

Statistical Physics / Thermal Physics.

- This course deals with and studies large assemblies of entities (atoms, molecules).
- The number of entities is measured in moles.
 - mole = The quantity of matter containing some number of entities as there are atoms in 12g of ^{12}C
 - $N_A = 6.02 \times 10^{23}$ (Avogadro's Number).
- Large quantities (number of entities) implies we can use average quantities
- Consider molecules of gas in container of volume V , temperature T . They exert an impulse ($I = FAt$) [F =Force, At =time for which F was applied]. We can also define a pressure ($P = \frac{F}{A}$). If the surface sampled is small, we need to worry about fluctuations in P . In this case, we reach a thermodynamic limit in which the fluctuations reach zero as surface area goes to infinity. P then appears uniform.

For most of the course we assume this case. Suppose kinetic energy of all molecules in the container adds up to U . They divide the container into 2 halves.

$$\boxed{\begin{matrix} E_{\text{kin}} = U \\ \vdots \end{matrix}}$$

$$\begin{array}{ll} \text{Full: } V \rightarrow & \text{Half: } \frac{V}{2} \\ U \rightarrow & \frac{U}{2} \\ P \rightarrow & P \\ T \rightarrow & T \end{array} \quad \begin{array}{l} \text{Extensive variables} \\ (\text{scale with system}) \end{array} \quad \begin{array}{l} \text{intensive variables} \\ (\text{don't scale}). \end{array}$$

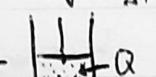
$$\frac{\text{Joule}}{\text{s}^2} \frac{1}{\text{m}^2}$$

$$\frac{\text{Kg}}{\text{s}^2} \frac{1}{\text{m}}$$

- The concept of heat is essential to thermal physics
 - "Heat is thermal energy in transit" - textbook defn
- Spontaneously transfers from hot \rightarrow cold object
- Can also transfer heat from cold \rightarrow hot (fridge) with an input of energy.
- Heat, Q , is measured in joules. $1\text{W} = 1 \frac{\text{J}}{\text{s}}$
- Rate of heating, $P^{(\text{heat})}$, is measured in watts
- $P = \frac{\Delta Q}{\Delta t}$

- The heat capacity, C , is the amount of heat required to raise T of an object by a small amount ΔT

$$C = \frac{dQ}{dT}$$

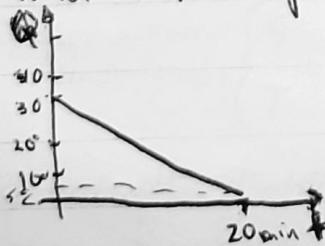
- It may be specific per unit volume $\Rightarrow C = \frac{dQ}{VdT}$
- It also may be specific per unit mass $\Rightarrow C = \frac{dQ}{mDT}$ (specific heat capacity)
- It also may be specific per mole $\Rightarrow C_m = c(mN_A)$ (molar heat capacity)
- Heat capacity can be measured under constant d : constant volume -  which $\Delta T \neq \Delta P$
 $C_V = \frac{Q}{\Delta T} = \left(\frac{\partial Q}{\partial T}\right)_V$
- constant pressure -  which ΔT , piston does work $\Rightarrow P$ is constant
 $C_P = \frac{Q}{\Delta T} = \left(\frac{\partial Q}{\partial T}\right)_P$
- Generally $C_P > C_V$ (requires energy to do work against atmosphere).
- Ex. Substance has mass per mole 50 g/mol , which 314.5 J to 30.0 g sample. T increases from 25.0°C to 45.0°C . For the substance what is the

(a) Specific heat? $C = \frac{dQ}{mDT} = \frac{314.5}{(30 \times 10^{-3} \text{ kg})(20 \text{ K})} = 523 \frac{\text{J}}{\text{kg}\cdot\text{K}}$

(b) molar specific heat? $C = c(mN_A) = 523 \cdot 3 \frac{\text{J}}{\text{kg}\cdot\text{K}} \left(50 \times 10^{-3} \frac{\text{kg}}{\text{mol}}\right) \approx 26 \frac{\text{J}}{\text{mol}\cdot\text{K}}$

(c) how many moles? $N = \frac{M}{mN_A} = \frac{30.0 \text{ g}}{(50 \times 10^{-3} \text{ kg})(6.02 \times 10^{23} \text{ mol}^{-1})} = 0.6 \text{ mol}$

- Ex. A 0.300 kg sample is placed in a cooling apparatus that removes energy or heat at a constant rate of 2.81 W . What is the specific heat of the sample?



$$\Delta Q = 25 \text{ J}$$

$$\Delta t = 20 \text{ min}$$

$$C = \frac{dQ}{dT} = \frac{\Delta Q}{\Delta T} = \frac{2.81 \frac{\text{J}}{\text{s}} (20 \text{ min} \cdot \frac{60 \text{ s}}{\text{min}})}{25 \text{ K}} = 134 \frac{\text{J}}{\text{K}}$$

$$C = mC = \frac{134}{0.3} = 450 \frac{\text{J}}{\text{kg}\cdot\text{K}}$$

Review of Probability

- Since thermal physics involves large numbers of entities probability is important
- Interpreting the behaviour on average.
- Need to extract average values from probability distributions.
- If event is impossible the $p=0$.

If event is certain the $p=1$

If event is possible but not certain $0 < p < 1$

- There are two types of probability distributions:

① discrete - discrete, random, variables (x_i) can only take on a finite number of values. (P_i)

- Ex: die, cards, coin etc. ~~etc.~~

~~Condition~~ $\sum P_i = 1$

- mean $\rightarrow \langle x \rangle = \sum x_i P_i$

- mean squared value $\rightarrow \langle x^2 \rangle = \sum x_i^2 P_i$

- mean value of $f(x) \rightarrow \langle f(x) \rangle = \sum f(x_i) P_i$

- Ex Game of chance.

Prob's if roll 5

$\frac{1}{2}$ if roll 2, 3

$$= 0.16 \cdot 5 + 0.33 \cdot 2 + 0.5$$

$\frac{1}{6}$ if roll 1, 4, 6. $= \frac{1}{6} \cdot 4$

a.) Find avg payout. $= \frac{1}{6} \cdot 4$

b.) Find mean squared value $\langle x^2 \rangle = \sum x_i^2 P_i$

$$= 5^2 \cdot \frac{1}{6} + 2^2 \cdot \frac{1}{3} + 6^2 \cdot \frac{1}{2} = \frac{155}{6}$$

② Continuous - If x is continuous there are infinite number of possible values it can take. Thus $P(x)$ for any value $\rightarrow 0$.

- Instead we say that x has probability $p(x)dx$ of lying within an interval dx located at x .

- Ex. Particle exhibiting STM or vibration decay.

- ~~Condition~~ $\int p(x)dx = 1$

- $\langle x \rangle = \int x p(x)dx$

- $\langle x^2 \rangle = \int x^2 p(x)dx$

- $\langle f(x) \rangle = \int f(x) p(x)dx$

Gaussian Distribution -

$\alpha \alpha \rightarrow$
compute for
integral.

- Let $P(x) = C e^{-\frac{x^2}{2\sigma^2}}$. Calculate $\langle x \rangle$ and $\langle x^2 \rangle$.

Step 1 Normalize - $\int_{-\infty}^{\infty} P(x) dx = 1 = C \int_{-\infty}^{\infty} e^{-\frac{x^2}{2\sigma^2}} dx = C \sqrt{\pi 2\sigma^2}$

$$C = \frac{1}{\sqrt{2\pi\sigma^2}}$$

$$P(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{x^2}{2\sigma^2}}$$

- $\langle x \rangle = \int_{-\infty}^{\infty} x e^{-\frac{x^2}{2\sigma^2}} dx = 0$ because for every (+) there is (-)
- $\langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 e^{-\frac{x^2}{2\sigma^2}} dx = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} x^2 e^{-\frac{x^2}{2\sigma^2}} dx = \frac{1}{2} 2\sigma^2 = \sigma^2$
-

Linear Transformation of a Random Variable.

* Assume $y = ax + b$; y, x one variables.
constants

* Then $\langle y \rangle = \langle ax + b \rangle = a\langle x \rangle + b$.

$$\langle y^2 \rangle = \langle (ax + b)^2 \rangle = \langle a^2 x^2 + 2abx + b^2 \rangle = a^2 \langle x^2 \rangle + 2ab\langle x \rangle + b^2$$

$$\langle y^2 \rangle = (a\langle x \rangle + b)^2 = a^2 \langle x^2 \rangle + 2ab\langle x \rangle + b^2$$

* The variance is the mean squared deviation defined by

$$\begin{aligned} \sigma_x^2 &= \langle (x - \langle x \rangle)^2 \rangle \\ &= \langle x^2 - 2x\langle x \rangle + \langle x \rangle^2 \rangle. \end{aligned}$$

$$= \langle x^2 \rangle - 2\langle x \rangle \langle x \rangle + \langle x \rangle^2 = \langle x^2 \rangle - \langle x \rangle^2 = \sigma_x^2$$

~~$$\begin{aligned} \sigma_y^2 &= \langle y^2 \rangle - \langle y \rangle^2, \\ &= a^2 \langle x^2 \rangle + 2ab\langle x \rangle + b^2 - a^2 \langle x \rangle^2 - 2ab\langle x \rangle - b^2 \\ &= a^2 \langle x^2 \rangle - a^2 \langle x \rangle^2 = a^2 [\langle x^2 \rangle - \langle x \rangle^2] = a^2 \sigma_x^2 \\ &= a^2 \sigma_x^2 = \sigma_y^2. \end{aligned}$$~~

* The standard deviation is:

$$\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2} = \sqrt{\sigma_x^2}$$

$$\sigma_y = a\sigma_x$$

- Ex. what are the standard deviation and variance for the:
 - a) Uniform Distribution:

$$\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2 = \sigma^2 - \bar{x}^2$$

$$\sigma_x = \sigma$$

- b) Game of chance:

$$\sigma_x^2 = 55 - 15^2 = 325$$

$$\sigma_x = \sqrt{325} = 1.8.$$

- c) Making game more enticing by offering a payout of

$y = 1.5x + 0.5$. when x is $\$x$ or $\$y$ are in dollars and x is again 5 for 1, 2, 3; 0 for 4, 5, 6. find the average payout, variance, and std dev.

$$\langle y \rangle = 1.5 \langle x \rangle + 0.5 = 1.5(15) + 0.5 = 27.5.$$

$$\sigma_y^2 = \sigma^2 \sigma_x^2 + 15^2(325) + 0.5^2 = 7.31.$$

$$\sigma_y = 2.7$$

Independent Variable

- Two random variables u & v are independent if knowing the value of one yields no info about value of other.

E.g. result of coin flip.

- Then the prob that u is in the range u_1 to u_2 and v is in the range v_1 to v_2 is:

$$P(u) = P(u)$$

$$P(u, v) = \int u \rho(u) P(v) dv du = \int_{u_1}^{u_2} \int_{v_1}^{v_2} \rho(u) P(v) dv du$$

- Example - Suppose there are n independent random variables x_i each with the same mean $\langle x \rangle$ and variance σ_x^2

$$y = x_1 + x_2 + \dots + x_n$$

$$\text{mean } \langle y \rangle = \langle x_1 + x_2 + \dots + x_n \rangle$$

$$\text{since } \langle x_i \rangle = \langle x \rangle$$

$$\langle y \rangle = n \langle x \rangle \text{ b/c}$$

$$\text{variance: } \sigma_y^2 = \langle y^2 \rangle - \langle y \rangle^2$$

$$\text{variance: } \sigma_y^2 = \frac{1}{n} \sum_{i=1}^n \langle x_i^2 \rangle - \langle x_i \rangle^2$$

$$\text{- Find } \langle y^2 \rangle = \langle x_1^2 + x_2^2 + \dots \rangle = \langle x_1^2 \rangle + \langle x_2^2 \rangle + \dots = n \langle x_i^2 \rangle = n(n-1) \langle x^2 \rangle$$

\rightarrow no choice.

$$\text{- } \sigma_y^2 = \langle y^2 \rangle - \langle y \rangle^2$$

$$= n \langle y^2 \rangle + n(n-1) \langle x^2 \rangle$$

$$= n \langle x^2 \rangle + n^2 \langle x^2 \rangle - n \langle x \rangle^2$$

$$= n \langle x^2 \rangle - \langle x \rangle^2$$

$$\therefore \sigma_y^2 = n \sigma_x^2 \quad \text{HLLV Confir.}$$

- Ex. In experimental physics it is important to repeat the experiments. Assuming errors are random and that the error in making a single measurement of a quantity x is Δ , find the error obtained after n measurements.

Solution: mean value \bar{x} :

$$\bar{x} = \frac{\sum x}{n} = \frac{x_1 + x_2 + \dots}{n}$$

$$\text{so } \langle y \rangle = \sum x_i = x_1 + x_2 + \dots = n\bar{x}$$

$$\sigma_y = \sqrt{n} \sigma_x = \sqrt{n} \Delta$$

$$\sigma_{\bar{x}} = \frac{\sigma_y}{\sqrt{n}} = \frac{\sqrt{n} \Delta}{\sqrt{n}} = \Delta$$

- Ex. $x = 3.05 \text{ m}, 3.02 \text{ m}, 3.06, 3.01, 2.99$.

$$\bar{x} = 3.026 \text{ m.}$$

$$\sigma_{\bar{x}} = 0.004 \text{ m}$$

$$\bar{x} = 3.026 \text{ m} \pm 0.004 \text{ m.}$$

- Coin toss is an example of a Bernoulli Trial, which is an experiment characterized by 2 possible outcomes.

