- We can now define the ensemble average of a quantity  $f(q, p)$

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

integration  
over whole Phase Space

- \* Note that  $\langle f \rangle$  may be a function of time.
- \* The ensemble is stationary if  $\rho$  does not depend on time explicitly

$$\boxed{\frac{\partial \rho}{\partial t} = 0}$$

This implies that  $\Rightarrow \frac{\partial \langle f \rangle}{\partial t} = 0$  as well

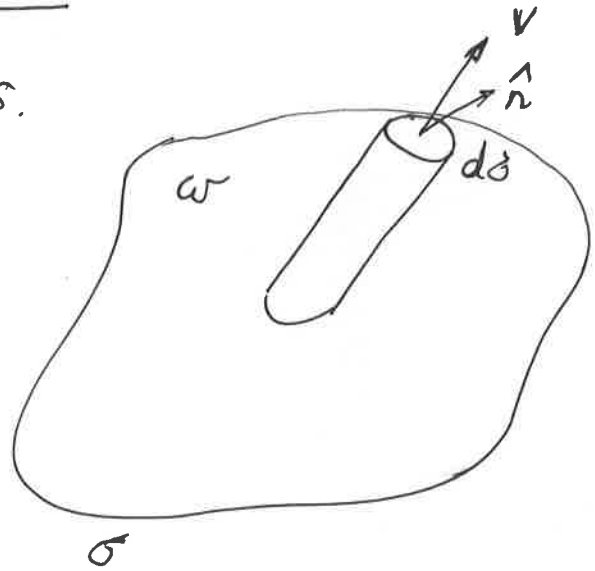
- \* Of course, a system at equilibrium is stationary.

# Liouville's theorem

Consider a volume  $\omega \in P.S.$   
with surface  $\sigma$

$$\left. \begin{array}{l} \text{rate of} \\ \text{change} \\ \text{\# systems} \end{array} \right\} = \frac{\partial}{\partial t} \int_{\omega} \rho \, d\omega$$

$$\text{where } d\omega = d^{3N}q \, d^{3N}p$$



On the other hand, the rate is also equal to  
the flux through the surface

$$\int_{\sigma} \rho \vec{v} \cdot \hat{n} \, d\sigma = \int_{\omega} \text{div}(\rho \vec{v}) \, d\omega$$

divergence theorem

Here, divergence is

$$\text{div}(\rho \vec{v}) = \sum_{i=1}^{3N} \frac{\partial}{\partial q_i} (\rho \dot{q}_i) + \sum_{i=1}^{3N} \frac{\partial}{\partial p_i} (\rho \dot{p}_i)$$

Since points do not appear/disappear spontaneously

$$\frac{\partial}{\partial t} \int_{\omega} \rho \, d\omega = - \int_{\omega} \text{div}(\rho \vec{v}) \, d\omega$$

$$\Rightarrow \int_{\omega} \left[ \frac{\partial \rho}{\partial t} + \text{div}(\rho \vec{v}) \right] d\omega = 0$$

$$\Rightarrow \boxed{\frac{\partial \rho}{\partial t} + \text{div}(\rho \vec{v}) = 0}$$

equation  
of  
continuity

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left( \frac{\partial \rho}{\partial q_i} \dot{q}_i + \rho \frac{\partial \dot{q}_i}{\partial q_i} \right) + \sum_{i=1}^{3N} \left( \frac{\partial \rho}{\partial p_i} \dot{p}_i + \rho \frac{\partial \dot{p}_i}{\partial p_i} \right) = 0$$

$$\Rightarrow \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left( \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) + \rho \sum_{i=1}^{3N} \left( \frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right) \equiv 0$$

$$\frac{\partial \dot{q}_i}{\partial q_i} = \frac{\partial^2 \mathcal{H}}{\partial p_i \partial q_i} \quad \frac{\partial \dot{p}_i}{\partial p_i} = \frac{\partial}{\partial p_i} \left( - \frac{\partial \mathcal{H}}{\partial q_i} \right) = - \frac{\partial^2 \mathcal{H}}{\partial p_i \partial q_i}$$

$$\Rightarrow \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left( \frac{\partial \rho}{\partial q_i} \frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial \mathcal{H}}{\partial q_i} \right)$$

this is the Poisson bracket  $[\rho, \mathcal{H}]$

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_{i=1}^{3N} \left( \frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) = \frac{\partial \rho}{\partial t} + [\rho, \mathcal{H}] = 0$$

Liouville's theorem The total time derivative

of the density vanishes.  $\rho$ : in a f.o.r.

moving with the systems  $\rho = \text{const.}$

\* The "fluid" in P.S. is incompressible.

\* If  $[\rho, \mathcal{H}] = 0$  then also  $\frac{\partial \rho}{\partial t} = 0$

Of course if  $\rho$  is independent of coordinates

$$[\rho, \mathcal{H}] = 0$$

This corresponds to an ensemble that uniformly distributed over all  $\mu$ -states at all times.

