STATISTICAL MECHANICS 611

A statistical description of matter provides the foundation for our understanding of thermodynamics & the description of the emergent properties of matter.

This course provides a thorough grounding in the methods of statistical mechanics at a graduate student level.

Our principal texts will be

Statistical Mechanics, 3rd edition (R.K. Pathria + P. Beale)
Elsevier, 2011.

Statistical Mechanics in a Nutshell (L. Peliti)
Princeton U. Press 2011.

OUTLINE OF THE COURSE

- Statistical basis of Thermodynamics (Ch 1)

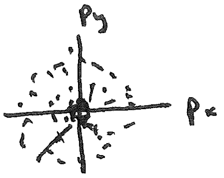
  $$S[\{X_i\}] = k \ln \Omega[\{X_i\}]$$

- Ensemble Theory. (Micro) Canonical, Grand Canonical. (Ch 2-4)

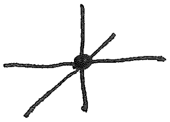
- Quantum Statistical mechanics. "Density Matrix" (Ch 5)

  $$\hat{\rho} = |n\rangle p_n \langle n| = e^{-\beta \hat{H}}$$

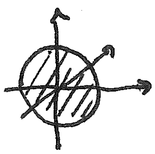
- Ideal Gases, general theory. (6)



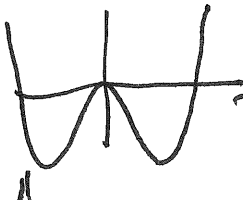
- Bosons, B.E.C. (7)



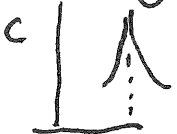
- Fermions, Fermi Liquid, electron gas (8)
  White Dwarfs.



- Phase transitions + Broken Symmetry. (12)
  Ising Model, Landau Theory



- Criticality, universality + scaling (13, 14)



HISTORY

"A 350 yr old struggle that continues"

c 1690	Newton, Principia Leibnitz. mv^2	MECHANICS WITHOUT ENERGY Heat = caloric, a fluid.

THE RISE OF THERMODYNAMICS.

c. 1790	Count Rumsford	Heat can be created from Work
1807	Thomas Young	"Energy"
1827	Coriolis	$K = \frac{1}{2} mv^2$
c. 1850	Joule	Energy conservation $E = Q + W$
	Thomson	
c. 1860	Clausius.	$\Delta S = \frac{\Delta Q_{rev}}{T}$.

EARLY STAT MECH.

Bernoulli 1738, Kronig 1856, Clausius 1857 $\quad P = \frac{1}{3} n m \overline{c^2}$

Maxwell $f(p,q)$ 1860, 1879 ENSEMBLES

Boltzmann "H-theorem" (entropy increases with time)

Gibbs 1902.

QUANTUM STAT MECH.

PLANCK 1900 $E = n\hbar\omega$ $\quad S = k \ln \Omega$ $\quad$ Einstein 1905/6 QUANTA

Bose, Einstein c. 1925. "B.E.C"

Pauli, Fermi, Dirac c. 1926/7.

Landau, von Neumann $\hat{\rho}$ 1927

MODERN ERA – QUANTUM INFO.

1948 SHANNON

1996 SREDNICKI "E.T.H"

1. STATISTICAL BASIS OF THERMODYNAMICS.

Micro & Macro States

Microstate $|\psi\rangle$

$$H|\psi\rangle = E|\psi\rangle$$

$$\hat{N}|\psi\rangle = N|\psi\rangle$$

e.g Free particles $|\psi\rangle = |n_1, n_2 \dots n_r\rangle$

$$\left.\begin{aligned} E &= \sum \epsilon_r n_r \\ N &= \sum n_r \end{aligned}\right\} \text{Discrete}$$

Macrostate (N, V, E) Consider system with macroscopic # of particles $N \sim N_{AV} \sim 10^{23}$.

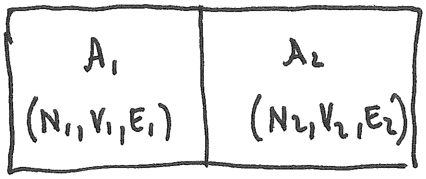
Formally $N \to \infty$ such that $N/V = \rho$ is fixed. Now the extensive properties become proportional to V. Intensive properties (energy density, particle density, magnetization etc) become independent of V.

When V is large $E = \sum \epsilon_r n_r$ becomes essentially a continuous variable. Many ways that the macrostate can be realized. We denote this by the symbol $\Omega(N, V, E)$.

The thermodynamics is determined by $\Omega(N,V,E)$.