- "success" with probability p .

- "failure" with probability $1-p$.

- The binomial distribution is the discrete probability distribution $P(n,k)$ of getting k successes out of n Bernoulli Trials.

$$\text{- } P(n,k) = \frac{n!}{k!(n-k)!} p^k (1-p)^{n-k} \rightarrow n-k \text{ failures.}$$

multiplicity
of ways of getting k success probability of
out of n trials. k success

3 heads out of 5 coins.

o

$${}^n C_S =$$

HHHTT
HHTHT
HHTTH
HTHHT
HTHTH
THHHHT

• See how this comes about:

- Assume 5 coins, "H" is success, "T" is failure

- Examine probability of obtaining 3H & 2T

- probability of 1st $p=0.5$

$$\text{2nd } " \quad p^2 = 0.25$$

$$\text{3rd } " \quad p^3 = 0.125$$

- " " 1st failure $(1-p) = 0.5$

$$\text{2nd failure } (1-p)^2 = 0.25$$

$$P(n,k) = {}^n C_k p^k (1-p)^{n-k}$$

- Select k H's out of n coins

- first from n coins.

$$\text{2nd } " \quad {}^{(n-1)} C_k "$$

$$\text{kth } " \quad {}^{(n-k+1)} C_1 "$$

$$\text{so total ways: } n(n-1)(n-2) \dots (n-k+1) \frac{(n-k)!}{(n-k)! (n-k)!} = \frac{n!}{(n-k)! (n-k)!}$$

- This assumes order is important.

- so need to divide by no of ways the 'k successes' can be organized i.e. $k!$

- ${}^n C_k = \frac{n!}{(n-k)! k!}$, sign "multiplicity of a macrostate containing k H's out of n coins."

$$P(n,k) = \frac{n!}{(n-k)! k!} p^k (1-p)^{n-k}$$

$$= \frac{5!}{2!3!} (0.125)(0.25) =$$

• Recall Binomial Theorem

$$(a+b)^n = a^n + n a^{n-1} b + \frac{n(n-1)}{1 \cdot 2} a^{n-2} b^2 + \dots + n a b^{n-1} + b^n$$

$${}^n C_n = \frac{n!}{(n-n)! n!} = 1$$

$${}^n C_{n-1} = \frac{n!}{(n-(n-1))!(n-1)!} = n$$

$${}^n C_{n-2} = \frac{n!}{(n-(n-2))!(n-2)!} = \frac{n(n-1)}{2}$$

$${}^n C_1 = \frac{n!}{(n-1)! 1!} = n$$

$${}^n C_0 = \frac{n!}{n! 0!} = n$$

• Thus can write:

$$(a+b)^n = \sum_{k=0}^n {}^n C_k a^k b^{n-k}$$

• Now put $a=p$ and $b=(1-p)$

$$(p+1-p)^n = 1^n = 1 = \sum_{k=0}^n {}^n C_k p^k (1-p)^{n-k} = \sum_{k=0}^n P(n,k).$$

- Let x be a random variable that takes on value 1 for success and 0 for failure (P is probability of success).

- $\langle x \rangle = 0(1-p) + 1(p) = p$.

- $\langle x^2 \rangle = 0^2(1-p) + 1^2(p) = p$.

$$\sigma_x^2 = \langle x^2 \rangle - \langle x \rangle^2 = p - p^2 = p(1-p)$$

- Since each Bernoulli trial is independent the expected number of success K in n trials is:

- $\langle K \rangle = n \langle x \rangle = np \quad (1)$

- i.e if n is doubled twice you expect no. of H's to be $2\langle x \rangle = 2(\frac{1}{2}) = 1$

- Also $\sigma_K^2 = n \sigma_x^2 = np(1-p)$

- Ex. - 1D Random Walk, Random Walker constrained along 1-D line. Length of step = ΔL . Walker has prob $p = \frac{1}{2}$ to step right and $p = \frac{1}{2}$ to take step to right. Each step independent of last, find mean distance after n steps and its STD, for n steps, how far which one to the right. Distance travelled.

$$x = k \Delta L \pm (n-k) \Delta L = (2k-n) \Delta L$$

- For binomial distribution with $p = \frac{1}{2}$.

$$\langle K \rangle = np = \frac{n}{2}$$

$$\therefore \sigma_K = \sqrt{np(1-p)} = \sqrt{n(0.25)} = \frac{\sqrt{n}}{2}$$

- Thus mean distance travelled is

$$\langle x \rangle = \langle (2K-n) \Delta L \rangle$$

$$= [2\langle K \rangle - n] \Delta L = [2 \cdot \frac{n}{2} - n] \Delta L = 0.$$

- But STD is

$$\begin{aligned} \sigma_x^2 &= \sqrt{\langle x^2 \rangle - \langle x \rangle^2} \\ &= \sqrt{\langle x^2 \rangle - \langle 2K-n \Delta L \rangle^2} \\ &= \sqrt{4\langle K^2 \rangle - 4n \langle K \rangle + n^2 \Delta L^2} \end{aligned}$$

$$\therefore \sigma_x = \sqrt{n} \Delta L$$

- Gives the root-mean-square length of a random walk of n steps

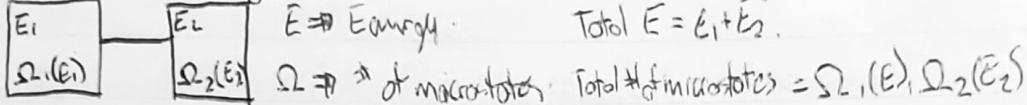
Statistical Interpretation of Temperature

- Thermalization: 2 objects at different T's; placed in contact will thermalize to the same temperature. Heat flows from Hot to cold.
 - Irreversible process
- Zeroth Law of Thermodynamics
 - 2 systems separately in thermal equilibrium with third, are in equilibrium with each other
- Measuring Temperature
 - place object in contact with object that has well-known T-dependence (thermometer).
 - When they come to thermal equilibrium, the T can be determined
 - Note: to work well, thermometer must have low heat capacity.
- A statistical approach can be used to define temperature.
- Need to understand distinction between macrostates and microstates.
- Ex.: 5 coins, all identical, tossed at same time.
 - Look to see how many H's, How many T's
 - 6 possible macrostates:

SH ₅	OT	microstates	1 state
4H ₁	TT		5 states
3H ₂	ZT ₂		10 states
2H ₃	ZT ₃		10 states
1H	TTT		5 states
0H	TTT		1 state

26 microstates.
 - Within each macrostate there are 1 or more microstates.
- Note: each micro-state is equally likely but each macrostate is not.
 - What one measures is determined by the macrostate which are not equally likely.
 - To specify the microstate for a thermal system would need to give microscopic configuration (eg. position, velocity) of each particle, which is generally impossible.
 - The macrostate of a system gives rise to macroscopic properties that are measurable (eg. pressure, volume, T, energy). will define properties.

- Consider 2 large systems that can exchange energy



- System chooses a macroscopic configuration that maximizes the # of microstates.
- Based on the following assumptions.

- ① All of the microstates are equally likely.
- ② The microstate configuration changes constantly.
- ③ Given enough time, system will sample all possible macrostates (ergodic hypothesis) and spend equal amount of time in each state.

- Implies system is most likely to be found in the macrostates, constituting the most microstates.

- most probable division of energy between 2 systems $E_1 \neq E_2$ in that which contains the most microstates.

- To find this maximize $\Omega_1(E_1) \Omega_2(E_2)$ wrt energy (E_i)

$$\frac{\partial \Omega_1(E_1)}{\partial E_1} \frac{\partial \Omega_2(E_2)}{\partial E_2} = 0$$

$$\Omega_1(E_1) \frac{\partial \Omega_2(E_2)}{\partial E_1} = \Omega_2(E_2) \frac{\partial \Omega_1(E_1)}{\partial E_2} = 0$$

$$\Omega_1(E_1) \frac{\partial \Omega_2(E_2)}{\partial E_1} = \Omega_2(E_2) \frac{\partial \Omega_1(E_1)}{\partial E_2} = 0$$

$$\frac{\partial \ln \Omega_2(E_2)}{\partial E_2} = \frac{\partial \ln \Omega_1(E_1)}{\partial E_1}$$

$$\text{recall: } \frac{C_v}{T} = \frac{1}{k_B T} = \frac{1}{\partial E_i / \partial T}$$

- gives most likely division of energy between the two systems.

- result is that two systems reach same temp. $T = T_1 = T_2$.

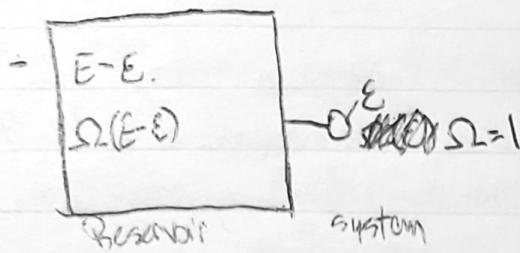
$$\text{Define: } \frac{1}{T_{\text{ST}}} = \frac{1}{\partial E_i / \partial T}$$

K_B - Boltzmann constant
 $k_B \approx 1.380700235 \frac{\text{J}}{\text{K}}$ • We will later see that entropy is defined by $S = k_B \ln \Omega$, which gives $\frac{1}{T} = \frac{1}{\partial S / \partial E}$

- Again consider two coupled systems that can exchange energy.

- One is extremely large (hot reservoir or bath) which has property that small amount of energy can be added or taken away without changing its temperature (significantly).

- The other much smaller one is referred to as the system.



exchange of energy

- This is called a canonical ensemble (small system in thermal contact with reservoir)
- Find probability that system is in microstate with energy E
- Reservoir will be in one of the large number $\Omega(E-E)$ possible microstates (all equally likely/accessible)
- Lower E implies higher $E-E$ and thus more possible microstates for reservoir \rightarrow thus probability that system is in microstate E will be proportional to $\Omega(E-E)$
- E.g. Consider 2 possible energies for reservoir (E_1, E_2) and assume $\Omega(E_2) = 2\Omega(E_1)$, since there are twice as many possible microstates

then system is most likely to have energy $E-E_1$

$$\text{Thus } P(E) \propto \Omega(E-E)$$

$$k_B T = \frac{d \ln \Omega}{d E} \text{ since } E \ll E \text{ use Taylor expansion around } E=0.$$

$$f(x+h) = f(x) + h f'(x) + \frac{h^2}{2!} f''(x) + \dots$$

$$\ln \Omega(E-E) = \ln \Omega(E) + E \frac{d \ln \Omega}{d E} + \dots$$

$$= \ln \Omega(E) - \frac{E}{k_B T}$$

Probability is proportional to this

$$\ln \left[\frac{\Omega(E-E)}{\Omega(E)} \right] = -\frac{E}{k_B T} \Rightarrow \frac{\Omega(E-E)}{\Omega(E)} = e^{-\frac{E}{k_B T}}, \text{ so.}$$

$$\Omega(E) = \frac{C}{e^{\frac{E}{k_B T}}} \text{ constant for given total } E$$

$P(E) \propto e^{-\frac{E}{k_B T}}$ \rightarrow Boltzmann factor.

- To find exact probability, need to normalize to probability that system is found in any one of all possible states

$$P(E_r) = \frac{e^{-\frac{E_r}{k_B T}}}{Z}$$

+ Partition function (usually denoted by Z)

$$Z = \sum e^{-\frac{E_i}{k_B T}}$$

$$P(E_r) = e^{-\frac{E_r}{k_B T}} / Z$$

often write $P = \frac{1}{Z} e^{-\frac{E_r}{k_B T}}$, which also equates to $\frac{c^{E_r}}{Z}$

• Ex. Thermal Excitation of Hydrogen Atoms

- Consider H-atom in atmosphere at sun ($T = 5800 \text{ K}$)

- Compare probability of finding atom in one of its 1^{st} excited states to that of finding it in the ground state

- Recall: $E = \frac{-13.6 \text{ eV}}{n^2}$ $E_1 = -13.6 \text{ eV}$

$E_2 = -3.4 \text{ eV}$

$\Delta E = -3.4 \text{ eV} - -13.6 \text{ eV} = 10.2 \text{ eV}$.

$$\begin{aligned} - \frac{P(E_2)}{P(E_1)} &= \frac{e^{-\frac{E_2}{kT}}}{e^{-\frac{E_1}{kT}}} \cdot \cancel{\frac{\cancel{E_2}}{\cancel{E_1}}} \\ &= e^{\frac{-(E_2 - E_1)}{kT}} \\ &= e^{\frac{-10.2 \text{ eV}}{(13.615 \times 10^{-19} \text{ eV})(1.38 \times 10^{-23} \text{ J/K})}} \\ &= 1.37 \times 10^{-9} \end{aligned}$$

- Actually, 1^{st} excited state has 4-fold energy degeneracy, so actually, $\frac{P(E_2)}{P(E_1)} = 4(1.37 \times 10^{-9})$
 $= 5.48 \times 10^{-9}$

- So ~~every~~ \approx billion atoms in ground state have \approx 5.48 in the 1^{st} excited state.

<u>n</u>	<u>l</u>	<u>m_l</u>
1	0	0
2	0	0
2	1	+1, 0, -1

Equipartition of Energy.

- Consider a system with an energy, E , that varies quadratically on some variable x
- Ex. $E = \frac{1}{2}Kx^2$ $E_K = \frac{1}{2}mv^2$
- In general, $E = \alpha x^2$
- Probability system has particular energy is proportional to the Boltzmann factor

- $P(E) \propto e^{-\frac{E}{kT}}$ ← system in contact with heat reservoir/bath at temp, T .