Then the ensemble average is

$$\langle f \rangle = \frac{1}{\omega} \int f(q, p) d\omega \quad \text{because } \rho = \rho_0$$

$\Rightarrow$  any point is equally likely  
[postulate of equal prob.]

\* Another way to satisfy  $\frac{\partial \rho}{\partial t} = 0$  is to

have  $\rho [H(q, p)]$   $\frac{\partial q_i}{\partial t}$   $(-\frac{\partial p_i}{\partial t})$

Then

$$\begin{aligned} & \frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \\ &= \frac{\partial \rho}{\partial H} \frac{\partial H}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial H} \frac{\partial H}{\partial p_i} \frac{\partial H}{\partial q_i} = 0 \end{aligned}$$

For example if  $\rho(q, p) \sim e^{-H(q, p)/T}$   $\frac{\partial \rho}{\partial t} = 0$

### 2.3 The microcanonical Ensemble

- Macrostate is defined by  $(N, V, E)$ .
- Equivalently we can define hypershell  $[E - \frac{\Delta}{2}, E + \frac{\Delta}{2}]$
- Each of the  $\mu$ -states is equally probable.
- The shell is defined  $E - \frac{1}{2}\Delta \leq H(q, p) \leq E + \frac{1}{2}\Delta$

\* The microcanonical ensemble is a collection of systems with a density function  $\rho$

$$\rho = \begin{cases} \rho(q, p) = \text{const.} & \text{in shell} \\ 0 & \text{outside} \end{cases}$$

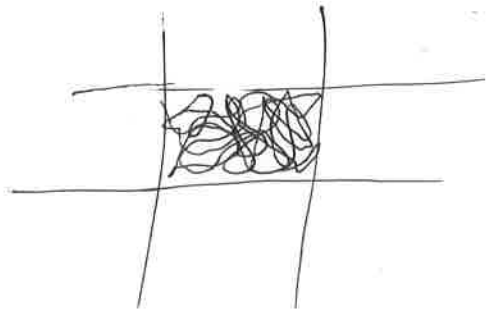
\* The ensemble average is stationary  $\frac{\partial \langle f \rangle}{\partial t} = 0$

$$\langle f \rangle = \overline{\langle f \rangle} \stackrel{\sim \text{time average}}{=} \langle \bar{f} \rangle \stackrel{\text{same for all members of ensemble}}{=} \bar{f} \stackrel{\text{measurement}}{=} f_{\text{exp}}$$

↑ averages are independent      ↑

Ensemble average of any physical quantity  $\langle f \rangle$  is equal to the expected value of measurement  $f_{\text{exp}}$

Ergodic theorem (Boltzmann): After long enough time, A  $\mu$ -state will pass through all states in the relevant phase space



We want to connect between the mechanics of  $\mu$ -states and the TD of the macrostate

We know that  $\Gamma \propto \omega$

↑ # of states      ↓ volume of hypershell

We need to find the fundamental volume  $\omega_0$  of 1  $\mu$ -state

Then  $\Gamma = \frac{\omega}{\omega_0} \Rightarrow S = \ln \Gamma = \ln \left( \frac{\omega}{\omega_0} \right)$  etc.

The scaling of  $\omega_0$  is  $(\Delta x \cdot \Delta p)^{3N} \sim h^{3N}$  | postpone

2.4 Examples

A. Ideal gas:

$$\sum_i \frac{p_i^2}{2m} = E$$

$$\omega = \int_{\Gamma} d^{3N}q \int d^{3N}p = V^N \int d^3p$$

$$E - \frac{\Delta}{2} \leq \sum \frac{p_i^2}{2m} \leq E + \frac{\Delta}{2}$$

We can compare to counting states

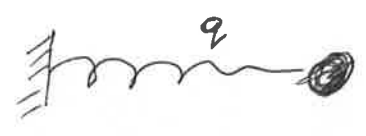
$$\left\{ \begin{aligned} \sum_{r=1}^{3N} n_r^2 &= \frac{8m V^{2/3}}{h^2} E = \left( \frac{V^{1/3} 2\sqrt{2mE}}{h} \right)^2 \\ \sum_{r=1}^{3N} p_r^2 &= (\sqrt{2mE})^2 \end{aligned} \right.$$

$$\omega \sim V^N (2mE)^{\frac{3N}{2}}$$

$$\Gamma \sim \left( \frac{V^{1/3} 2\sqrt{2mE}}{h} \right)^{3N} \frac{1}{2^{3N}} = \frac{V^N (2mE)^{3N/2}}{h^{3N}}$$

$$\rightarrow \omega_0 = h^{3N}$$

B. Harmonic oscillator



$$H(q, p) = \frac{1}{2} k q^2 + \frac{p^2}{2m}$$

$$\left. \begin{aligned} \text{Hamilton's} \\ \text{equations} \end{aligned} \right\} \begin{aligned} \dot{q} &= \frac{p}{m} \\ \dot{p} &= m\ddot{q} = -kq \end{aligned} \quad \text{Newton's law}$$

