

Motivation:

Usefulness

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. (Predictability vs. uncertainty)
- * This approach is very fundamental and general and can be applied almost in any field of physical sciences (and non-physical sciences) 10^7
 10^{23}

1 THE STATISTICAL BASIS OF THERMODYNAMICS

Historical Note

- * Around the middle of 19th century,
TD = study of macroscopic behavior of physical systems became an established discipline of physics.
with the first and second laws. (energy conservation)
- * Around the same time, the kinetic theory of gases which aims to understand the properties of gases based on the motion of molecules. (MAXWELL)
- * 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.

TD kinetic theory
 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 d.o.f

Hence the term STATISTICAL MECHANICS

[Predictability vs. uncertainty]

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 $\sim 10^{20}$. (How many molecules are in the class)
- Even if we could follow the dynamical equations of each particle, it would not teach us much. 22.4 l
per
mole

* 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 $N \sim 10^{23}$

[Another example] $\epsilon_i = \{0, 1\}$

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

n_i \ ϵ_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} .

Example

$$N = 10$$

→ total # states = 2^N

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

$$E = 5$$

$$\Omega = \binom{10}{5} = \frac{10!}{5!5!} = \frac{10 \cdot 9 \cdot 8 \cdot 7 \cdot 6}{8 \cdot 4 \cdot 3 \cdot 2 \cdot 1} = 36 \cdot 7 = 252$$

In general for N and $E = \frac{N}{2}$

$$\Omega = \binom{N}{\frac{N}{2}} = \frac{N!}{\left(\frac{N}{2}\right)! \left(\frac{N}{2}\right)!}$$

$$\ln \Omega = \ln N! - 2 \ln \left(\frac{N}{2}\right)!$$

$$= N \ln N - N - 2 \left(\frac{N}{2} \ln \frac{N}{2} - \frac{N}{2} \right)$$

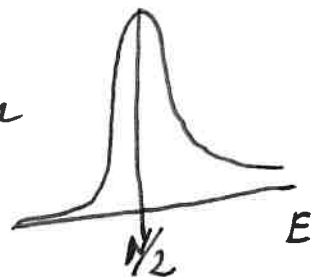
$$= N \ln N - N \ln \frac{N}{2} = N \ln 2$$

$$\Omega \approx 2^N$$

but even if we don't specify the energy

$$\Omega = 2^N$$

which implies sharp distribution



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.

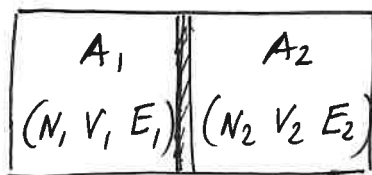
We denote the actual number of microstates as $\Omega(N, V, E)$.

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 Ω

- 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, $\Omega_1(E_1)$ states of A_1
 $\Omega_2(E_2)$ states of A_2

The overall Ω

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

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 Ω is more probable.



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

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

$$\boxed{\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T}} \quad (\text{usually } > 0)$$

By comparing the two conditions Boltzmann found

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

which leads to

$$\boxed{S = k_B \ln \Omega}$$

$$k_B = 1.38 \cdot 10^{-23} \frac{\text{J}}{\text{OK}}$$

or

$$k_B = 1 \text{ if } [T] = [E]$$

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

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

* Relation to 2nd law of TD: $\Delta S \geq 0$

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

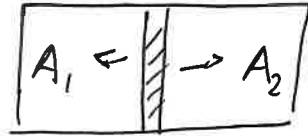
Total order implies $S = 0 \leftrightarrow \Omega = 1$

[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

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

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

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

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

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

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

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

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

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

This follows what we know from TD

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

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

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

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

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

9 / We can use this formula to write

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

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

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

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

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

while

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

We could derive these formula directly from

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

We can get the usual definitions

$$\boxed{E = -PV + TS + \mu N} \quad (\text{intensive} \times \text{extensive})$$

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

Now we define the usual TD potentials

(also "F") $A = E - TS = -PV + \mu N$: Helmholtz free energy (F)

$G = A + PV = \mu N$: Gibbs free energy

$H \equiv E + PV = \mu N + TS = G + TS$: Enthalpy

10 / The specific heats, at constant volume and pressure are

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

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

$$dH = TdS + VdP + \mu dN$$



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

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

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

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

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

$$\boxed{PV = N k_B T = n R T} \quad \text{with } R = k_B N_A = 8.3 \frac{\text{J}}{\text{mol} \cdot \text{K}}$$

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

* To derive the full TD we need to know how Ω 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

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

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

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

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,

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

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

* 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 $\left(\frac{E}{V} \cdot V^{5/3}\right) PV^{5/3} = \text{const.}$ 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 $\Omega(N, V, E) = \Omega_N(E^*)$

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

What we actually look for is

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

13 A

Hyper sphere volume

Integrate hyper-Gaussian

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

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

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

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

$$\Gamma\left(\frac{N}{2}\right) \approx \left(\frac{N}{2}-1\right)!$$

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

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

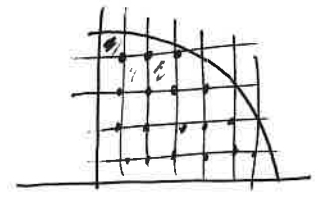
$$S_{N-1}(R) = \frac{2\pi^{N/2}}{\Gamma\left(\frac{N}{2}\right)} R^{N-1} \rightarrow \mathcal{A}(R) = R^N$$

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 ($R = \sqrt{E^*}$)

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

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

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

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

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

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 $E + \frac{1}{2}\Delta$

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

$$\ln \Gamma = \ln \Sigma + \underbrace{\left\{ \ln \frac{3N}{2} + \ln \frac{\Delta}{E} \right\}}_{\text{negligible}} \approx \ln \Sigma \quad \left(\begin{array}{l} \text{in other words} \\ \text{most states are} \\ \text{at the interface} \end{array} \right)$$

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

From all this,

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

We can insert this and get

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

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

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

The specific heat at constant volume

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

15/

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

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

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

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

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

* 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

$$\Delta S = S_f - S_i = N \ln \frac{V_f}{V_i} \quad \left(\text{since } S = N \ln \left[\frac{V}{h^3} \left(\frac{4\pi m E}{3N} \right)^{3/2} \right] \right)$$

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

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

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

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

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

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 α the entropy does not increase by α

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

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

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

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

$$S_i = N_i \log \left(\frac{V}{\lambda_i^3} \right) + \frac{3}{2} N_i \quad \lambda_i = \frac{h}{\sqrt{2\pi m_i T}}$$

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:

$m_1 = m_2$ 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 Ω 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. $N \dots$

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

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

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

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 ϵ_1 , n_2 in ϵ_2 and so on.

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

If we exchange particles between two energies, then in the old counting method there are two μ -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 $\sum_j n_j \epsilon_j = E$ and $\sum_j n_j = N$

If our particles were distinguishable all these permutations were different μ -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

$$\left\{ S = \ln \Omega \right\}$$

- $\left\{ \Omega(E, V, N) \right\}$ 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: $PV = NT$

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

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

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

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