Assuming $x \rightarrow$ \bullet Normalizing: $P(x) = \frac{C}{\int_{-\infty}^{\infty} e^{-\frac{\alpha x^2}{kT}} dx}$ - constant
 not equal probability of having any value

• The mean energy:

$$- \langle E \rangle = \int_{-\infty}^{\infty} EP(x)dx = \int_{-\infty}^{\infty} \alpha x^2 C e^{-\frac{\alpha x^2}{kT}} dx$$

$$\text{So } \langle E \rangle = \alpha \frac{1}{2} \sqrt{\frac{\pi}{\left(\frac{k_B T}{\alpha}\right)^2}} = \alpha \frac{1}{2} \left(\frac{k_B T}{\alpha}\right) = \frac{k_B T}{2}$$

• For n -independent quadratic terms

- $E = \sum \alpha_i x_i^2$ then $\langle E \rangle = \frac{n}{2} k_B T$ + Equipartition Theory.

• Each such quadratic term is called a degree of freedom

• Assumptions - x can take any value with equal probability (not given)
- have ignored anharmonic terms in the potential

Ex. Gas,

① Translational motion in a monoatomic gas:

$$E = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2$$

using equipartition, $\langle E \rangle = \frac{3}{2} k_B T$.

② Rotational motion in a diatomic gas

$$E = \frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2 + \frac{1}{2} I_{xx}^2 + \frac{1}{2} I_{yy}^2$$

$$\langle E \rangle = \frac{5}{2} k_B T$$

③ Vibration energy in diatomic gas

- 2 additional DOF (Degrees of freedom)

$$\langle E \rangle = \frac{7}{2} k_B T$$

④ Heat Capacity in a solid.

- Each spring connects to at least 2 atoms

- So if there are N atoms there are $3N$ springs

$$\text{so } \langle E \rangle = 3N \times \frac{7}{2} k_B T = 3N k_B T$$

$$\text{Total } \langle C \rangle = \frac{\partial}{\partial T} \langle E \rangle = 3N k_B T$$

OR for one : $C = 3N k_B = 3R$ { Dulong - Petit Rule } N_A = Avogadro Number

R "gas constant" - $R = 8.314 \frac{\text{J}}{\text{mol K}}$

• Ex. 19.3 A particle at position r in a potential well

given by $V(r) = \frac{A}{r^n} - \frac{B}{r^2}$, $A, B = \text{constants}$, $n > 2$

Show bottom of well is approximately quadratic in r and therefore find mean energy of particle assuming the validity of equipartition.

• Problem 19.3: Find minimum

$$\frac{dV(r)}{dr} = 0$$

$$\frac{d}{dr} \left[\frac{A}{r^n} - \frac{B}{r} \right] = \frac{d}{dr} [Ar^{-n} - Br^{-1}] \\ = -nAr^{n-1} + Br^{-2}$$

• Put $r = r_0$ at min.

$$-\frac{nA}{r_0^{n+1}} + \frac{B}{r_0^2} = 0 \Rightarrow B = \frac{nA}{r_0^{n+1}} \Rightarrow B = \frac{nA}{r_0^{n-1}}$$

$$\text{so } r_0^{n-1} = \frac{nA}{B}$$

• Take Taylor Expansion of $V(r)$ about r_0

$$f(x) = f(a) + (x-a) \left(\frac{df}{dx} \right)_{x=a} + \frac{(x-a)^2}{2!} \left(\frac{d^2f}{dx^2} \right)_{x=a} + \dots$$

$$V(r) = V(r_0) + (r-r_0) \left(\frac{\partial V}{\partial r} \right)_{r=r_0} + \frac{(r-r_0)^2}{2!} \left(\frac{\partial^2 V}{\partial r^2} \right)_{r=r_0} + \dots \\ = V(r_0) + \underbrace{\frac{(r-r_0)^2}{2!} \left[n(n+1) \frac{A}{r_0^{n+2}} - \frac{2B}{r_0^2} \right]}_{\text{quadratic dep. const.} = \beta}$$

quadratic dep. const. $\equiv \beta$.

$$v = V_0 + \alpha (r-r_0)^2$$

Find Energy near bottom of the well where potential is quadratic and exhibits SHM.

$$\langle E \rangle = 2 \times \frac{1}{2} k_B T = k_B T$$

Kinetic Theory of Gases

- Individual gas atoms behave according to the Boltzmann Distribution.

- Consider only translational motion, ignore rotational & vibrational motion → strictly speaking only applicable to monoatomic gases
- Assumptions - ① molecular size is \ll intermolecular separation
Molecules don't "bump" often
- ② ignore intermolecular forces.
- ③ Molecules exchange energy via collisions
- ④ Each molecule behaves as if it is a small system connected to a heat reservoir at temp T which is all the other molecules in the gas.

- Energy of given molecule:

$$\frac{1}{2}mv^2 = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2$$

- The velocity distribution function gives

- g fraction of molecules with velocities in x-direction.

- Proportional to Boltzmann factor for energy in that direction

- $g(v_x) \propto e^{-\frac{mv_x^2}{2k_B T}}$ (ave for each direction)

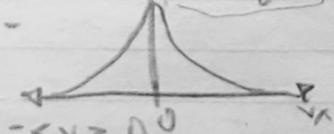
- Normalizing!

$$A \int_{-\infty}^{\infty} g(v_x) dv_x = 1.$$

$$A \left(\sqrt{\frac{2k_B T}{m}} \right) = 1$$

$$\sqrt{\frac{m}{2k_B T}} = \frac{1}{A}$$

$$g(v_x) = \frac{1}{\sqrt{\frac{m}{2k_B T}}} e^{-\frac{1}{2} \frac{mv_x^2}{k_B T}}$$



Analogous results would be obtained for v_y & v_z , thus the fraction of molecules in the (v_x, v_y, v_z) is

$$\langle v_x v_y v_z \rangle = \int_{-\infty}^{\infty} v_x v_y v_z g(v_x) g(v_y) g(v_z) dv_x dv_y dv_z$$

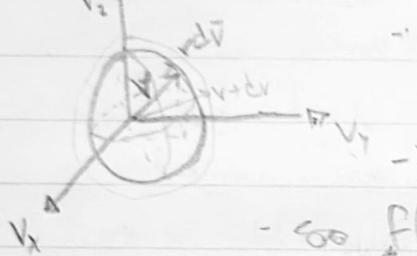
$$\langle v_x^2 \rangle = \frac{k_B T}{m}$$

$$\langle \left(\frac{m}{2k_B T} \right)^{3/2} e^{-\frac{1}{2} \frac{mv^2}{k_B T}} \rangle$$

- $g(v_x)$ gives us fraction of molecules with velocities between $\bar{v} = (v_x, v_y, v_z)$ and $\bar{v}' = (v_x + dv_x, v_y + dv_y, v_z + dv_z)$
- $g(v_1)g(v_2)dv_x dv_y dv_z = \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2k_B T}}$

• Next we find distribution of speeds.

- need to find fraction of molecules with speeds between $v = |\bar{v}|$, & $v dv = |\bar{v} + d\bar{v}|$



- corresponds to spherical shell in \bar{v} -space

- Volume of shell $4\pi v^2 dv$

$$- \infty f(v) dv \propto v^2 e^{-\frac{mv^2}{2k_B T}} dv.$$

need to normalize, \therefore drop constants.
fraction with speeds
between v & $v + dv$.

$$\begin{aligned} - A \int_{-\infty}^{\infty} v^2 e^{-\frac{mv^2}{2k_B T}} dv &\quad \leftarrow \int_{-\infty}^{v+dv} x^2 e^{-\frac{mx^2}{2k_B T}} dx = \frac{1}{4} \sqrt{\frac{\pi}{a^3}} \\ = \frac{A}{2} \sqrt{\frac{8k_B^3 \pi T^3}{m^3 \pi}} &= \frac{A}{4} \sqrt{\frac{8k_B^3 \pi T^3}{m^3 \pi}} \Rightarrow A = \frac{4}{\sqrt{\pi}} \sqrt{\frac{m^3}{8k_B^3 T^3}} \\ &\stackrel{oc}{=} \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T}\right)^{\frac{3}{2}}. \end{aligned}$$

$$- f(v) dv = \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T}\right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2k_B T}} dv$$

- This is the Maxwell-Boltzmann speed distribution

$$\textcircled{1} \quad \langle v \rangle = \int_0^{\infty} v f(v) dv = \int_0^{\infty} v \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T}\right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2k_B T}} dv$$

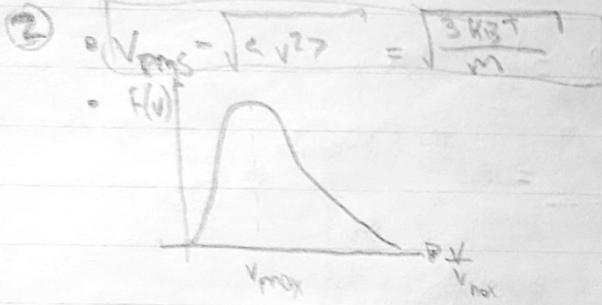
$$= \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T}\right)^{\frac{3}{2}} \cdot \frac{2m^2}{(2k_B T)^2} \cdot \frac{1}{2} \left(\frac{m}{2k_B T}\right)^2$$

$$= \frac{2}{\sqrt{\pi}} \left(\frac{2k_B T}{m}\right)^{\frac{1}{2}} = \sqrt{\frac{8k_B T}{\pi m}}$$

$$\langle v^2 \rangle = \int_0^{\infty} v^2 f(v) dv = \frac{3k_B T}{m}$$

$$\text{Result, for } g(v_x) \rightarrow \langle v_x^2 \rangle = \frac{k_B T}{m}$$

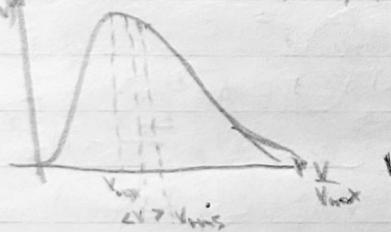
$$\text{so } \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = \frac{3k_B T}{m} = \langle v^2 \rangle.$$



• find V_{max} :

$$\begin{aligned} \frac{d(F(v))}{dv} = 0 &= \frac{d}{dv} \left[\frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{\frac{3}{2}} v^2 e^{-\frac{mv^2}{2k_B T}} \right] \\ &= \frac{4}{\sqrt{\pi}} \left(\frac{m}{2k_B T} \right)^{\frac{3}{2}} \left[2v e^{-\frac{mv^2}{2k_B T}} + v^2 \left(-\frac{m}{2k_B T} \right) e^{-\frac{mv^2}{2k_B T}} \right] \\ 0 &= 1 - \frac{v^3}{2k_B T} \Rightarrow V_{\text{max}} = \frac{2k_B T}{\sqrt{m}} \quad (3) \end{aligned}$$

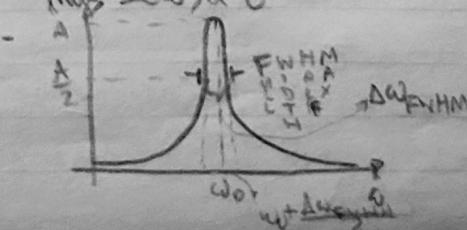
• Thus from ①, ②, ③ we see that $V_{\text{max}} < \langle v \rangle < V_{\text{rms}}$



• Application: Doppler Broadening of Spectral Lines.

- When hot gas atoms in excited state makes a transition to a lower energy level it emits light at frequency ω_0 .
- However atoms moving towards/away from detector at time t emission will be doppler-shifted
- $\omega = \omega_0 (1 \pm \frac{v_x}{c})$, + for towards, - for away.
- $\frac{\omega}{\omega_0} = 1 \pm \frac{v_x}{c} \Rightarrow v_x = \pm c \frac{\omega_0 - \omega}{\omega_0}$

- $v_x^2 = \frac{c^2}{\omega_0^2} (\omega_0 - \omega)^2$
- Thus spectral lines will broaden according to $f(\omega)$
- Thus $I(\omega) \propto e^{-\frac{N \cdot \frac{c^2}{2k_B T} \frac{1}{\omega_0^2} (\omega_0 - \omega)^2}{\omega_0}}$



$$I(w_0 + \frac{\Delta w_{\text{FWHM}}}{2}) = \frac{1}{2}$$

$$I(w_0) = e^{-\frac{m}{2k_B T} \frac{(w_0 - v)^2}{w_0^2} \Delta w_{\text{FWHM}}^2} = e^{-\frac{m}{2k_B T} \frac{v^2}{w_0^2} \Delta w_{\text{FWHM}}^2}$$

$$\ln \frac{1}{2} = -\frac{m}{2k_B T} \frac{v^2}{w_0^2} \Delta w_{\text{FWHM}}^2$$

$$\Delta w_{\text{FWHM}} = \sqrt{\frac{8k_B T \ln 2}{m v^2}} \text{ depend on } T \text{ & } m.$$

$$1 \text{ Pa} = \frac{N}{\text{m}^2} \text{ (SI)}$$

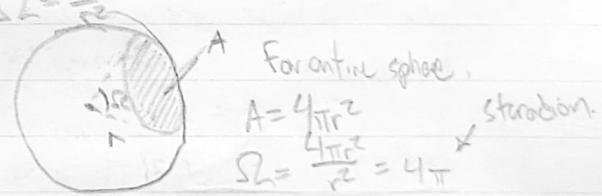
$$1 \text{ Bar} = 10^5 \text{ Pa}$$

$$1 \text{ atm} = 1.01325 \times 10^5 \text{ Pa}$$

$$1 \text{ Torr} = 1 \text{ mmHg} = 133.32 \text{ Pa}$$

Application: Equation of State of an Ideal Gas

- Consider pressure of gas: $P = \frac{F}{A}$, units: $\text{N/m}^2 = 1 \text{ Pa}$, Bar, torr, atm
- no. of molecules travelling with speeds between v and $v+dv$ is $n f(v) dv$ (per unit volume) $\leftarrow \frac{dN}{dt}$
- Solid angle $\Omega = \frac{\pi}{2}$