1.2 Connection between Statistics & Thermodynamics

Consider two systems A_1 & A_2 in thermal equilibrium



Total energy fixed $\quad E = E_1 + E_2$

Equal à priori probability : equally likely for A_1 to be in any one of the $\Omega_1(N_1,V_1,E_1)$ states of A_1. Similarly for A_2.

Total number of states with energy (E_1,E_2) $\quad \Omega^0(E,E_1) = \Omega_1(E_1)\,\Omega_2(E-E_1)$

The composite-system will select the E_1 that is maximally likely, i.e the value that maximizes $\Omega^0(E,E_1)$.

In practice Ω^0 is very sharply peaked around the most likely value of E_1 $\quad E_1 \propto N \quad \delta E_1^2 \propto N \quad \sqrt{\delta E_1^2}/E_1 \sim 1/\sqrt{N}$.

$$\frac{\partial \Omega^0}{\partial E_1}(E, E_1) = \frac{\partial \Omega_1}{\partial E_1}\Omega_2 - \Omega_1 \frac{\partial \Omega_2}{\partial E_2} = 0$$

$$\Rightarrow \left(\frac{\partial \ln \Omega_1}{\partial E_1}\right)_{E_1 = \bar{E}_1} = \left(\frac{\partial \ln \Omega_2}{\partial E_2}\right)_{E_2 = E - \bar{E}_1}$$

Equilibrium corresponds to the equality of the parameters β_1 & β_2 of the two subsystems, where

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

Energy will exchange between A_1 & A_2 until $\beta_1(\bar{E}_1) = \beta_2(E - \bar{E}_1)$.

β is somehow related to the THERMODYNAMIC TEMPERATURE.

Recall

$$\left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{1}{T} \qquad (dE = T\,dS - P\,dV + \mu\,dN)$$

$$\left.\begin{aligned} \Delta \ln \Omega &= \beta \Delta E \\ \Delta S &= \frac{1}{T}\Delta E \end{aligned}\right\} \qquad \frac{\Delta S}{\Delta \ln \Omega} = \frac{\frac{1}{T}\cancel{\Delta E}}{\beta \cancel{\Delta E}} = \frac{1}{\beta T} = k_B$$

A universal constant. $k_B = 1.38 \times 10^{-23}\ \mathrm{J/K}$.

$$\Rightarrow \quad \boxed{\frac{1}{kT} = \beta}$$

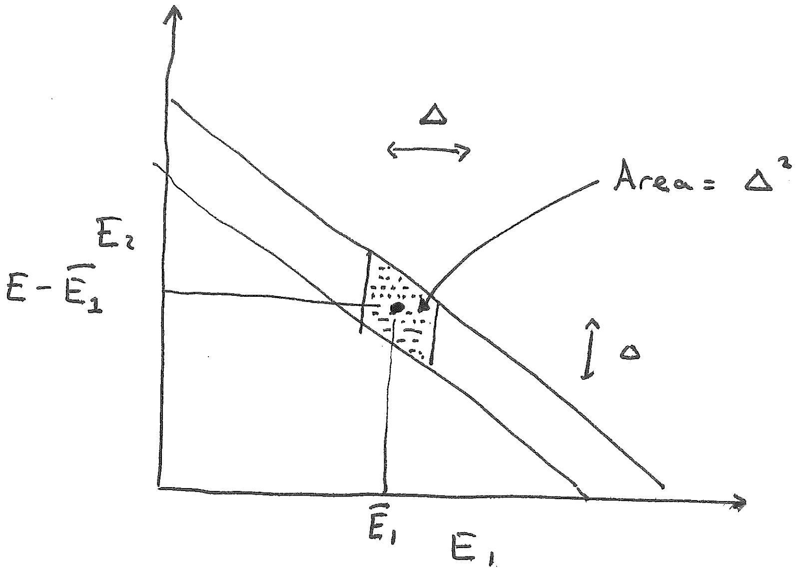
$$S = k \ln \Omega \quad + \quad C$$

$\Omega = 1 \iff S = 0$ absolute zero $\quad C = 0.$

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

k_B = Boltzmann's Constant.

Thermodynamics tells us that entropy increases inexorably in irreversible processes. We can now understand this as the inexorable rises in the disorder of the macrosystem.