$$q = A \cos(\omega t + \phi)$$

$$\omega = \sqrt{\frac{k}{m}}$$

$$p = m\dot{q} = -m\omega A \sin(\omega t + \phi)$$

$$E = \frac{1}{2}kq^2 + \frac{p^2}{2m} = \frac{1}{2}kA^2 \cos^2(\omega t + \phi) + \frac{\omega^2 A^2}{2m} \sin^2(\omega t + \phi)$$

$$= \frac{1}{2}kA^2 = \frac{1}{2}m\omega^2 A^2 = \text{const.}$$

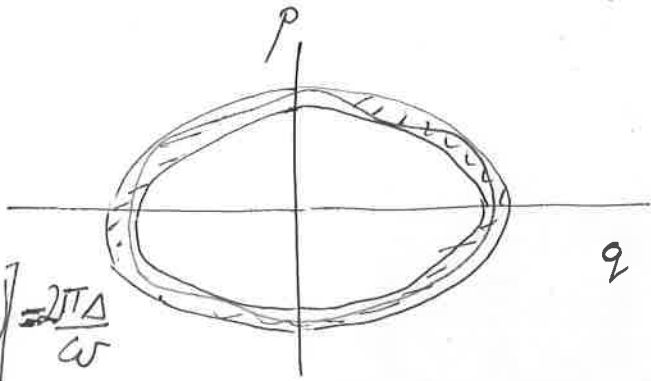
This defines phase-space

$$\frac{p^2}{2mE} + \frac{q^2}{(2E/m\omega^2)} = 1 \quad \text{an ellipse}$$

$$\text{Area} = \pi ab = \frac{2\pi E}{\omega}$$

As usual we consider the hypershell  $(E - \frac{\Delta}{2}, E + \frac{\Delta}{2})$

With volume



$$W = \int dq dp = \frac{2\pi}{\omega} \left[ (E + \frac{\Delta}{2}) - (E - \frac{\Delta}{2}) \right] = \frac{2\pi\Delta}{\omega}$$

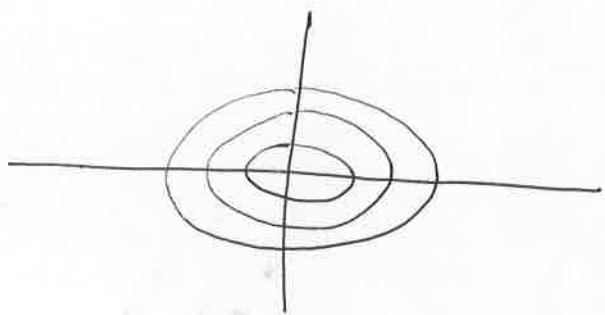
From Q.M we know the energies of the oscillator

$$E_n = (n + \frac{1}{2})\hbar\omega \quad n = 0, 1, 2, \dots$$

So the shell that corresponds to one state has  $\Delta E = \hbar\omega$

So that

$$\omega_0 = \frac{2\pi}{\omega} \hbar\omega = 2\pi\hbar = h$$



If  $E \gg \Delta \gg \hbar\omega$  the number of eigenstates is  $\frac{\Delta}{\hbar\omega}$

Similar for N oscillators  $\omega_0 = h^N$



## (2.5) Quantum States and the Phase Space

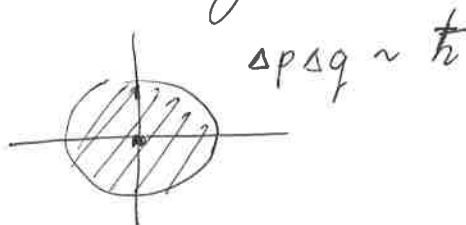
Why  $h$  is so significant?

The uncertainty principle:

We cannot specify simultaneously both the position and momentum of a particle.

$$(\Delta q \Delta p) \geq \hbar$$

This tells that around energy point  $(q, p)$  there is a region where the system could be



So we can think of P.S. cells where all positions in a cell are non-distinct.

Relativistic particles (photons)

$$p = \hbar k = \hbar \frac{\omega}{c}$$

Then

$$\int d^3q d^3p = V \cdot 4\pi p^2 dp = V 4\pi \left(\frac{\hbar}{c}\right)^3 \omega^2 d\omega$$

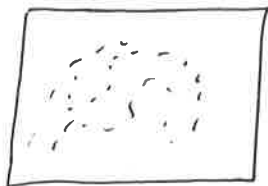
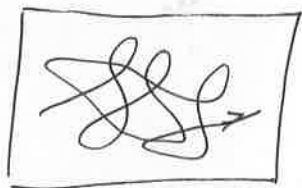
Rayleigh had an expression for # of states

$$V \cdot (4\pi) (2\pi)^3 \frac{\omega^2 d\omega}{c^3}$$

from which we see that  $\omega_0 = h^3$

## Summary CH. 2

\* Ensembles in Phase Space:



$$dw = d^{3N}q d^{3N}p$$

$$\bar{f} = \langle f \rangle$$

\* Density function  $\rho(q, p, t)$

obey Liouville's theorem  $\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + [\rho, H] = 0$