- If all molecules are equally likely to travel in any direction the fraction in an elemental solid angle $d\Omega$ is $\frac{d\Omega}{4\pi}$

- Choose particular direction



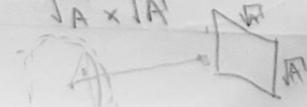
- Solid angle corresponding to fraction of molecules travelling with θ and $\theta + d\theta$ of the particular direction

$$d\Omega = \frac{dA}{A} = 2\pi r^2 \sin \theta d\theta$$

$$\frac{d\Omega}{4\pi} = \frac{1}{2} \sin \theta d\theta$$

- The no. of molecules per unit volume travelling at speeds between v and $v+dv$ and travelling at angles between θ and $\theta+d\theta$ will be given by $n f(v) dv \frac{1}{2} \sin \theta d\theta$

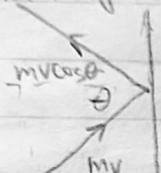
- Assume the direction is 1 to a wall of area $\sqrt{A} \times \sqrt{A}$



$$\frac{vdt \cos\theta}{dt} \sqrt{A}$$

Volume swept out in time dt is
thus $\sqrt{A} \sqrt{A} v dt \cos\theta$

- No. of molecules hitting wall of area A in time dt , with speeds v to $v+dv$ at angles $\theta+\dfrac{d\theta}{2}$ is $A v dt \cos\theta n f(v) dv \frac{1}{2} \sin d\theta$.
- Each molecule bounces back from the wall imparting an impulse equal to:



$$Ap = 2mv \cos\theta = F A$$

$$so \quad df = \frac{Ap}{A} = \frac{2mv \cos\theta}{A}$$

- Force due to all molecules ($v \rightarrow v+dv$; $\theta \rightarrow \theta + d\theta$) in the dt is:

$$A v dt \cos\theta n f(v) dv \cdot \frac{1}{2} \sin d\theta \frac{2mv}{A} \star$$

$$\begin{aligned} - \text{Pressure is } & \int \frac{df}{A} = \frac{Ap}{A} = \frac{2mv}{A} \int v^2 f(v) dv \cdot \frac{1}{2} \sin \cos^2 \theta dv \\ & = \frac{2mv}{A} \int v^2 dv \end{aligned}$$

$$\begin{aligned} - \text{Thus } P = \frac{NkT}{V} \Rightarrow PV = nRT. \quad \text{Equation of state} \\ & \text{for an ideal gas} \end{aligned}$$

- Assume \rightarrow no molecular force
 \rightarrow point char.

$$\frac{3k_B T}{m}$$

Dalton's Law

- for mixture of gases in equilibrium.
- $P = \sum_i n_i k_B T = \sum_i \bar{P}_i$ Partial pressure of i th species.
where $n_i = \frac{N_i}{V}$

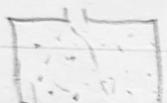
Molecular Flux

- no. of molecules striking (or flowing) wall per unit area per unit time.
- $\Phi = \frac{\text{no. of molecules}}{A \times dt} = \frac{A v dt \cos\theta n f(v) dv \cdot \frac{1}{2} \sin d\theta}{A \times dt}$

$$\cdot \frac{1}{2} \int_0^{\infty} v f(v) dv \int_0^{\infty} \sin \theta \cos \theta d\theta = \frac{\pi}{4} \bar{v}^2$$

From ideal gas law $n = \frac{P}{RT}$ $\bar{v}^2 = \sqrt{\frac{3k_B T}{m}}$
 $\text{so } I = \frac{1}{4} \frac{P}{RT} \int \frac{3}{m} dT = \frac{P}{m} \int \frac{3k_B T}{m} dT$
 $\overline{v^2} = \frac{P}{2\pi k_B T}$ prop. $\propto T^{1/2}$

- Effusion - process by which gas escapes from a tiny hole

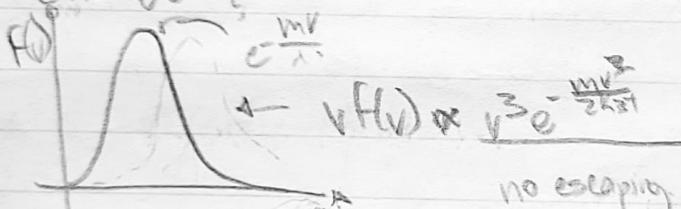


Effusion

$$m \overline{v^2} A = \frac{P}{2\pi k_B T}$$

no molecules escape

- E.g. isothermal box contains Maxwellian distribution speeds but faster molecules have higher chance!



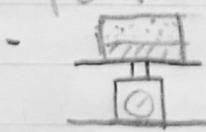
- Rate at which mass is lost inside box is.

$$\frac{dM}{dt} = m \overline{v^2} A = \frac{m \overline{v^2} A}{\sqrt{2\pi k_B T}} = \frac{P A}{\sqrt{2\pi k_B T}}$$

$$\therefore \text{pressure in box } P = \sqrt{2\pi k_B T}$$

- Applications: Knudsen method of measuring vapor pressure.

A closed vessel is partially filled with liquid Hg; there is a tiny hole of area 10^{-7} m^2 above liquid level. Vessel is placed in region of high vacuum at 273K and after 30 days is found to be lighter by $2.4 \times 10^{-5} \text{ kg}$. Estimate vapor pressure of Hg. (molecular mass Hg is 200.59)



$$P = \frac{\sqrt{2\pi k_B T}}{m} \frac{dM}{dt}$$

$$P = \frac{2 \times (1.38 \times 10^{-23})(273)}{200.59 \times 10^{-3}} \times \frac{6.022 \times 10^{23} \text{ mol}^{-1}}{10^{-7} \text{ m}^2} \times \frac{2.4 \times 10^{-5}}{30 \text{ days}}$$

$$P = 0.6247 \text{ Pa}$$

Mean Free Path and Collisions

- In dilute gas, molecules spend most of their time between collisions (treat classically)
- Assume after collisions velocities are random.
- Calculate average time between collisions.
- Assume molecule travelling at speed v , in a stationary sea of like molecules.
- The cross sectional area of molecule is σ .
- In time dt , sweeps out volume $\sigma v dt$.
- If collides with any other molecules in that volume.
- Assume density, n , molecules/volume.
- Probability of a collision is $n \sigma v dt$.
- Let $P(t)$ be probability molecule does not collide in time t

Then $P(t+dt) = P(t) + \frac{dP}{dt} dt = P(t)(1 - n \sigma v dt)$

First term of Taylor expansion: $\frac{dP}{dt} dt$
 prob of no collision till next interval, dt .
 prob not collide in next interval, dt .

$P + \frac{dP}{dt} dt = P - P n \sigma v dt$

$\frac{dP}{dt} dt = - P n \sigma v dt$

$\frac{1}{P} \frac{dP}{dt} = - n \sigma v$

$P(t) = e^{-n \sigma v t}$ where $P(0) = 1$

100% probability, no collisions
 at $t=0$

- Prob of surviving to time t , but then colliding in next interval dt is:

$e^{-n \sigma v t} n \sigma v dt$

- To find mean scattering time multiply + and integrate over all possible values

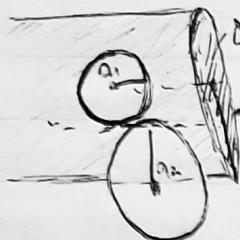
$$T = \int_0^\infty t e^{-n \sigma v t} n \sigma v dt \quad | \text{Change of variables } x = n \sigma v t \quad \frac{dr}{dt} = n \sigma v, dt = \frac{dr}{n \sigma v}$$

$$= \left[\int_0^\infty r e^{-r} dr \right] \frac{1}{n \sigma v} = \frac{1}{n \sigma v}$$

$P(t) = e^{-\frac{t}{T}}$

- Assuming hard spheres the collision cross-section between two molecules of radii a_1, a_2 is given by:

$$\sigma = \pi (a_1 + a_2)^2$$



σ i.e. collision takes place if centers of molecules lie within tube of radius $a_1 + a_2$.

As T molecules are less rigid and σ becomes smaller.

- The mean free path is given by $\lambda = \frac{1}{2\langle v \rangle}$, distance molecule moves between collisions so $\lambda = \frac{\langle v \rangle}{2\langle v \rangle}$ now, this shall be the relative velocity between 2 molecules

$$\text{Then } \langle v \rangle, \vec{v}_r = \vec{v}_1 - \vec{v}_2, \quad v_r^2 = v_1^2 + v_2^2 - 2(v_1 \cdot \vec{v}_2)$$

$$\langle v_r^2 \rangle = \langle v_1^2 \rangle + \langle v_2^2 \rangle - 2 \langle v_1 v_2 \rangle$$

$$\langle v_r^2 \rangle = \langle v_1^2 \rangle + \langle v_2^2 \rangle = 2 \langle v^2 \rangle$$

- For the Maxwell Boltzmann distribution

$$\langle v \rangle \equiv \sqrt{\langle v^2 \rangle} \quad \langle v \rangle = \sqrt{\frac{3}{\pi}} \sqrt{\frac{k_B T}{m}}$$

$$\text{so } \langle v_r^2 \rangle \approx 2 \langle v^2 \rangle \quad \sqrt{\langle v^2 \rangle} = \sqrt{3} \sqrt{\frac{k_B T}{m}}$$

$$\text{so } \lambda = \frac{\langle v \rangle}{\text{now} \sqrt{2} \langle v \rangle} = \frac{1}{\sqrt{2} \text{ now}} \quad P = n k_B T$$

$$\text{or } \lambda = \frac{k_B T}{\sqrt{2} m P}$$

- Example: No. density of the gas (mainly Hydrogen, H_2) that fills interstellar space is one molecule per cubic cm (10^6 m^{-3}), diff molecule is 10^{-10} m , what is ~~MED~~ in interstellar space?

$$\lambda = \frac{1}{\sqrt{2} m P} = \frac{1}{\sqrt{2} (10^6) (\pi) (10^{-10})} = 2.23 \times 10^{13} \text{ m.}$$

- b) what is collision frequency of a hydrogen molecule in collision per centur, if $T = 10^\circ \text{C}$.

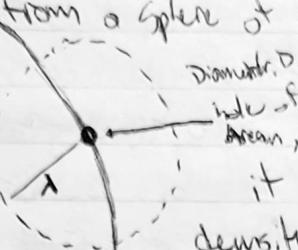
$$f = \frac{1}{T} = \frac{\langle v \rangle}{\lambda} = \frac{\sqrt{8k_B T}}{\pi m \lambda} = \frac{\sqrt{8(1.38 \times 10^{-23})}}{\pi (1.67 \times 10^{-27})} \frac{1}{2.23 \times 10^{13}} = 3.153 \times 10^9 \frac{1}{\text{century}}$$

= 0.05 century.

- Return to concept of effusion to consider how small hole must be (do not want to appreciably alter equilibrium state of gas in container)
- Molecules move on average distance λ between collisions.
- Density of molecules at a given location is determined by the flow of molecules from a sphere of radius λ one surface area $4\pi\lambda^2$.

- Flow of over A be so small that it does not appreciably affect molecular density at center of sphere ($A \ll 4\pi\lambda^2$)
- $A \ll 4\pi\lambda^2 \Rightarrow \frac{\pi D^2}{4} \ll 4\pi\lambda^2 \Rightarrow D^2 \ll 16\lambda^2$
Arbitrarily say, $D^2 \leq 100(16\lambda^2) \Rightarrow D = 0.4\lambda \Rightarrow \lambda = \frac{D}{0.4}$
(or smaller) (larger)

- Since $\lambda \propto \frac{1}{P}$ there is an upper limit to pressure for which effusion occurs



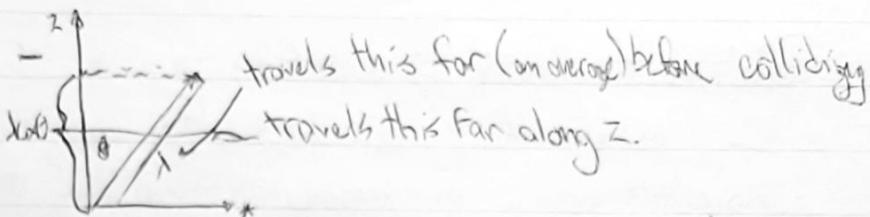
Transport Properties in Gases

- η Viscosity = consider a fluid (gas) between two plates of area A.



Top plate slid at speed, u ,
keeping the bottom plate stationary (shear force).

- There will be a gradient in the x-component of molecules velocities as a function of distance along the z-axis
- $\frac{du_x}{dz}$ i.e. use average since extra motion in x-axis is superimposed on the Maxwell-Boltzmann speed distribution
- Note that molecules travelling in +z direction move from a layer where $<u_x>$ is less to one where it is more, thereby transporting translational momentum
- $\Pi_z = -\eta \frac{du_x}{dz}$, Π_z = momentum flux, η = viscosity.
- Consider molecules travelling at θ with to z-axis.