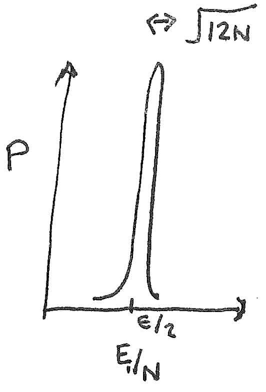
$\#$ states in parallelogram

$$= \tilde{\Omega}_1(\bar{E}_1)\,\tilde{\Omega}_2(E-\bar{E}_1)\,\Delta^2$$

e.g suppose $\Omega(E) \propto E^{3N/2}$ & $E_1 + E_2 = N\epsilon$

$$\Omega_1 \Omega_2 \sim [E_1(E-E_1)]^{3N/2}$$

Peak is at $\bar{E}_1 = \bar{E}_2 = \left(\frac{\epsilon}{2}\right)N$



$$\Omega_1 \Omega_2 \sim \left[\left(\frac{\epsilon N}{2} + \delta E_1\right)\left(\frac{\epsilon N}{2} - \delta E_1\right)\right]^{3N/2}$$

$$\sim \left(\frac{\epsilon N}{2}\right)^{3N}\left(1 - \left(\frac{2\delta E_1}{\epsilon N}\right)^2\right)^{3N/2}$$

$$\sigma^2 = \frac{N\epsilon^2}{12}$$

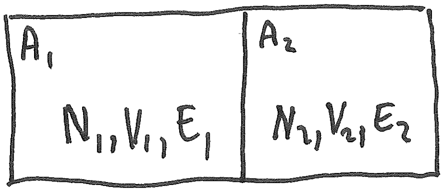
$$\sim \left(\frac{\epsilon N}{2}\right)^{3N} \exp\left[\frac{3N}{2}\ln\left(1 - \left(\frac{2\delta E_1}{\epsilon N}\right)^2\right)\right]$$

$$\sim \left(\frac{\epsilon N}{2}\right)^{3N} \exp\left[-\frac{6\,\delta E_1^2}{N\epsilon^2}\right] = \left(\frac{\epsilon N}{2}\right)^{3N} \exp\left[-\frac{\delta E_1^2}{2\sigma^2}\right]$$

1.3 Further contact between Statistics + Thermodynamics:

Previously we just allowed the exchange of energy.

Suppose though that the wall seperating the two systems is movable



$$E = E_1 + E_2 ; \quad V = V_1 + V_2$$

Now in addition to $\frac{\partial \ln \Omega_1}{\partial E_1} = \frac{\partial \ln \Omega_2}{\partial E_2}$, we must have

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

$$\| \qquad\qquad\qquad \|$$

$$\eta_1 \qquad = \qquad \eta_2$$

Likewise particle transfer.

$$\delta \ln \Omega = \frac{\partial \ln \Omega}{\partial E} \delta E + \frac{\partial \ln \Omega}{\partial V} \delta V + \frac{\partial \ln \Omega}{\partial N} \delta N$$

$$= \beta dE + \eta dV + \zeta dN$$

$$\delta k_B \ln \Omega = k_B \beta dE + k_B \eta dV + \zeta k_B dN$$

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

$$\Rightarrow \quad dS = \frac{dE}{T} + \frac{P}{T}\,dV - \frac{\mu}{T}\,dN$$

$$\Rightarrow \quad \beta = \frac{1}{k_B T}, \quad \eta = \frac{P}{k_B T}, \quad \zeta = -\frac{\mu}{k_B T}.$$

In equilibrium through a moveable, permeable membrane

$$\beta_1 = \beta_2, \quad P_1 = P_2, \quad \mu_1 = \mu_2 .$$

So the entropy in that state is

$$\boxed{S(N,V,E) = k \ln \Omega(N,V,E).}$$

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

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

and

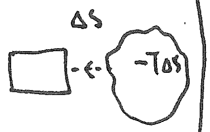
$$\mu = -\left(\frac{\partial S}{\partial N}\right)_{E,V} \Big/ \left(\frac{\partial S}{\partial E}\right)_{N,V} = \left(\frac{\partial E}{\partial N}\right)_{V,S}.$$

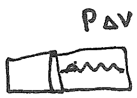
while

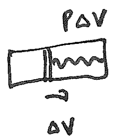
$$T = \left(\frac{\partial E}{\partial S}\right)_{N,V}.$$

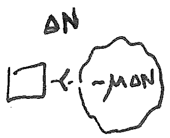
$dE = TdS - PdV + \mu dN$

From this the rest of Thermodynamics









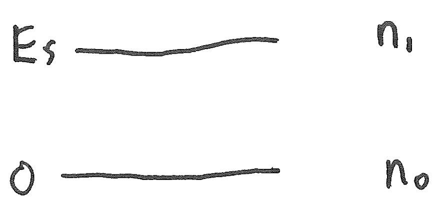
Includes energy of bath maintaining const T, P, N	$E(S,V,N)$
Helmholtz Free Energy. (Energy available once contact heat at fixed temperature)	$A(T) = E - TS$ $dA = -SdT - PdV + \mu dN$
Gibbs Free Energy (Energy available at constant pressure constant temperature)	$G = A + PV = E - TS + PV.$ $= \mu N$ $dG = -SdT + VdP + \mu dN$
Enthalpy (Energy available at constant Pressure)	$H = E + PV$ $dH = TdS + VdP + \mu dN$
LANDAU	$F = E - TS - \mu N$ $= -SdT - PdV - Nd\mu$