\* Stationary system  $\frac{\partial \rho}{\partial t} = 0$  equilibrium

\* Microcanonical Ensemble

Macrostate  $(E, V, N)$

constant  $E$  manifold  $\mathcal{H} = E$

$$\Omega = \frac{1}{h^{3N} N!} \int dw \delta(\mathcal{H} - E)$$

$\mu$ -canonical ensemble:

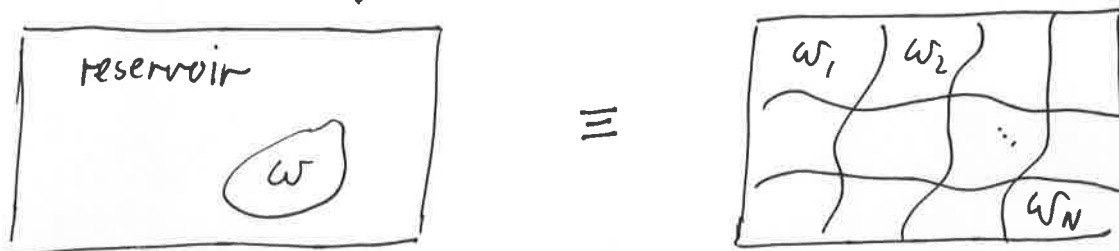
- Determine  $\Omega(E, V, N)$  for given  $E$ , then derive  $T, D$ .

Problems:

- \* Usually it's hard to determine  $\Omega$  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



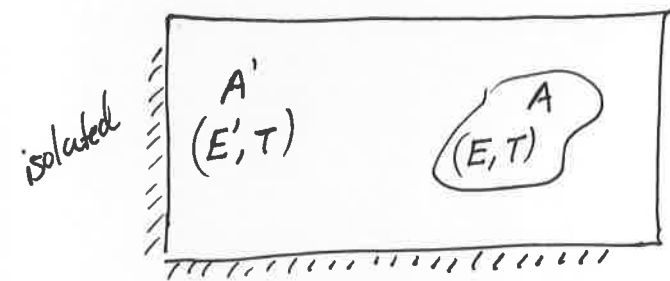
- \* This is the canonical ensemble = many systems with the same  $(T, V, N)$
- \* The energy of the system can now vary and we will look for  $P_f(E_f)$

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



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

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!  
( $\mu$ -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  $\mu$ -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  $F\{n_r\}$

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 Lagrangian'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  $\alpha$

To find  $\beta$  use the second constraint

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

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

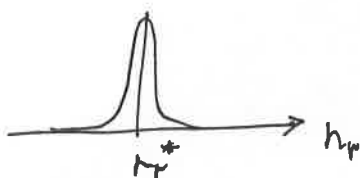
from which we can solve for  $\beta$ .

[This must be the TD  $\beta$  we got 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

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

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

$$dA = dU - d(TS) = dU - Tds - SdT$$

$$= -SdT - pdV + \mu dN$$

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

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

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

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:

$$(1) C_V = \left(\frac{\partial U}{\partial T}\right)_{V, N} = \frac{\partial}{\partial T} \left( A - T \frac{\partial A}{\partial T} \right) = \frac{\partial A}{\partial T} - \frac{\partial A}{\partial T} - T \left( \frac{\partial^2 A}{\partial T^2} \right)_{N, V}$$

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

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 "3<sup>rd</sup> 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

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

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

$$I = \int e^{-p_i^2/2mT} d^3 p_i =$$

$$= \int e^{-(p_x^2 + p_y^2 + p_z^2)/2mT} dp_x dp_y dp_z$$

$$= \left( \int e^{-\frac{p_x^2}{2mT}} dp_x \right) \left( \int \dots dp_y \right) \left( \int dp_z \right) = (2\pi mT)^{3/2}$$

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

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  $\Omega$ !

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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  $\mu$ -canonical result

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

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  $\mu$ -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

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

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

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

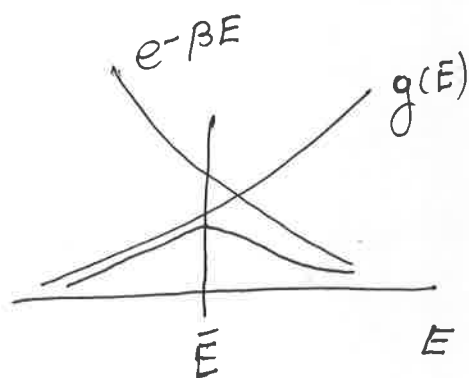
$$e^{-\beta E} \left( \frac{\partial g}{\partial E} - \beta g(E) \right) = 0$$

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

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  $\frac{\ln N}{N} \rightarrow 0$ .