- In travelling λ_{coll} along z , passes through viscosity gradient $\frac{\partial u(x)}{\partial z}$
- Thus velocities will increase by $\lambda_{\text{coll}} \frac{\partial u(x)}{\partial z}$
- Since travelling to where u_x is higher, it transfers deficit of momentum $-m \left(\frac{\partial u(x)}{\partial z} \right) \lambda_{\text{coll}}$.
- Thus momentum flux is:

$$\begin{aligned} \Pi_z &= \int_0^{\infty} \int_0^{\pi} v \cos \theta n f(v) \sin \theta d\theta - m \left(\frac{\partial u(x)}{\partial z} \right) \lambda_{\text{coll}} \\ &= \frac{1}{2} n m L \int_0^{\infty} v f(v) \cos \theta \left(\frac{\partial u(x)}{\partial z} \right) \int_0^{\pi} \sin \theta d\theta d^3v \\ &= \frac{1}{2} n m L \langle v \rangle \left(\frac{\partial u(x)}{\partial z} \right)^2 \frac{2}{3} \end{aligned}$$

- Thus $\eta = \frac{1}{3} n m L \langle v \rangle$, viscosity.
- Consider its dependence on various quantities.

$$\begin{aligned} L &= \sqrt{2} n \rightarrow \pi d^2, \langle v \rangle = \left(\frac{8 k_B T}{\pi m} \right)^{1/2} \\ \eta &= \frac{1}{3} n m L \left(\frac{8 k_B T}{\pi m} \right)^{1/2} \frac{1}{\sqrt{2} \pi} \\ \eta &= \frac{2}{3} \frac{1}{\pi d^2} \left(\frac{k_B T m}{\pi} \right)^{1/2}, L \gg \lambda \gg d. \end{aligned}$$

- Find the viscosity of oxygen gas at STP (standard temp/pressure).

$$\eta = \frac{2}{3 \pi} \frac{1}{(3.6 \times 10^{-10})^2} \left(\frac{1.3807 \times 10^{-23} \text{ J/K} / 273 \text{ K} / (0.032 \text{ kg/mol})}{\pi / (6.022 \times 10^{23} \text{ mol})} \right)$$

$$= 1.3 \times 10^{-5} \text{ Pa}\cdot\text{s}$$

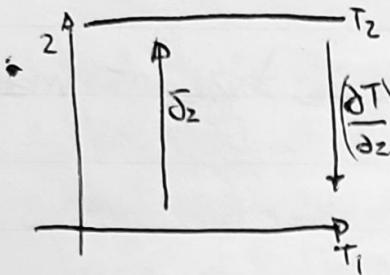
or using another result

$$\eta = 1.5 \times 10^{-5} \text{ Pa}\cdot\text{s.}$$

When the Maxwell-Boltzmann distribution change is taken into account, it is

$$\eta = \frac{5}{16} \frac{L}{d^2} \left(\frac{k_B T m}{\pi} \right)^{1/2}$$

Thermal Conductivity.



- Assume $T_1 > T_2$
 - heat flows from warmer to colder region
 - ∵ heat flux vector whose magnitude
 if the ^{heat} energy per unit time per unit area $(\frac{J}{sm} = \frac{W}{m^2})$
 is given by $\vec{J}_z = -k \left(\frac{\partial T}{\partial z}\right)$

- k is thermal conductivity, the negative sign tells
 us heat flows in the opposite direction of ~~mean~~ gradient

• Recall for gas at reasonably low T that mean energy is $\frac{3}{2}k_B T$

• So to increase T of gas by $1K$ need to increase average energy $\frac{1}{2}$ per molecule

• But heat capacity is heat reqd to raise by ~~1K~~ $1K$.
 so: $C_{molecule} = \frac{3}{2}k_B$

• molecule moving $\lambda \cos\theta$ in z -direction will carry excess thermal energy: $C_{molecule} \Delta T = C_{molecule} \left(\frac{\partial T}{\partial z}\right) \cos\theta$.

• Thus heat δQ :

$$\delta Q = \int_0^\infty CV \left(-C_{molecule} \left(\frac{\partial T}{\partial z}\right) \lambda \cos\theta \right) v \cos\theta n f(v) \frac{1}{2} \sin\theta dv.$$

$$= -\frac{1}{2} C_{molecule} \lambda n \left(\frac{\partial T}{\partial z}\right) \int_0^\infty v^2 f(v) \cos^2\theta \sin\theta dv$$

$$= -\frac{1}{2} C_{molecule} n \lambda \left(\frac{\partial T}{\partial z}\right)^2$$

$$K = \frac{1}{2} C_{molecule} n \lambda$$

$$C_V = n C_{molecule} = \text{heat capacity per mol volume}$$

• Sub in for $\lambda \propto v^2$ or above:

$$K = \frac{1}{2} C_{molecule} \frac{1}{2} \left(\frac{k_B T}{\pi m}\right)^2$$

Monatomic

Other eqn.

$$K = \frac{2S}{3B} C_{mol} \frac{1}{2} \left(\frac{k_B T}{\pi m}\right)^2$$

Diffusion.

- Consider a distribution of the same type of molecules along z-axis $\rightarrow n^*(z)$

- Assume n^* are labelled.

- Flux of labelled molecules along z:

$$\Phi_z = -D \frac{dn^*}{dz} \quad \text{in 3D, } \Phi = -D \nabla n^*$$

\hookrightarrow coefficient of self-destruction

- Number of labelled particles that flow out of a closed surface S , is: $\int_S \Phi_z dS$ and must equal the decrease in number labelled molecules in volume, V , surrounded by S .

$$\int_S \Phi_z dS = -\frac{\partial}{\partial z} \int_V n^* dV = \int_V \nabla \Phi_z dV.$$

$\underbrace{\qquad\qquad\qquad}_{\text{DIVERGENCE THEOREM}}$

Thus, $\frac{\partial}{\partial z} n^* = \nabla \cdot \Phi_z = \nabla \cdot (-D \nabla n^*)$

$$\frac{\partial n^*}{\partial z} = D \nabla^2 n^* \quad \text{Diffusion equation.}$$

- To find D , use an approach similar to that of thermal conductivity

$$\Phi_z = \int_0^L d\theta \int_0^\pi d\phi \cos\theta f(\theta) \frac{1}{2} \sin\theta \left(\frac{dn^*}{dt} \right) \lambda \cos\theta$$

$$D = \frac{1}{3} \lambda \langle v_r \rangle$$

$$\frac{1}{3} \lambda \langle v_r \rangle = \frac{1}{3} \lambda C V \frac{\partial n^*}{\partial z} \Rightarrow \frac{2}{3D} \frac{1}{nd^2} \left(\frac{k_B T}{\pi m} \right)^{1/2}$$

Boundary condition.

Recall: $\frac{1}{3} \lambda \langle v_r \rangle = \frac{1}{3} \lambda \sqrt{v_r^2} \Rightarrow \frac{1}{3} \lambda \sqrt{v_r^2} = D$ (at const T)

- Example: How does D depend on i) λ (constant), ii) T (constant)?

i) $D \propto \frac{1}{3} \lambda \langle v_r \rangle$, $\langle v_r \rangle$ is constant if T const., $\lambda \propto \frac{1}{T} \Rightarrow D \propto \frac{1}{T}$.

$$D \propto \frac{1}{T}$$

ii) $D \propto \frac{1}{3} \lambda \langle v_r \rangle^2 \Rightarrow \langle v_r \rangle \propto T$.

$$D \propto \sqrt{T}$$

- If instead we have different types of molecules diffusing against one another, replace $d \rightarrow \frac{d_1 + d_2}{2}$ any molecule diameter

$$D = D_{12} = \frac{2}{3\pi n_1 \left[\frac{d_1 + d_2}{2} \right]^2} \left(\frac{k_B T (m_1 + m_2)}{2\pi m_1 m_2} \right)^{1/2} + \frac{2\pi m_1}{m_1 + m_2} \text{ reduced mass}$$

\downarrow
molecules 1 diffusing against molecules 2.

Thermal Diffusion.

- Heat flux: $\vec{J} = -k \nabla T$
- Heat flow out of closed surface: $\int_S \vec{J} \cdot d\vec{s}$
- Must equal rate at change of thermal energy inside volume surrounded by S , $\int_S \vec{J} \cdot d\vec{s} = -\frac{\partial}{\partial t} \int_V C \rho T dV$, C = per unit volume.
- Thus $\nabla \cdot \vec{J} = -C \frac{\partial T}{\partial t}$.

$$-k \nabla^2 T = -C \frac{\partial T}{\partial t}$$

$$\frac{\partial T}{\partial t} = \frac{k}{C} \nabla^2 T, \quad \frac{k}{C} \text{ thermal diffusivity or } D$$

$$\frac{\partial^2 T}{\partial t^2} = D \nabla^2 T \quad \text{Thermal Diffusivity Equation (Heat Equation).}$$

- Heat equation has the form of a wave equation:

$$T \propto e^{i(kx - \omega t)}$$

- Consider 1-D case: $\frac{\partial^2 T}{\partial t^2} = D \frac{\partial^2 T}{\partial x^2}$. ①

$$\text{Try } T(x,t) = A e^{i(kx - \omega t)}, \quad k = \frac{2\pi}{L}, \quad \omega = 2\pi f.$$

$$\text{Sub into ①: } A e^{i(kx - \omega t)} = D A e^{i(\omega t - kx)} e^{i(kx - \omega t)}$$

$$-i\omega T(x,t) = -Dk^2 T(x,t). \quad k^2 = \frac{i\omega}{D} \Rightarrow \frac{(i\omega)^2 \omega}{2D} \quad k = \pm \sqrt{\frac{\omega}{2D}} (i\omega)^2$$

$$\cdot \text{Consider: } e^{ikx} = e^{-i(kx)} e^{i\frac{\omega}{2D} x} = e^{i\frac{\omega}{2D} x} \text{ x. & blows up as } x \rightarrow 0$$

- Assume we have a boundary condition at $x=0$. want $\#$ solutions for $x>0$, thus $k = \pm \sqrt{\frac{\omega}{2D}} (i\omega)$

$$\text{General sol.: } T(x,t) = \sum_{\omega} A(\omega) e^{-i\omega t} e^{i\frac{(i\omega)^2 \omega}{2D} x} = \sum_{\omega} A(\omega) e^{-i\omega t} e^{i\frac{(i-1)\omega^2}{2D} x} \quad \#$$

- Applying to a specific boundary condition: propagation of harmonic waves into ground eg due to day/night (period T_0)

due to sun/moon (period T_0)

Then:

$$\begin{cases} T(x,t) = T_0 + A T_0 \cos \Omega t \\ \text{at } x=0 \end{cases}$$

$$T(0,t) = T_0 + A T_0 \cos \Omega t.$$

$$= T_0 + \frac{\Delta T}{2} e^{i\Omega t} + \frac{\Delta T}{2} e^{-i\Omega t}$$

$$\text{Comparing with } \# \quad A(0) = T_0$$

$$A(-\Omega) = \frac{\Delta T}{2}$$

$$A(\Omega) = \frac{\Delta T}{2}$$

$$\text{Solution: } T(x,t) = T_0 + \frac{\Delta T}{2} e^{i\Omega t} e^{i\frac{(i-1)\omega^2}{2D} x} + \frac{\Delta T}{2} e^{-i\Omega t} e^{i\frac{(i-1)\omega^2}{2D} x}.$$

$$\omega = \Omega$$

$$\omega = \Omega$$

$$\omega = -\Omega$$

$$\begin{aligned}
 \text{Reduced: } T(x,t) &= T_0 + \frac{\Delta T}{2} e^{-\frac{\sqrt{\pi}}{2}t} \left[e^{i(\frac{\pi}{2} + \frac{\sqrt{\pi}}{2}x)} + e^{i(\frac{\pi}{2} - \frac{\sqrt{\pi}}{2}x)} \right] \\
 &= T_0 + \cancel{\Delta T} \frac{\sqrt{\pi}}{2} \cos(\frac{\pi}{2}t - \frac{\sqrt{\pi}}{2}x) \quad \frac{\Delta T}{2} = \frac{1}{2} \quad S = \text{skin depth} \\
 &= T_0 + \Delta T e^{-\frac{x}{S}} \cos(\frac{\pi}{2}t - \frac{x}{S})
 \end{aligned}$$

→ falls off exponentially

→ initially constant

→ falls off by $\frac{1}{2}$ is distance equal to skin depth

- Assume ΔT for soil at 1×10^{-3} $\text{cm}^2/\text{s}^{-1}$

For Diurnal cycle (period = 1 day)

$$\Omega_1 = \frac{2\pi}{T} = \frac{2\pi}{24 \times 3600} = 7.27 \times 10^{-5} \text{ s}^{-1}$$

$$S_{\text{Diurnal}} = \frac{(2\pi)^2}{\Omega_1} \Rightarrow S = 24 \text{ cm}$$

For Annual cycle (period = 1 yr.)

$$\Omega_2 = \frac{2\pi}{T} = 1.99 \times 10^{-7} \text{ s}^{-1}$$

$$S_4 = \frac{(2\pi)^2}{\Omega_2} \approx 1 \text{ m}$$

In other steady state, properties are time independent.
 $\frac{\partial^2 T}{\partial t} = 0$.