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

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

Example

Consider a system of $N \gg 1$ non interacting identical particles in which the energy of each particle can acquire two values, 0 & E_s. Suppose n_0 particles are in



the lower level and n_1 particles are in the upper level. Let the total energy be U.

a) Find the entropy of the system

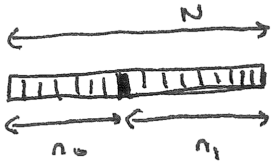
b) Find the temperature as a function of U

For what values of n_0 is $T > 0$?

c) If T is negative in one system & positive in another which way will the heat flow ?

a) $U = n_1 E_s$

Number of ways of putting n_0 particles in to lower level & n_1 particles in to upper level is



$$\Omega = \frac{N!}{n_0!\,n_1!} = \frac{N!}{n_0!\,(N-n_0)!} = \binom{N}{n_0}$$

The entropy is then

$$S = k_B \ln \Omega = k_B \ln \binom{N}{n_0}$$

$\left(\ln p! \sim p \ln \frac{p}{e} + \ln\sqrt{2\pi p}\right)$

Using Stirlings formula $\ln p! \simeq p \ln(p/e)$ for large p, it follows that

$$S = k_B\left(N \ln \frac{N}{e} - n_0 \ln \frac{n_0}{e} - n_1 \ln \frac{n_1}{e}\right)$$

$$= k_B\left(N \ln N - n_0 \ln n_0 - (N-n_0)\ln(N-n_0)\right)$$

$$= k_B N\left[\ln N - \frac{n_0}{N}\ln n_0 - \left(1-\frac{n_0}{N}\right)\ln(N-n_0)\right)$$

$$= -k_B N\left[\frac{n_0}{N}\ln\frac{n_0}{N} + \left(1-\frac{n_0}{N}\right)\ln\left(1-\frac{n_0}{N}\right)\right]$$

11b

$$E = n_1 u = (N - n_0) u = Nu\left(1 - \frac{n_0}{N}\right)$$

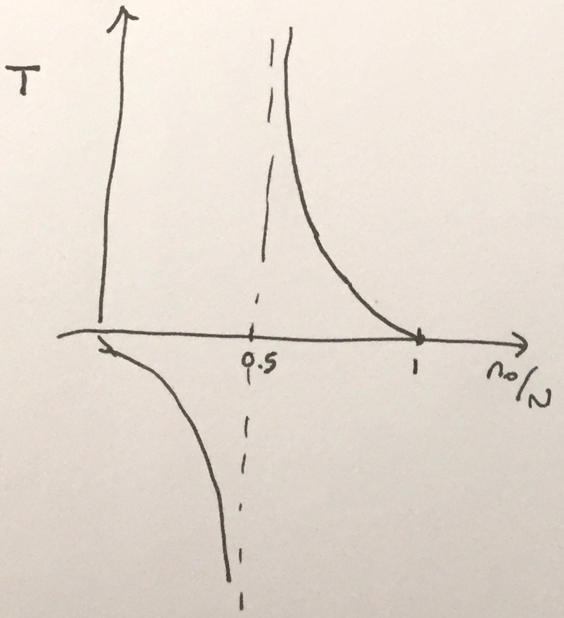
$$\Rightarrow \quad \left(1 - \frac{n_0}{N}\right) = \frac{E}{Nu} \qquad \frac{n_0}{N} = \left(1 - \frac{E}{Nu}\right)$$

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

$$\frac{1}{T} = \frac{\partial S}{\partial E} = + \frac{k_B \cancel{N}}{\cancel{N} u} \left[\ln\left(1 - \frac{E}{Nu}\right) - \ln \frac{E}{Nu} \right]$$

$$\Rightarrow \qquad T = \frac{u}{k_B} \frac{1}{\ln\left(\frac{Nu - E}{E}\right)} = \frac{u/k_B}{\ln\left(\frac{n_0/N}{1 - n_0/N}\right)}$$

$$T > 0 \Rightarrow n_0/N > 1 - n_0/N \Rightarrow \frac{n_0}{N} > 1/2$$



If $n_0/N < \frac{1}{2}$ we have an inverted population.