### Summary

\* Canonical ensemble

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

\* Average energy

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

\* 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  $\rightarrow = \int x_i \left( \frac{\partial \mathcal{H}}{\partial x_j} e^{-\beta \mathcal{H}} \right) dx_j d\omega_{\text{rest}} = \int \dots d\omega \text{ deriv of } x_j$

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

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

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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

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

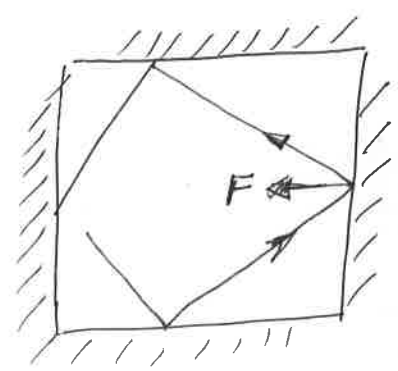
Why the virial is an interesting quantity?

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

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



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

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

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)

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

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

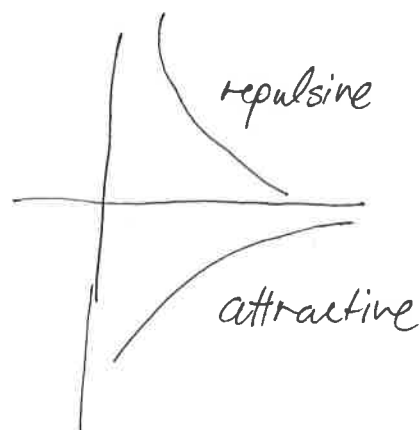
From which we get

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

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 photons and protons.

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

$$S1 \quad - \mu = \left( \frac{\partial A}{\partial N} \right)_{T,V} = T \ln \left( \frac{\hbar \omega}{T} \right) \quad \leftarrow \text{Some TD}$$

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

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

$$= N + (-N) \log(\hbar \omega \beta) = N \left[ 1 - \log(\beta \hbar \omega) \right]$$

$$- U = NT$$

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

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

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

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

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

(B) By actual inverse Laplace

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

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

QM oscillator

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

For a single oscillator

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

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

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

Free energy

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

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

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

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

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

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

→ The QM oscillators do not obey equipartition

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

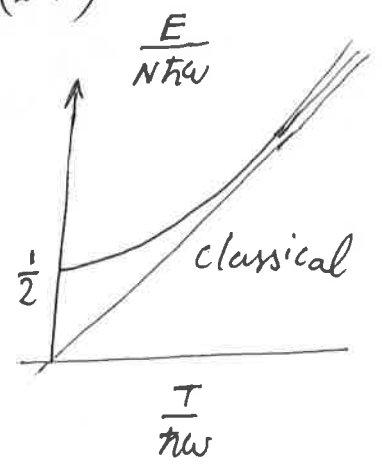
Only at high  $T$  (small  $\beta$ )  $\coth(x) \approx \frac{1}{x}$   $U = \frac{1}{2} NT$



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

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

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



Next, let's calculate the density of states

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

One way described in the book is the

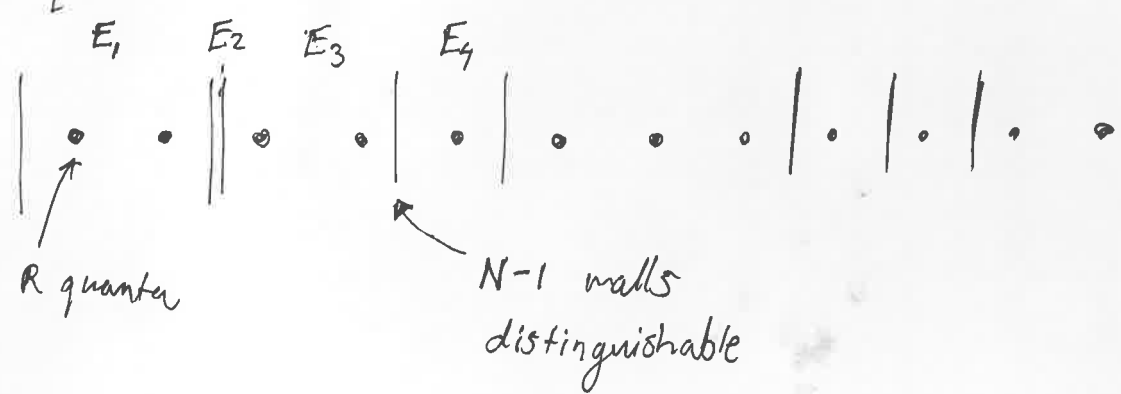
inverse Laplace transform  $\Omega(E) = \mathcal{L}^{-1}[Q_N(\beta)]$

- 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

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

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

$N-1 \approx N$

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

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

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

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

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

as in the canonical ens.