$\Delta^2 T = 0$, Laplace's

- Example: Assume plane $x=0$ is held at T_1 and plane $x=L$ is held at T_2 , $T_2 < T_1$.

$$\frac{\partial^2 T}{\partial x^2} = 0 \quad \text{solution is of form } T(x) = Ax + B$$



Boundary Condition: $T=T_1$ at $x=0$, $T_1 = A(0) + B$

$$T_1 = B$$

$$T=T_2 \text{ at } x=L, \quad T_2 = A(L) + B$$

$$A = \frac{T_2 - T_1}{L}$$

$$\text{Thus } T(x) = \frac{T_2 - T_1}{L}x + T_1$$

$$= \frac{\Delta T}{L}x + T_1 \quad \text{for } 0 \leq x \leq L$$

$$\text{Heat flux } \dot{Q} = -K \frac{\partial T}{\partial x} = -K \frac{\Delta T}{L} = -\frac{\Delta T}{L} K$$

$\frac{1}{L} = \text{thermal conductance}$
 $\frac{1}{R} = \text{thermal resistance}$

- Thermal Diffusion Equation for a Sphere.

In spherical coordinates,

$$\nabla^2 T = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial T}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 T}{\partial \phi^2}$$

If T is independent of θ, ϕ (spherical symmetry) then,

$$\nabla^2 T = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right)$$

$$\Rightarrow \frac{\partial T}{\partial r} = \frac{D}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) \text{ where } D = \frac{B}{C}.$$

Example sphere is steady-state, i.e. $\frac{\partial T}{\partial t} = 0$

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) = 0$$

Solutions, $T = \text{constant}$.

$$r^2 \frac{\partial T}{\partial r} \Rightarrow \text{constant} \Rightarrow T \propto \frac{1}{r}.$$

General Solution: $T = f(r) \frac{B}{r}$.

Newton's Law of Cooling.

-  $T > T_{\text{air}}$ Heat loss of a solid or liquid surface to the outer surrounding gas is proportional to the area of contact & the temperature difference between the two media.

• The heat flux $\bar{J} = \bar{h} \Delta T$, where \bar{h} is a number \perp to the surface and $\bar{h} = |h|$ is the heat transfer coefficient

• $\bar{J} A = h A (T - T_{\text{air}})$, note C. is required to change to

heat energy K (Celsius to Kelvin)

put in place

$$\therefore \bar{J} = -C \frac{\partial T}{\partial t} = \bar{J} A = h A (T - T_0)$$

$$\frac{\partial T}{\partial t} = -\frac{h}{C} A (T - T_0) \quad (\text{*)(})$$

is (-) cooling (+) is heating.

• Solution is of the form $T = \alpha e^{-\beta t} + \beta$

$$\frac{\partial T}{\partial t} = -\beta \alpha e^{-\beta t} \quad (\text{**})$$

$$\text{At } t=0, T=T_H \Rightarrow \beta T = \alpha + \beta$$

$$\text{At } t \rightarrow \infty, T=T_{\text{air}} = \beta$$

$$T_H = \alpha + T_{\text{air}} \Rightarrow \alpha = T_H - T_{\text{air}}$$

$$T = T_{\text{HOT}} \text{ App.}$$

• Sub into ①

$$\frac{\partial T}{\partial t} = \frac{1}{c} A [(T_{H0} - T_{air}) e^{-\lambda t} + T_{air}] \\ = -\frac{h}{c} A (T_{H0} - T_{air}) e^{-\lambda t}$$

• Comparing with ② $\lambda = \frac{h}{c} A$

• Note having ignored convective heat transfer by motion within the fluid

• Convection dominates if heat convection is larger dominated by momentum & diffusion.

• Define! Kinetic ν_{sp} s^{-1} , Viscosity characteristic of momentum diff / P. C.f.

• Thermal diffusivity \rightarrow characteristic heat diff

$$D = \frac{K}{\rho c_p} \quad K, \text{Kappa}$$

$$\cdot \text{ Prandtl Number! } \text{Pr}_p = \frac{\nu}{D} \Rightarrow \frac{\nu_{sp}}{K}, \text{ unitless}$$

• If $\text{Pr}_p \gg 1$, convection dominates,

$\ll 1$, conduction dominates.

- It can be shown that the Prandtl number for an ideal gas $\text{Pr}_p = \frac{1}{3} \rightarrow$ both conduction and convection are important.

• Note: When there is also heat input:

$$\nabla \cdot \vec{j} = -c \frac{\partial T}{\partial t} + H$$

$$\text{So } \nabla \cdot (K \nabla T) = -c \frac{\partial T}{\partial t} + H$$

$$\nabla^2 T = \frac{1}{K} \frac{\partial T}{\partial t} + \frac{H}{K}$$

$$\text{or } \frac{\partial T}{\partial t} = \nabla^2 T \frac{K}{c} + \frac{H}{c}$$

$$\frac{\partial T}{\partial t} = \nabla^2 T D + \frac{H}{c}$$

$$D = \frac{K}{c}$$

Particle Diffusion

- Particle Diffusion is treated the same way as thermal diffusion.
- i.e. particles will be represented as a concentration gradient
- The analogous diffusion equation
 $\frac{\partial n}{\partial t} = D \nabla^2 n$ D = diffusion constant
- Problem 10.8 - A sphere is placed in an infinite medium containing particles of number density n_0 . Sphere absorbs particles at such a rate that no number density at surface of sphere is zero. Find rate of absorption of particles by sphere.



In steady state $\frac{\partial n}{\partial t} = 0$
 $\text{so } \nabla^2 n = 0$
 and $\frac{1}{r^2} \frac{d}{dr} (r^2 \frac{dn}{dr}) = 0$

as before $n \equiv \text{constant}$ is a possible solution
 also $r^2 \frac{dn}{dr} \equiv \text{constant}$ is a possible solution.
 $\therefore n \propto \frac{1}{r}$

General Solution $n = A + \frac{B}{r}$. at $r=a$, $n=0$ so
 $A = -\frac{B}{a}$. & at $r=\infty$, $n=n_0$ $n_0 = A + \frac{B}{r} \Rightarrow B/a = -A = -n_0$
 $n = n_0 - \frac{n_0}{r} = n_0(1 - \frac{1}{r})$

Rate of particle flow at surface (flux).

$$\Phi = -D \left(\frac{\partial n}{\partial r} \right)_{r=a} \iff J = -D \frac{\partial T}{\partial r}$$

$$\frac{\partial n}{\partial r} = \frac{\partial n_0}{\partial r}$$

$$\Phi = -D \left(\frac{\partial n_0}{\partial r} \right) = -D \left(\frac{n_0}{a} \right)$$

Rate of absorption

$$|E|A = \frac{D n_0}{a} 4\pi a^2$$

$$= 4\pi D n_0 a \quad \star \text{It's proportionality to } a.$$

- Has implications in biology (breathing absorption, prop to size, limit size w.r.t. oxygen absorption) Ex 10.5

- Thermo equilibrium - Macroscopic observables are constant with respect to time (pressure, temp.)
- Function of State - A physical quantity that has a well defined value for equilibrium states of the system (volume, pressure, temp...)
- Consider state of system defined by variables x

$$x = (x_1, x_2, x_3, \dots)$$

Different parameters that x depends on.

and $f(x)$ is a function of state. If a system's parameters change from x_{initial} to x_{final} , then change in $f(x)$ is

$$\Delta f = f(x_{\text{final}}) - f(x_{\text{initial}}) \quad (\text{only depends on endpoints})$$

If final state depends on path taken it is an inexact differential and is not a function of state.

- First Law of Thermo - Energy is conserved and heat and work are both forms of energy. The internal energy, U , of a system is a function of state.
- The change in internal energy, ΔU , is
- $$\Delta U = \Delta Q + \Delta W, \quad (Q, W \text{ not fnm of state}).$$

$$\partial U = \partial Q + \partial W$$

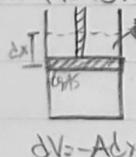
A Thermally Isolated System

- Does not exchange heat with surroundings ($\Delta Q = 0$)

$$\text{so } \Delta U = \Delta W$$

- Recall $dW = Fdx$

- Ex. Piston compressing gas



$$\begin{aligned} dW &= Fdx \\ dW &= -pAdx \\ &= -pdV \end{aligned}$$

- Generally consider, $U = U(V, T)$

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

- From (1) + (2) $dQ = dU + pdV \quad (3)$

$$dQ = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT + pdV.$$

$$\frac{\partial Q}{\partial T} = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \frac{\partial V}{\partial T} \quad (3)$$

- For a system at constant volume,

$$\frac{\partial Q}{\partial T} = \left(\frac{\partial U}{\partial T}\right)_V, \quad \text{but } C_V = \left(\frac{\partial Q}{\partial T}\right),$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

- For a system at constant pressure,

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \frac{\partial V}{\partial T}_P. \quad (3)$$

$$C_P = C_V + \left[\left(\frac{\partial U}{\partial T}\right)_V + p\right] \frac{\partial V}{\partial T}_P$$

$$\text{Define, } \gamma = \frac{C_P}{C_V}$$

- Reversible process, is a process that can be changed by an infinitesimally small change in some property.

- The are no dissipative forces.

- Generally, if processes such as compression of gas is done slowly enough it can be treated as reversible.

- Ex Isothermal Expansion of an Ideal Gas

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

for ideal gas $U = \frac{3}{2}RT$, so.

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

so if $dT = 0$ (isothermal), $dU = 0$

$$\text{so from } dU = dQ + dW \Rightarrow dQ = -dW = pdV$$

So heat absorbed upon isothermal expansion from V_1 to V_2 for one mole of ideal gas,

$$\Delta Q = \int dQ = \int pdV$$

$$pV = RT$$

$$= RT \int \frac{dV}{V}$$

$$= [RT \ln V]_V^{V_2}$$

$$= [RT \ln V]_V^{V_2} = RT \ln \frac{V_2}{V_1}$$

$$1 - \gamma = \frac{2}{3}$$

$$\gamma = \frac{2}{3}$$

$$\begin{aligned} & \frac{2}{3} + \frac{2}{3} - \frac{3}{3} - \frac{3}{3} \\ & = \frac{8}{3} - \frac{4}{3} \end{aligned}$$

$$Y = -2 - 3 = \frac{3}{3}$$

- Ex. Adiabatic Expansion of Ideal Gas
Reversible $\Delta Q = 0$.

Then $dU = dW$

$$C_V dT = -pdV = -\frac{RT}{V} dV$$

$$\frac{C_V}{T} dT = -\frac{R}{V} dV$$

$$C_V \sqrt{\frac{T_1 T}{T_2}} = -R \sqrt{\frac{V_2}{V_1}}$$

$$C_V \ln \frac{T_1}{T_2} = -\frac{R}{C_V} \left(\frac{V_2}{V_1} \right)^{\gamma}$$

$$\text{From } (1) \quad C_p = C_V \left(\frac{R}{C_V} \right) \left[\frac{V_2}{V_1} \right]^{\gamma} + R \left[\frac{V_2}{V_1} \right]^{\gamma}$$

$$C_p = C_V + pR$$

$$C_p = C_V + R \quad \text{for ideal gas (Mayer's Eqn)}$$

$$\text{so } \frac{C_p}{C_V} = \gamma = 1 + \frac{R}{C_V} \Rightarrow \frac{R}{C_V} = \gamma - 1$$

$$\text{Sub in } (2) \quad \ln \frac{T_2}{T_1} = (1-\gamma) \ln \left(\frac{V_1}{V_2} \right) = \ln \left(\frac{V_1}{V_2} \right)^{\gamma}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{1-\gamma} \Rightarrow \left(\frac{V_1}{V_2} \right)^{\gamma-1}$$

$$T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1} = \text{constant}$$

or equivalently, $pV^\gamma \propto T \Rightarrow V \propto \frac{1}{p}$.

$$T \left(\frac{1}{p} \right)^{\gamma-1} = \text{constant}$$

$$T^{\gamma-1+\frac{1}{\gamma}} p^{1-\frac{1}{\gamma}} = \text{constant}$$

$$T^{\gamma} p^{\frac{1}{\gamma}} = \text{constant}$$

Similarly, $pV^{\gamma} = \text{constant}$.

- Ex. An ideal monoatomic gas having initial pressure P_0 and initial volume V_0 , undergoes an adiabatic expansion in which the volume is doubled. Find the final pressure.

$$pV^\gamma = \text{constant} \Rightarrow P_0 V_0^\gamma = P_f V_f^\gamma$$

$$P_0 V_0^\gamma = P_f \left(\frac{V_f}{V_0} \right)^\gamma$$

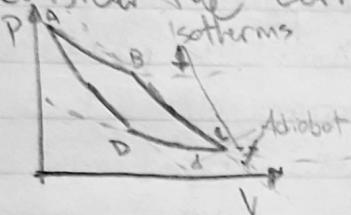
$$\gamma = \frac{C_p}{C_V} = \frac{C_V + R}{C_V} = \frac{\frac{5}{3}R}{\frac{3}{2}R} = \frac{5}{3}$$

$$\text{Thus } P_f = \frac{P_0 V_0^\gamma}{2^{\gamma}} = \frac{P_0}{2^{\frac{5}{3}}} = 0.314 P_0$$

~~Expansion from Adiabatic Process~~
~~Adiabatic~~

Second Law of Thermodynamics

- "No process is possible whose sole result is the transfer of heat from a colder to hotter object (Carnotian)"
- "No process is possible whose sole result is the conversion of heat into work" (Kelvin).
- Define an engine ^{operating} cyclic process to convert heat into work
- Consider the Carnot Engine



Carnot Cycle; AB, CD are isotherms (reversible)
 - heat enters/leaves system
 - BC, DA are adiabats
 $\Delta Q = 0$.