c)

$$\boxed{T_1 < 0} \xleftarrow{\delta E_1} \boxed{T_2 > 0}$$

$$S = S_1 + S_2$$

$$= S_1(E_1) + S_2(E - E_1)$$

$$\delta S = \frac{\partial S}{\partial E}\delta E_1 - \frac{\partial S_2}{\partial E}\delta E_1 = \underbrace{\left(\underset{<0}{\frac{\partial S_1}{\partial E}} - \underbrace{\frac{\partial S_2}{\partial E}}_{<0}\right)}_{<0} \underset{<0}{\delta E_1} > 0$$

$$\Rightarrow \boxed{\delta E_1 < 0}$$

Heat flows to the +ve temperature material!

$$\boxed{T_1 < 0} \dashrightarrow \boxed{T_1 > 0}$$

1.4 The Classical Ideal Gas

Non-interacting particles $\Omega(N,E,V) \propto V^N$

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

$$\Rightarrow \boxed{\begin{array}{l}\boxed{PV = Nk_BT = nRT}\\ \text{IDEAL GAS LAW}\end{array}}$$

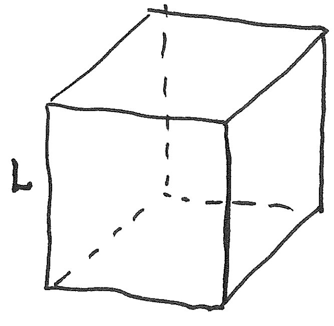
$n = \frac{N}{N_A}$, $R = k_BN_A = 8.31$ J/mol/K.

$k_B = 1.38\times10^{-23}$ J/K.

$$E = \sum_{r=1}^{3N} \epsilon_r$$

3 degrees of freedom / particle

$r \in [1, 3N]$



Box with periodic boundary conditions

$$\psi = \frac{1}{\sqrt{V}}\exp[i\vec{k}\cdot\vec{x}]$$

$$\psi(x,y,z) = \psi(x+L,y,z)$$

$$k_xL = 2\pi n_x \Rightarrow k_x = \left(\frac{2\pi}{L}\right)n_x$$

$$\vec{k} = \frac{2\pi}{L}(n_x, n_y, n_z) \quad (n_{x,y,z} \in \mathbb{Z})$$

$$E(n_x,n_y,n_z) = \frac{\hbar^2k^2}{2m} = \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2(n_x^2+n_y^2+n_z^2) = \frac{h^2}{2mL^2}\vec{n}^2$$

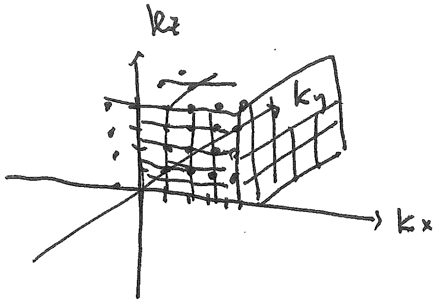
$$\hbar = h/2\pi$$

n.b.

(Had we chosen hard walls, then $\psi = \sqrt{\frac{8}{V}} \sin k_x x \sin k_y y \sin k_z z$

$k_x L = \pi n_x \qquad k_x = \left(\frac{\pi n_x}{L}\right) \qquad \bar{k} = \frac{\pi}{L}(n_x, n_y, n_z)$

$n_{x,y,z} > 0$)



$\bar{k} = \frac{2\pi}{L}(n_x, n_y, n_z)$

$n_{x,y,z} \in \mathbb{Z}$

Ω_1 : # of solutions for which

$$\vec{n}^2 = (n_x^2 + n_y^2 + n_z^2) = \frac{2m}{h^2} V^{2/3} \epsilon = \epsilon^*$$

$\Omega(N,\epsilon,V)$ = # of solutns for which

$$\sum_{r=1}^{3N} n_r^2 = \bar{n}_{3N}^2 = \frac{2m}{h^2}\underbrace{(V^{2/3}E)}_{\text{note combination.}} = E^*$$

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

$V^{2/3}E$ = constant in an adiabatic process. $E \propto \frac{1}{V^{2/3}}$

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

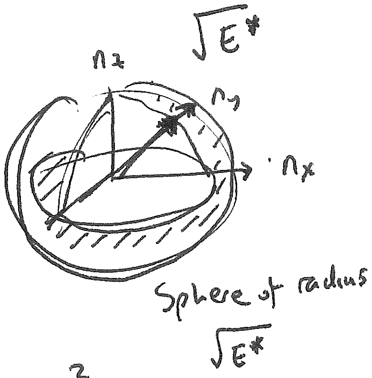
$$\Rightarrow \boxed{PV^{5/3} = \text{constant}}$$ ADIABATIC.