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

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

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

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

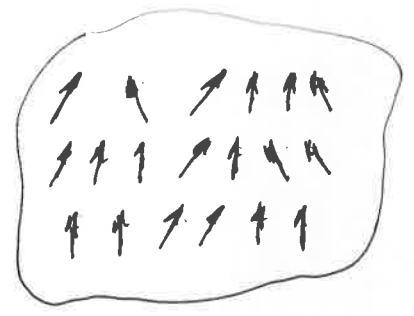
~~$$= N \left(1 + \ln \frac{E}{N\hbar\omega} + \frac{1}{2} \frac{N\hbar\omega}{E}\right) = N \left(1 + \ln \frac{1}{2} \left(\coth\left(\frac{\hbar\omega}{2T}\right) - 1\right)\right)$$~~

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
- $\mu$  - magnetic dipole
- $H$  - external field



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

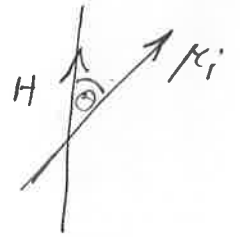
$T \rightarrow 0$  order, dipoles are aligned - magnetization

\* 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

$$Q_N = \int e^{-\frac{H}{\mu} \sum_i \cos \theta_i} \prod_i d\theta_i = \prod_i \left[ \int e^{-H_i} d\theta_i \right] = Q_1^N$$

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

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

The average magnetization

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

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

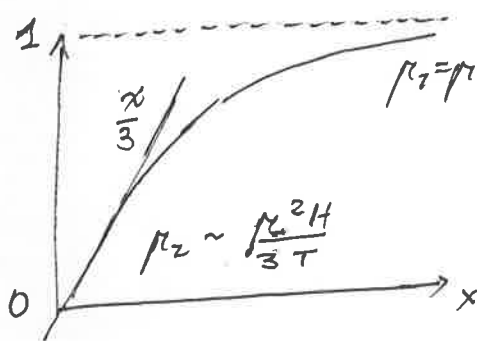
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$$\mu_z = \frac{1}{\beta} \frac{\partial \ln Q_1}{\partial \beta} = \frac{1}{\beta} \frac{\partial}{\partial \beta} \left[ \ln [\sinh(\beta \mu H)] - \ln \beta \mu H \right]$$

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

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  $\mu_z$  are both quantized

gyromagnetic ratio

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

angular momentum

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

5r

$g$  is Lande's  $g$ -factor

$g = 2$  if angular momentum is from electron spin

$g = 1$  if from orbital motion of electron

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

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

$$a_1 \left( \frac{q^{n-1}}{q-1} \right)$$

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

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

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

5b / The mean magnetic moment is

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

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

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

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

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

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

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

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

QM Curie's law and note that the coefficient relates directly to the QM eigenvalues of  $\mu^2$

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  $m = -1, +1$

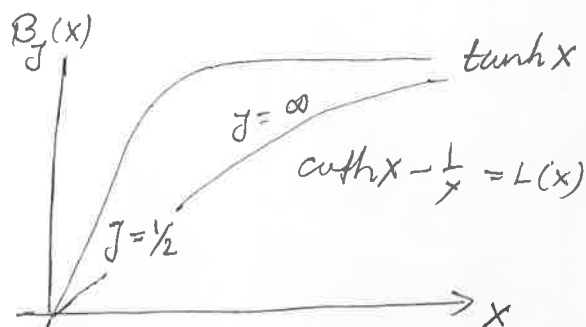
$$J = \frac{1}{2} \quad B_J(x) = 2 \coth 2x - \coth x = \tanh x$$