- $\downarrow @A, Q, T_h \leftarrow$ initial heat
- $\downarrow @B, Q + Q_h \leftarrow$ heat enters
- $\downarrow @C, Q + Q_h \leftarrow$ heat stays same
- $\downarrow @D, Q + Q_h + Q_c = Q_i \leftarrow$ heat loss
- $\downarrow @A, Q \leftarrow$ heat stay same

$$\oint dU = 0 \text{ (cycle)}$$

$$\text{thus } W = Q_h - Q_c$$

- Consider isotherm AB; $\Delta Q = Q_h = T_h V_B \ln \frac{V_B}{V_A} \quad (1)$

$$\text{Consider adiabat BC; } T_h V_B^{\gamma-1} = T_L V_L^{\gamma-1}$$

$$T_h = \left(\frac{V_L}{V_B} \right)^{\frac{1}{\gamma-1}} \quad (2)$$

$$\text{Consider isotherm CD; } Q_c = -T_L V_L \ln \frac{V_D}{V_C} \text{ negative.} \quad (3)$$

$$\text{Consider adiabat DA; } T_h = \left(\frac{V_D}{V_A} \right)^{\frac{1}{\gamma-1}} \quad (4)$$

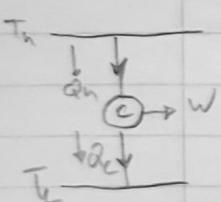
$$\text{From (2) & (4); } \left(\frac{V_B}{V_C} \right)^{\frac{1}{\gamma-1}} = \left(\frac{V_A}{V_D} \right)^{\frac{1}{\gamma-1}} \Rightarrow \frac{V_B}{V_C} = \frac{V_A}{V_D} \text{ or } \frac{V_B}{V_h} = \frac{V_c}{V_D}$$

$$\text{" (1) & (3); } \frac{Q_h}{Q_c} = \frac{T_h}{T_L} \leftarrow \text{important}$$

- Efficiency is defined: $\eta = \frac{W}{Q_h} \quad \eta < 1$

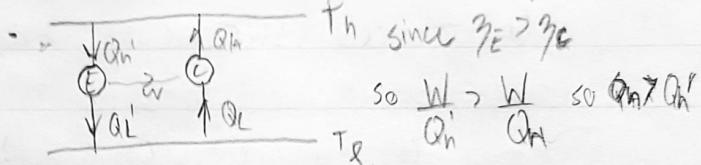
$$\eta_{\text{Carnot}} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h} \text{ or } 1 - \frac{T_L}{T_h}$$

- Carnot Theorem: No engine operating between two reservoirs can be more efficient than the Carnot engine operating between those reservoirs.



• Proof by Contradiction - Consider engine, E, is not engine, C and assume $\eta_E > \eta_C$

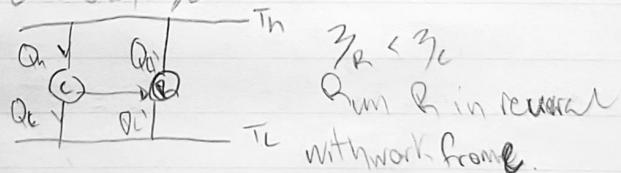
- Since Carnot engine is reversible, it can be run in reverse by the work produced by E



- But $W = Q_H - Q_L = Q_H - Q_L$
net heat input $Q_H - Q_L = Q_H - Q_L'$
into reversible T_H positive net heat extracted from T_L

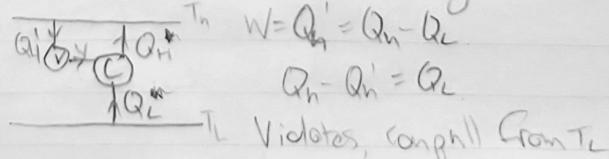
- Heat transferring from Q_L to Q_H which violates the ~~Second~~ Law of Thermodynamics.

- A consequence is that all reversible engines working between two temp's have same efficiency: η_C



$$\frac{W}{Q_H} < \frac{W'}{Q_H} \text{ so } Q_H' > Q_H, Q_H' - Q_H = Q_L' - Q_L$$

- Also a violation of the second law.
- Imagine system that violates Kelvin's statement of 2nd Law (converts heat into only work).
- Use work to run a Carnot engine.



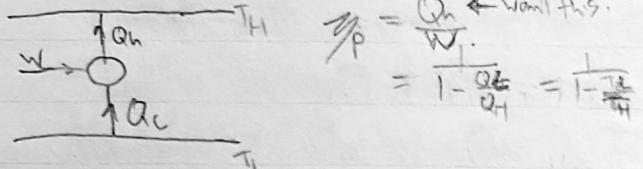
- Note: for engines running in reverse the definition of efficiency above is not useful

For a Fridge

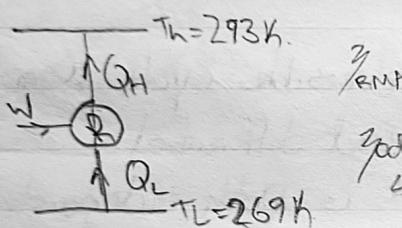
$$\frac{W}{Q_L} = \frac{T_H}{T_L}, \eta_{\text{Carnot}} = \frac{1}{\frac{Q_H}{Q_L} - 1} = \frac{1}{\frac{T_H}{T_L} - 1}$$

$\eta < 1$

- For a heat pump, (pump heat from reservoir into a house)



- Example: A cooling system is designed to maintain a refrigerator at -4°C in a room at 20°C . If 10^4 J of heat leaks in the system each minute and system works at 40% max thermal efficiency, what are the power requirements?



$$\eta_{\text{max}} = \frac{269}{293 - 269} = 11.268$$

$$\eta_{\text{actual}} = 0.4 \eta_{\text{max}} \leq 4.483 = \frac{Q_L}{W}$$

$$4.483 = \frac{Q_L}{W}$$

$$W = \frac{10^4}{4.483} = \frac{10000 \text{ J/min}}{4.483} = 2230.48 \text{ W}$$

$$P = \frac{W}{\text{Time}} = \frac{2230.48}{60} = 37.2 \text{ W} \approx 2230.48 \text{ J/m}$$

Clausius' Theorem

- Carnot cycle: $\frac{Q_H}{Q_L} = \frac{T_H}{T_L} \Rightarrow \frac{Q_H}{Q_L} - \frac{T_H}{T_L} = 0 \quad (\star)$

In one cycle heat enters at Q_H enters at temp T_H & heat Q_L leaves at T_L .

- Let ΔQ_i be heat energy entering the particular point in the cycle

$$\sum \frac{\Delta Q_i}{T_i} = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0 \quad (\text{from } \star)$$

- Replace sum with integral $\int dQ_i / T_i = 0$ and imagine more than 2 points where heat enters and leaves the system, generalizing

$T \partial Q_i$:

$$\Delta W = \sum \Delta Q_i$$

Imagine ΔQ_i is supplied by a Carnot engine.

work gain

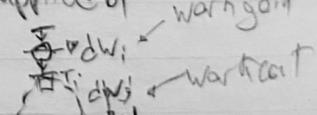


ΔW

$\rightarrow \Delta W$ (total work extracted from cycle).

$$\frac{\partial Q_i}{T_i} = \frac{\partial Q_i}{T} = \frac{\partial Q_i + \partial W_i}{T}$$

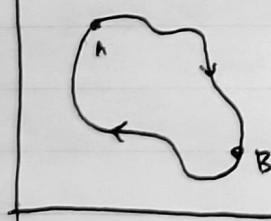
$$\frac{T \partial Q_i}{T_i} = \partial Q_i + \partial W_i \Rightarrow \Delta W_i = \partial Q_i (T_i - T)$$



- To ensure this total work produced per cycle
 $\Delta W + \sum_i dQ_i \leq 0$.
- ∴ $\sum_{\text{cycle}} dQ_i + \sum_{\text{cycle}} dQ_i \left(\frac{1}{T} - 1 \right) \leq 0$
 $\sum_{\text{cycle}} dQ_i \left(1 + \frac{1}{T} - 1 \right) \leq 0$
 $T \sum_{\text{cycle}} \frac{dQ_i}{T} \leq 0$, since $T > 0$, $\sum \frac{dQ_i}{T} \leq 0$
- Replacing sum with integral
 $\oint \frac{dQ}{T} \leq 0 \rightarrow \text{ Clausius Inequality}$.

Clausius Inequality

- Equality holds in a reversible cycle (Carnot cycle, $\oint \frac{dQ_{\text{rev}}}{T} = 0$).
- Thus $\frac{dQ_{\text{rev}}}{T}$ is an exact differential
- Also implies $\int_A^B \frac{dQ_{\text{rev}}}{T}$ is path independent.
- $\frac{dQ_{\text{rev}}}{T} = dS$, entropy
- ∴ $S(B) - S(A) = \Delta S = \int_A^B \frac{dQ_{\text{rev}}}{T}$
- Adiabatic process; $dQ = 0 \rightarrow dS = 0 \rightarrow \oint dS = 0$
- A system without changes in entropy are called "isentropic"
- Consider a loop in PV space. Define A, B, A → B is irreversible & B → A is reversible.



$$\begin{aligned} & - \int_A^B \frac{dQ}{T} + \int_B^A \frac{dQ_{\text{rev}}}{T} \leq 0 \\ & - \text{In the limit } A \rightarrow B, dS = \frac{dQ_{\text{rev}}}{T} \geq \frac{dQ}{T}; \\ & - \int_A^B \frac{dQ}{T} = \int_A^B \frac{dQ_{\text{rev}}}{T} \geq 0 \\ & - \int_A^B \frac{dQ_{\text{rev}}}{T} \geq \int_A^B \frac{dQ}{T}. \end{aligned}$$

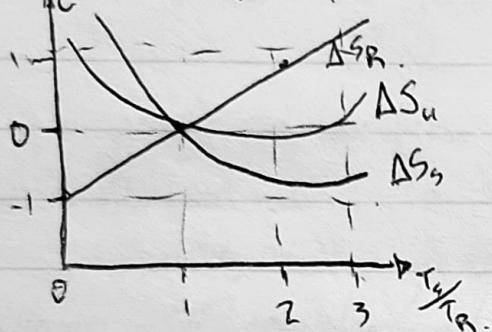
- Consider a thermally isolated system: $dQ = 0$. Then $dS \geq 0$, equal for a reversible system
- Apply to the universe assuming it is isolated:
 - $dU = dQ + dW \Rightarrow dQ = dW = 0$ for isolated dU
 - Total Energy of the universe is constant.
- $dS \geq 0$, Entropy can only increase.

- E_g- Universe consists of large reservoir at T_R in thermal contact with a small system at T_S .
 - Both thermalize to T_R . Heat transfer from res \rightarrow sys is $\Delta Q = C\Delta T = C(T_R - T_S)$. If $T_R > T_S$, $\Delta Q > 0$; otherwise $\Delta Q \leq 0$
 - Net $\Delta Q \neq 0$. System warms up, ΔS if $\Delta Q > 0$; ΔS , if $\Delta Q < 0$.

$$\Delta S_R = \int \frac{dQ}{T_R} = \frac{1}{T_R} \int dQ = \frac{-C(T_R - T_S)}{T_R} = C\left(-1 + \frac{T_S}{T_R}\right)$$

$$\Delta S_S = \int_{T_S}^{T_R} \frac{dQ}{T_S} = C \ln\left(\frac{T_R}{T_S}\right)$$

$$\Delta S_u = \Delta S_R + \Delta S_S = C\left(\ln\left(\frac{T_R}{T_S}\right) + \frac{T_S}{T_R} - 1\right)$$



$\Delta S_u \geq 0$ and has its minimum at $\frac{T_S}{T_R} = 1$.

First Law of Thermodynamics (Reversible).

- $dU = dQ + dW$ but for rev. change, $dS = \frac{dQ}{T}$ $\Rightarrow dQ = TdS$
- $dU = TdS - pdV$.

First Law of Thermodynamics (Irreversible).

- $dQ \leq TdS$ and $dW \geq -pdV$ since T, S, p, V, d are all function of state (in integral around a closed path are all ≥ 0).
- $dU = TdS - pdV$ (also valid).

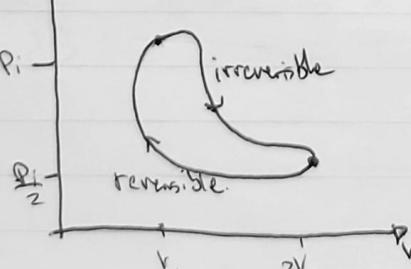
Entropy and the First Law

- T & P are 'intensive variables' \rightarrow don't depend on the size of the system
- S & V are 'extensive variables' \rightarrow scale with system, S and V are the 'natural variables' of the system.
- Can write $dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$.
- So $T = \left(\frac{\partial U}{\partial S}\right)_V$ and $-P = \left(\frac{\partial U}{\partial V}\right)_S$.
- Take $\frac{P_f}{T_f} \rightarrow \frac{P_f}{T_f} = -\left(\frac{\partial U}{\partial S}\right)_V \left(\frac{\partial S}{\partial U}\right)_V$ (\because reciprocity theorem).
- Reciprocity Theorem: $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = -1$
- Gives $\frac{P_f}{T_f} = \left(\frac{\partial S}{\partial U}\right)_V$.

Free Expansion

- Is irreversible; a process by which gas in a smaller container suddenly expands into a larger one. Assume the large container is thermally isolated from surroundings.
- Assume we start with n mol of gas. Initial volume V_0 , initial pressure and temp. P_i and T_i .
- Ideal Gas Law: $P_i V_0 = RT_i$; $P_f (2V_0) = RT_f$
- Since system is thermally isolated, $\Delta V = 0$ (Recall $dU = Cdt$) for an ideal gas: $\Delta T = 0$ and $T_i = T_f$
- $P_i V_0 = 2P_f V_0 \Rightarrow P_f = \frac{1}{2}P_i$
- Is isothermal for an ideal gas.