Now let.

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

i.e.

$$\Sigma_N(E) = \sum_{E' < E} \Omega_N(E').$$



e.g. $$\Sigma_1 = \sum_{|\vec{n}| < \frac{2mL^2}{h^2}} = \frac{4\pi}{3} n^3$$

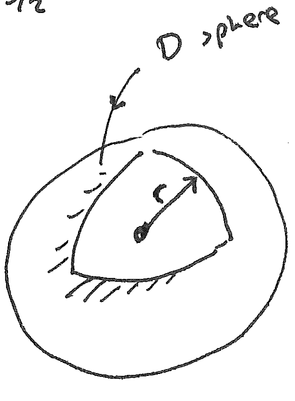
$$E = \frac{h^2}{2mL^2}(n_x^2+n_y^2+n_z^2) = \frac{h^2}{2mL^2}\vec{n}^2 \qquad |\vec{n}| < \frac{2mL^2}{h^2}$$

$$n^2 = \frac{2mL^2}{h^2}E = E^* \longrightarrow |n| < \sqrt{E^*}.$$

$$n^3 = (E^*)^{3/2}$$

$$\Sigma_1 = \frac{4\pi}{3}(E^*)^{3/2} = \frac{4\pi}{3}\left[\left(\frac{2mE}{h^2}\right)V^{2/3}\right]^{3/2}$$

$$= \left(\frac{V}{h^3}\right)\frac{4\pi}{3}(2mE)^{3/2}$$



Similarly,

Σ_N : volume of 3N dimensional sphere

$$V_D = \Lambda_D r^D$$

$$\Lambda_D = \frac{\pi^{D/2}}{\Gamma(\frac{D}{2}+1)} = \frac{\pi^{D/2}}{(D/2)!}$$

Proof of Volume of D dimensional sphere

Recall. $\int dx\, e^{-x^2} = \sqrt{\pi}$

c.f. $\left(\int dx\, e^{-x^2}\right)^2 = \int dx\,dy\, e^{-x^2+y^2} = \int 2\pi r\,dr\, e^{-r^2}$

$u = r^2$
$du = 2r\,dr$

$$= \int \pi\, du\, e^{-u}$$

$$= \pi \Rightarrow \int dx\, e^{-x^2} = \sqrt{\pi}.$$

$$\boxed{\begin{array}{l} A_D = S_D r^{D-1} \\ dV = S_D r^{D-1} dr \end{array}}$$

$$\pi^{D/2} = \left(\int dx\, e^{-x^2}\right)^D = \int \prod_{r=1}^{D} dx_r\, e^{-\sum x_r^2}$$

area of a D-sphere.

$$= \int S_D r^{D-1} dr\, e^{-r^2}$$

$u = r^2$
$du = 2r\,dr$
$r^{D-1}dr$
$= r^{D-2} r\,dr$
$= \frac{r^{D-2}du}{2}$

$$= \frac{S_D}{2}\int du\, r^{D-2} e^{-u}$$

$$= \frac{S_D}{2}\int du\, u^{\left(\frac{D-2}{2}\right)} e^{-u}$$

$$= \frac{S_D}{2}\left(\frac{D}{2}-1\right)! = \left(\sqrt{\pi}\right)^D$$

$$\Rightarrow S_D = \frac{2\pi^{D/2}}{\left(\frac{D}{2}-1\right)!}$$

$$dV = S_D r^{D-1} dr$$

$$\boxed{V = \int S_D r^{D-1} dr = \frac{S_D}{D} r^D = \Lambda_D r^D}$$

$$\Rightarrow \Lambda_D = \frac{S_D}{D} = \frac{\pi^{D/2}}{\underbrace{\frac{D}{2}\left(\frac{D}{2}-1\right)!}_{\frac{D}{2}!}} = \boxed{\frac{\pi^{D/2}}{\left(\frac{D}{2}\right)!}}$$

$$\boxed{V_D = \frac{\pi^{D/2}}{\left(\frac{D}{2}\right)!} R^D}$$

volume of a D-sphere

$0! = 1 = \Gamma(1)$

$\Gamma(\frac{1}{2}) = -\frac{1}{2}! = \sqrt{\pi}$

$\Gamma(\frac{3}{2}) = \frac{1}{2}\Gamma(\frac{1}{2}) = \frac{\sqrt{\pi}}{2} = \frac{1}{2}!$