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

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



### (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  $E = \mp \mu_B H$

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

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

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

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

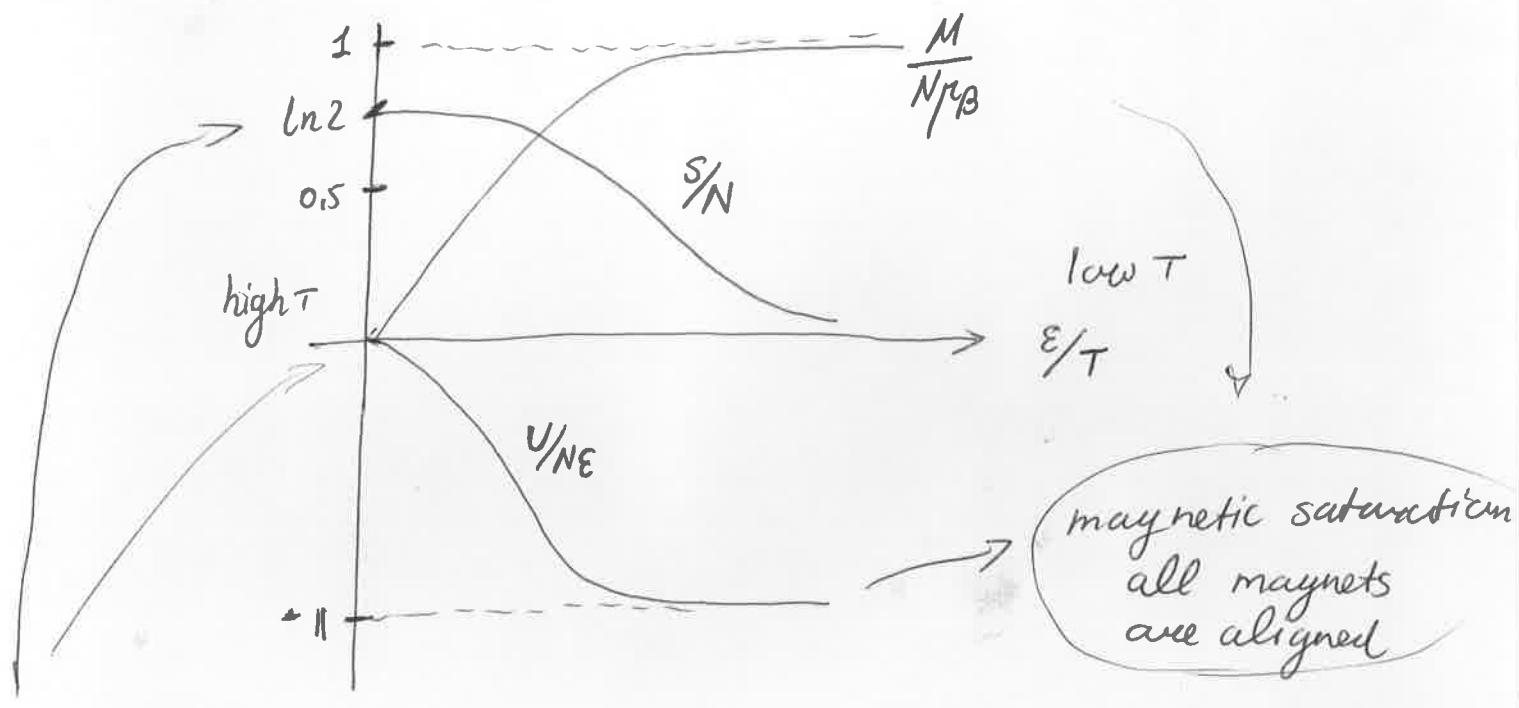
$$= N \left[ \ln \left( 2 \cosh\frac{\epsilon}{T} \right) - \frac{\epsilon}{T} \tanh\left(\frac{\epsilon}{T}\right) \right]$$

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

$$M = -\left(\frac{\partial A}{\partial H}\right)_T = +NT \frac{\sinh(\epsilon/T)}{2 \cosh(\epsilon/T)} \cdot \left(+\frac{\mu_B}{T}\right) = N\mu_B \tanh\left(\frac{\epsilon}{T}\right)$$

Finally, specific heat

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

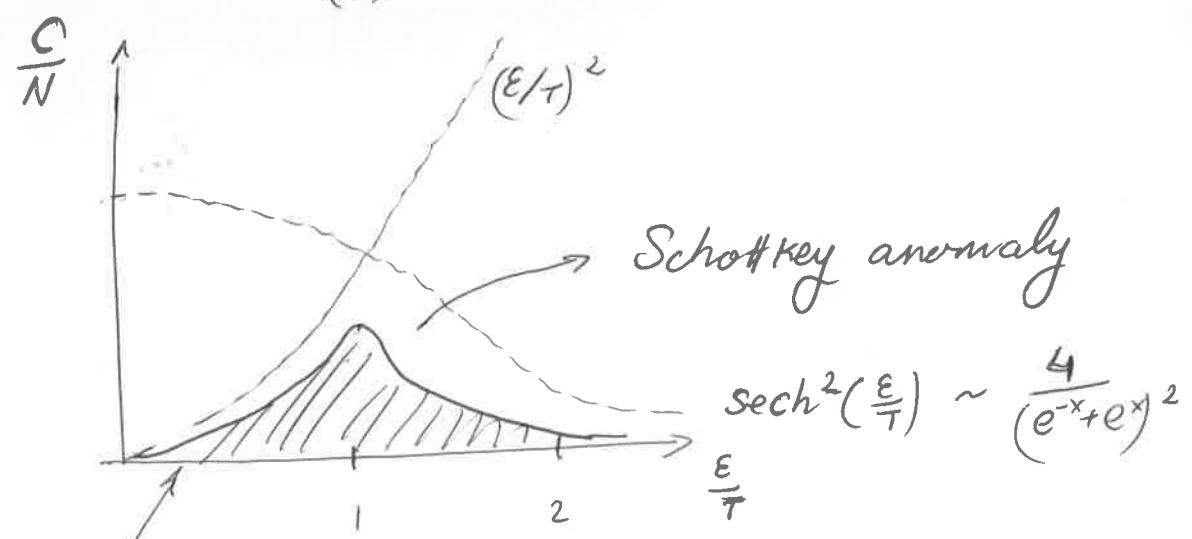


\* At high T both states  $\pm\epsilon$  are equally likely so  $\frac{S}{N} = \ln 2$   
 Random state



# 61 / Specific heat

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



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

What is the temperature?

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

However, if the energy states have a maximum there is no problems.

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

If  $U < 0 \rightarrow T > 0$

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

But if  $U > 0 \rightarrow T < 0$ !

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

To get  $S$  use

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

$$\frac{S}{N} = \ln \left( 2 \cosh \frac{\epsilon}{T} \right) - \underbrace{\frac{\epsilon}{T} \tanh \frac{\epsilon}{T}}_{-U/NT}$$

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

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

$$= \frac{1}{2} \ln \frac{4(N\epsilon)^2}{(N\epsilon)^2 - U^2} + \frac{U}{N\epsilon} \cdot \frac{1}{2} \ln \frac{N\epsilon - U}{N\epsilon + U}$$

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

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

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

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

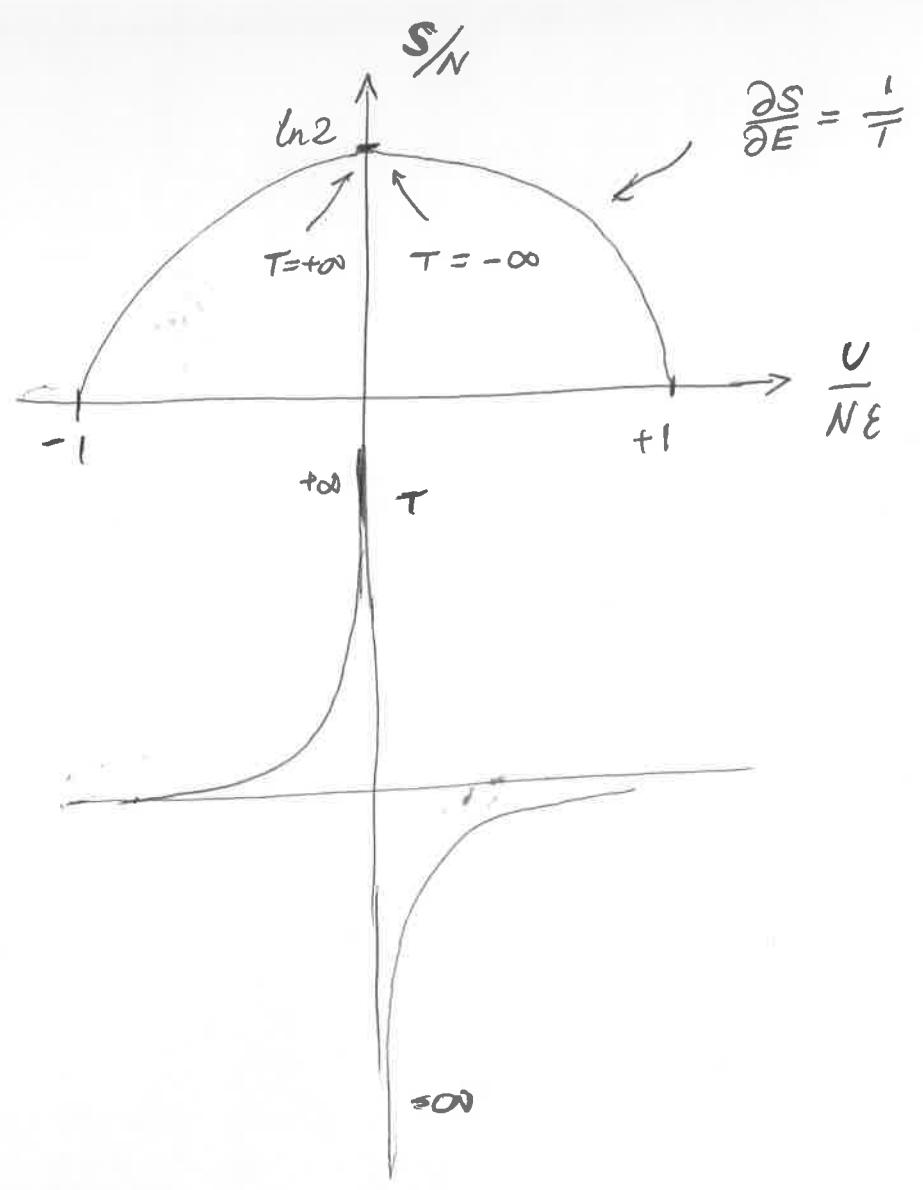
As  $U$  increases both  $T$  and  $S$  increase

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

$$S_{\max} = N \ln 2$$

However if we now increase  $U$   $U \rightarrow 0+$  the entropy decreases so  $\frac{dS}{dU} \rightarrow 0_-$  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  $NT \gg E_f$  any energy

At very high  $T$  we can assume non-interacting particles

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

$$Q_N(\beta) \approx \left[ \sum_n \left( 1 - \beta E_n + \frac{1}{2} \beta^2 E_n^2 \right) \right]^N$$

Now if there are  $g$  states we can write

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

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

$$A = -T \ln Q_N$$

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

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

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

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

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

We see that  $S$  is an even function of  $\beta$  while  $U$  is odd which leads to

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