$\Gamma(2) = 1! = 1$

$\Gamma(\frac{5}{2}) = \frac{3}{2}! = \frac{3}{2}\,\frac{1}{2}! = \frac{3}{4}\sqrt{\pi}$

$\Gamma(3) = 2! = 2$

n	$-\frac{1}{2}$	0	$\frac{1}{2}$	1	$3/2$	2
$n!$	$\sqrt{\pi}$	1	$\frac{\sqrt{\pi}}{2}$	1	$\frac{3\sqrt{\pi}}{4}$	2

$$\frac{\partial V}{\partial R} = S_D = \frac{2\pi^{D/2}}{\left(\frac{D}{2}-1\right)!} R^{D-1}$$

$$V_1 = \frac{\sqrt{\pi} R}{\sqrt{\pi}/2} = 2R$$

$$V_2 = \pi R^2$$

$$V_3 = \frac{\pi^{3/2} R^3}{\frac{3}{4}\sqrt{\pi}} = \frac{4}{3}\pi R^3$$

$$V_4 = \frac{\pi^2 R^4}{2} = \frac{1}{2}\left(\pi R^2\right)^2$$

$$\Sigma_N = \frac{\pi^{3N/2}}{\left(\frac{3N}{2}\right)!}\left(E^*\right)^{3N/2}.$$

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

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

$$= \frac{1}{\left(\frac{3N}{2}\right)!}\left(2\pi mE\right)^{3N/2}\left(\frac{V}{h^3.}\right)^{N} \qquad \ln\left(\frac{3N}{2}\right)! \approx \frac{3N}{2}\ln\left(\frac{3N}{2e}\right)$$

$$\boxed{\ln\Sigma = N\ln\left[\frac{V}{h^3}\left(\frac{4\pi mEe}{3N}\right)^{3/2}\right]}$$

$$\Sigma \sim E^{3N/2}V^{N}.$$

# of states in a small increment of energy ΔE.

$$\Gamma(N,V,E,\Delta) = \frac{\partial \Sigma}{\partial E}\Delta \simeq \frac{3N}{2}\left(\frac{\Delta}{E}\right) \Sigma_N$$

$$\frac{S}{k_B} = \ln\Gamma = \underbrace{N \ln\left[\frac{V}{h^3}\left(\frac{4\pi m E e_N}{3N}\right)^{3/2}\right]}_{O(N)} + \underbrace{\cancel{\ln\left(\frac{3N}{2E}\Delta\right)}}_{O(1)}$$

$$E = \frac{3h^2N}{4\pi m V^{2/3}} \exp\left[\frac{2S}{3Nk_B} - 1\right]$$

$$\frac{\partial E}{\partial S} = T = \frac{2E}{3Nk_B} \Rightarrow \boxed{E = \frac{3Nk_BT}{2} = \frac{3}{2}nRT}$$

$$P = -\left.\frac{\partial E}{\partial V}\right)_S = \frac{2E}{3V} = \frac{Nk_BT}{V} \Rightarrow PV = nRT$$

$$C_V = \left.\frac{\partial E}{\partial T}\right)_{V,N} = \frac{3}{2}Nk_B = \frac{3}{2}nR$$

$$C_P = \left.\frac{\partial}{\partial T}(E+PV)\right)_{P,N} = \frac{3nR}{2} + nR = \frac{5}{7}nR$$

If we expand the gas at constant T, E

$$S_2 - S_1 = k_B N \ln \frac{V_2}{V_1}$$

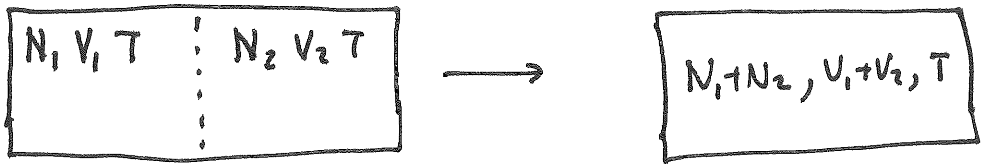
$$\gamma = \frac{C_P}{C_V} = \frac{5}{3}.$$

Adiabatic $VE^{3/2} = \text{cons}$

$VT^{3/2} = \text{cons} \Rightarrow T \sim V^{-2/3}$

$PV = nRT \sim V^{-2/3} \Rightarrow PV^{5/3} = \text{cons}$

GIBBS ENTROPY OF MIXING PARADOX



Gives rise to an entropy of mixing.

BUT If the two gases are identical we do not expect an entropy of mixing

Lets examine :

$$S_i = N_i k_B \ln \frac{V}{h^3} + \frac{3Nk_B}{2} \ln\left[2\pi m k_B T e_N\right]$$

$$S_T = (N_1+N_2) k_B \ln V + \frac{3(N_1+N_2)k_B}{2} \ln\left(\frac{2\pi m k_B T e}{h^2}\right)$$

$$S_1+S_2 = N_1 k_B \ln V_1 + N_2 k_B \ln V_1 + 3\left[\ \cdots\ \right]$$

$$S_T-(S_1+S_2) = (N_1+N_2) k_B \ln V - N_1 k_B \ln V_1 - N_2 k_B \ln V_2$$

$$= N_1 \ln \frac{V_1+V_2}{V_1} + N_2 \ln \frac{V_1+V_2}{V_2}$$

OK if 1 & 2 are distinct gases.

But if A & B are identical

$$x! \sim x \ln \frac{x}{e}$$

$$S_M = N_1 \ln \frac{N_1+N_2}{N_1} + N_2 \ln \frac{N_1+N_2}{N_2}$$

$$\simeq (N_1+N_2)\ln\left(\frac{N_1+N_2}{e}\right) - N_1 \ln \frac{N_1}{e} - N_2 \ln \frac{N_2}{e}$$

$$\simeq \ln \binom{N_1+N_2}{N_1} \neq 0$$

Gibb's resolution to the paradox.

$$\tilde{\Omega} = \frac{\Omega}{N!}$$

$$\ln \tilde{\Omega} = \ln \Omega - N \ln\left(\frac{N}{e}\right)$$

$$S = N k_B \ln \left[\frac{V e^{5/2}}{N} \left(\frac{4\pi m E}{3 N h^2} \right)^{3/2} \right]$$

$$\boxed{S \doteq N k_B \ln \frac{V}{N} + \frac{3}{2} N k_B \left\{ \frac{5}{3} + \ln \frac{2\pi m k_B T}{h^2} \right\}}$$

SACKUR · TETRODE FORMULA

Rearranged

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

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

$$= \frac{5}{3} k_B T - \frac{ST}{N} = \frac{G}{N}$$

$$\mu = k_B T \ln\left[\frac{N}{V}\left[\frac{h^2}{2\pi m k_B T}\right]^{3/2}\right]$$

CORRECT EVALUATION OF MICROSTATES

$$E = \sum n_i \epsilon_i$$

$$\frac{N!}{n_1! \cdots n_r!} = \text{Total \# of permutations lead to same } \{n_i\}$$

$$\Omega_{\text{classical}} = \sum \delta\left(E - \frac{\hbar^2}{2m}\left(\frac{2\pi}{L}\right)^2 \sum n_i^2\right)$$

$$= \sum \frac{N!}{n_1! \cdots n_r!} \delta(E - n_i \epsilon_i)$$

$$\Omega_{\text{Gibbs}} = \frac{\Omega_{\text{classical}}}{N!} = \sum \frac{1}{n_1! \cdots n_r!} \delta(E - n_i \epsilon_i)$$

OK if the $n_1! = n_r! = 1$ (i.e singly occupied)

But

$$\Omega_{\text{correct}} = \sum_{\{n_i\}} 1 . \, \delta(E - n_i \epsilon_i)$$

how ?

QUANTUM STAT MECH

Proof of Volume of D dimensional sphere

Recall. $\int dx\, e^{-x^2} = \sqrt{\pi}$

c.f. $\left(\int dx\, e^{-x^2}\right)^2 = \int dx\, dy\, e^{-x^2+y^2} = \int 2\pi r\, dr\, e^{-r^2}$

$u = r^2$
$du = 2r\,dr$

$$= \int \pi\, du\, e^{-u}$$

$$= \pi \Rightarrow \int dx\, e^{-x^2} = \sqrt{\pi}.$$

$$\boxed{\begin{aligned} A_D &= S_D r^{D-1} \\ dV &= S_D r^{D-1} dr \end{aligned}}$$

$$\pi^{D/2} = \left(\int dx\, e^{-x^2}\right)^D = \int \prod_{r=1}^{D} dx_r\, e^{-\sum x_r^2}$$

area of a D-sphere.

$$= \int S_D r^{D-1} dr\, e^{-r^2}$$

$u = r^2$
$du = 2r\,dr$
$r^{D-1}dr$
$= r^{D-2} r\,dr$
$= \frac{r^{D-2}du}{2}$

$$= \frac{S_D}{2} \int du\, r^{D-2} e^{-u}$$

$$= \frac{S_D}{2} \int du\, u^{\left(\frac{D-2}{2}\right)} e^{-u}$$

$$= \frac{S_D}{2} \left(\frac{D}{2} - 1\right)! = \left(\sqrt{\pi}\right)^D$$