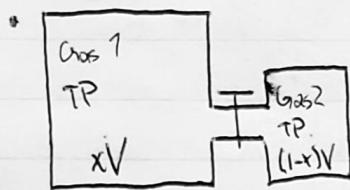
Calculating Entropy

- Calculate Entropy in Free expansion
- 
- Expansion takes a complicated path; difficult to calculate; choose instead a reversible path
- Since S is a state function it does not depend on path taken

- Choose a reversible isotherm $\Rightarrow \Delta U = 0$ since $\Delta T = 0$
- $\Delta U - T\Delta S - P\Delta V \Rightarrow T\Delta S = P\Delta V$
- $\Delta S_{\text{gas}} = \int_{V_1}^{V_2} dS = \int \frac{P}{T} dV = \int_{(gas law)}^R \frac{1}{V} dV = R \int_{V_1}^{V_2} \frac{1}{V} dV \Rightarrow R \ln 2$

- This is the same regardless of path taken
- For rev. 'isothermal expansion': $\Delta S_{\text{univ}} = 0 = \Delta S_{\text{gas}} + \Delta S_{\text{surrounding}}$.
- Therefore, $\Delta S_{\text{surrounding}} = -\Delta S_{\text{gas}} = -R \ln S$
- For the Joule expansion, system is thermally isolated $\Rightarrow \Delta S_{\text{surrounding}} \circledcirc$
- i.e., $\Delta S_{\text{univ}} = \Delta S_{\text{gas}} + \Delta S_{\text{surrounding}}$
 $= R \ln 2.$
- If you want to compress gas back into original container:
 - at least work is to do it reversibly (very slowly) by a reversible isothermal expansion
 - work for 1 mol of gas: $W = P\Delta V$ (irreversible: $W \neq -P\Delta V$)
 - $\Delta W = - \int_{V_2}^{V_1} P dV = - \int_{V_2}^{V_1} \frac{RT}{V} dV = -RT \int_{V_2}^{V_1} \frac{1}{V} dV = RT \ln \frac{V_1}{V_2} = RT \ln 2.$
 • limits of integration should be flipped.

The Entropy of Mixing



$$\begin{aligned} \text{Total Volume} &\equiv V \\ P = \frac{Nk_B T}{V} &\Rightarrow N = \frac{PV}{k_B T} \\ N_1 = \frac{P}{k_B T} \times V &= xN \\ N_2 = \frac{P(1-x)}{k_B T} &= (1-x)N \end{aligned}$$

$$\text{Total } N = N_1 + N_2.$$

- Open valve \rightarrow gases mix & entropy increases.

- Gas 1 expands from volume xV to V
 " 2 " " " "(1-x)V " "

- Isothermal ~~Expansion~~ Expansion ($\Delta U=0 \rightarrow$ for ideal)

$$dU = TdS - pdV,$$

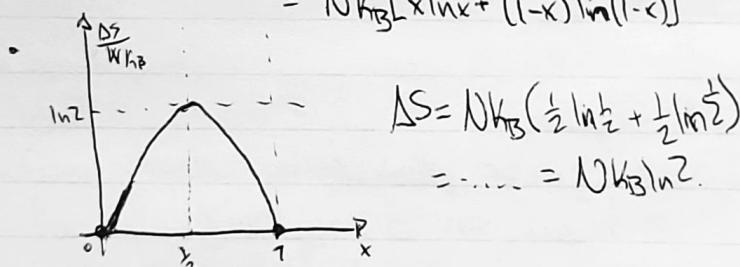
$$dS = \frac{P}{T} dV = Nk_B \frac{dV}{V}$$

$$\text{Thus, } \Delta S = xNk_B \int_{xV}^V \frac{dV}{V} + (1-x)Nk_B \int_{(1-x)V}^V \frac{dV}{V}$$

$$= xNk_B [\ln V - \ln xV] + (1-x)Nk_B [\ln V - \ln (1-x)V]$$

$$= xNk_B [\ln V - \ln x - \ln V] + (1-x)Nk_B [\ln V - \ln (1-x) - \ln V]$$

$$= Nk_B [x \ln x + (1-x) \ln (1-x)]$$



$$\Delta S = Nk_B \left(\frac{1}{2} \ln \frac{1}{2} + \frac{1}{2} \ln \frac{1}{2} \right)$$

$$= \dots = Nk_B \ln 2.$$

Maxwell's Demon

- Performing Joule Expansion of a gas
- Gas initially in one chamber, connected via a side which can open and close ~~to~~ a hole between both chambers.
- Hole is opened \rightarrow gas expands into both chambers
-



- Joule Expansion is irreversible.

- Maxwell proposed the ~~statis~~ following 'demon' who does no work in the PdV sense by opening & closing the 'massless', 'frictionless' slide, selectively opens the slide ~~selectively~~ to allow molecules from B back into A until all are.
- It appears that Maxwell's Demon can control entropy to decrease with consequent number increase etc
- So it turns out to be that Demon needs to store info
- Results in ~~an increase~~ in an increase ~~of~~ of entropy that cancels the decrease brought by the demon, placing them ~~out~~ atoms back inside

Statistical Interpretation

- $dU = TdS - PdV = \left(\frac{\partial U}{\partial V}\right)_S dV + \left(\frac{\partial U}{\partial S}\right)_V dS$
- We see $T = \left(\frac{\partial U}{\partial S}\right)_V$ or $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V$.
- Recall: $\frac{1}{k_B T} = \frac{d \ln \Omega}{d E}$ $\Rightarrow \frac{1}{T} = \frac{d \ln \Omega}{d E}$
 - suggests $\rightarrow S = k_B \ln \Omega$ + entropy of system
 - ~~Microscopic~~ Microscopic
- Ex.- Double Expansion
 - After expansion each molecule can be in LHS & RHS of container. (2 possible way of placing)
 - Consider first energy levels, 2 molecules + 2 possible O, E
 - Before expansion molecule 1 molecule 2

O	O	④ Macrostate.
E	O	
O	E	
E	E	

- After expansion Chamber 1 Chamber 2.

2^2 microstates for each state before.	m_1	m_2
	m_2	m_1
	$m_1 m_2$	-
		$m_1 m_2$

- Total no. of microstates after is 2^{Ω}
- For 1 mole of ~~molecules~~ molecules, there will be 2^{N_A} ways of placing them.
- Now no. of states in system is 2^{N_A} larger than original number.
- $S_{\text{before}} = \cancel{K_B} \ln \Omega$
- $S_{\text{After}} = K_B \ln \Omega 2^{N_A} = K_B [\ln \Omega + \ln 2^{N_A}]$
- $\Delta S = S_{\text{After}} - S_{\text{before}} = K_B N_A \ln 2 = R \ln 2$

Entropy and Probability.

- Assume system with N microstates which belong to i macrostates containing n_i microstates each.
- $N = \sum_i n_i$
- Probability of finding system in i^{th} macrostate is $P_i = \frac{n_i}{N}$
- Note: $\sum P_i = \frac{\sum n_i}{N} = \frac{N}{N} = 1$.
- Total Entropy $\rightarrow S_{\text{tot}} = K_B \ln N$
- The entropy we measure is associated with the number of macrostates (i.e. ~~#~~ of experimentally states the system can be in).
- Consider a specific ~~macrostate~~ example
 - Assume N has N_m macrostates, then
 - $S = K_B \ln N_m$
 - Assume N_m has N_μ microstates
 - ~~$\Omega = N_m N_\mu$~~
 - $S_{\text{tot}} = K_B \ln \Omega = K_B \ln N_m N_\mu = K_B \ln N_m + K_B \ln N_\mu$.
 - $= S + S_{\text{micro}}$.
- Going back to general example
- Each macrostate has n_i microstates so entropy of microstates in i^{th} macrostates is: $S_i = K_B \ln N_i$, and total energy due to the microstate is: $S_{\text{micro}} = \sum_i P_i S_i = \langle S_i \rangle$
- \uparrow probability of finding S_i
 in i^{th} macrostate

$$\bullet S = S_{\text{TOT}} - S_{\text{micro}}$$

$$\begin{aligned}
 &= k_B \ln N - \sum P_i (k_B \ln n_i) \\
 &= k_B \left[\sum P_i \ln N - \sum P_i \ln n_i \right] \\
 &= k_B \left[P_1 \ln N - \ln n_1 \right] \\
 &= k_B \sum P_i \ln \frac{N}{n_i} \\
 &= -k_B \sum P_i \ln \left(\frac{n_i}{N} \right)
 \end{aligned}$$

$S = -k_B \sum P_i \ln(P_i)$ Gibbs Expression for Entropy.

• Example: Use Gibbs entropy to derive formula for entropy of mixing

- Probability of molecule being type 1 is $x \rightarrow P_1$
 " " " " " " " 2 is $(1-x) \rightarrow P_2$

$$- \sum P_i = P_1 + P_2 = x + (1-x) = 1$$

$$- \text{For } N \text{ molecules, } S = \sum [-k_B \sum P_i \ln P_i]$$

$$= -Nk_B \sum P_i \ln P_i$$

$$= -Nk_B [x \ln x + (1-x) \ln (1-x)]$$

• Recall: S, U, V, T, P are functions of state.

• Any combination of functions of state is also a function of state

• Some particularly useful ones:

$$H = U + PV \rightarrow \text{Enthalpy}$$

$$F = U - TS \rightarrow \text{Helmholtz Function. (Helmholtz free Energy Function)}$$

$$G = U + PV - TS \rightarrow \text{Gibbs Functions. (Gibbs free Energy Function)}$$

• 1st review some properties of U (internal energy)

- 1st Law: $dU = TdS - pdV$, changes in S or V

lead to changes in U , vice versa.

$$- dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV, \text{ thus } T = \left(\frac{\partial U}{\partial S}\right)_V, p = -\left(\frac{\partial U}{\partial V}\right)_S$$

- Isochoric $\rightarrow dV=0 \Rightarrow dU = TdS$

- Reversible Isochoric $\rightarrow dU = dQ_{\text{rev}} = C_V dT$

$$\Delta U = \int_{T_1}^{T_2} C_V dT, \text{ take at constant } V$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

• Consider enthalpy: $H = U + PV$.

$$dH = dU + pdV + Vdp$$

$$= TdS - pdV + pdV + Vdp$$

$$= TdS + Vdp$$

Isochoric Process ($dp=0$)

Natural
Variables

$$dU = TdS$$

$$= dQ_{\text{rev}}$$

$$= C_V dT \Rightarrow$$

$$C_V = \left(\frac{\partial H}{\partial T}\right)_P \Rightarrow \Delta H = \int_{T_1}^{T_2} C_V dT$$

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP \Rightarrow dH = TdS + VdP.$$

$$T = \left(\frac{\partial H}{\partial S}\right)_P, V = \left(\frac{\partial H}{\partial P}\right)_S$$

• Next Helmholtz function

$$- F = U - TS$$

$$dF = dH - TdS \Rightarrow TdS - pdV - TdS - SdT = -pdV - SdT$$

- for an isothermal process

$$dF = -pdV \Rightarrow dF = -\int_{V_1}^{V_2} -pdV = -\int dW$$

- If dF is positive, reversible work is done on system by surroundings

- If dF is negative, work is done on the surroundings by system ($dW = pos$)

$$- dF = \left(\frac{\partial F}{\partial V}\right)_T dV + \left(\frac{\partial F}{\partial T}\right)_V dT, P = -\left(\frac{\partial F}{\partial V}\right)_T, S = -\left(\frac{\partial F}{\partial T}\right)_V$$

• Gibbs Function

$$- G = H - TS \Rightarrow dG = dH - TdS - SdT = TdS + VdP - TdS - SdT$$

$$= VdP - SdT \quad \text{Variables}$$

$$- dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT$$

- $\delta u = TdS - pdV \rightarrow$ For fixed natural variables, equilibrium state is obtained by minimizing $U/H/F/G$.
- $\delta H = TdS + VdP$
- $\delta F = -SdT + pdV$
- $\delta G = -SdT + VdP$

• Consider $dF_2 = -SdT + pdV$.

$$\left(\frac{\partial F}{\partial T} \right)_V = \left(\frac{\partial F}{\partial V} \right)_T dT + \left(\frac{\partial F}{\partial V} \right)_T dV, S = -\left(\frac{\partial F}{\partial T}\right)_V, P = -\left(\frac{\partial F}{\partial V}\right)_T$$

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

$$\left(\frac{\partial P}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T \quad \leftarrow \text{a Maxwell relation}$$

• Maxwell Relationships

$$- (1) \left(\frac{\partial P}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T$$

from F

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

" U

$$- (3) \left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P$$

" H

$$- (4) \left(\frac{\partial S}{\partial P} \right)_T = -\left(\frac{\partial V}{\partial T} \right)_P$$

" G

Variables of interest

- Find an expression for $(\frac{\partial Q}{\partial T})_V$ in terms of R, V, T

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V, \quad dQ = dU + pdV$$

$$= \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial V}{\partial T}\right)_P dT + pdV$$

$$\frac{\partial Q}{\partial T} = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial V}{\partial T}\right)_P + p\right] dT \leftarrow \text{lost } V \text{ term} \Rightarrow 0 \text{ for const. } p,$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \quad \text{but } dU = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial S}\right)_T dS.$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V$$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \frac{\partial}{\partial V} \left(T \left(\frac{\partial S}{\partial T}\right)_V \right) = T \frac{\partial}{\partial V} \left(\frac{\partial S}{\partial T} \right)_V = T \left(\frac{\partial}{\partial T} \left(\frac{\partial S}{\partial V} \right)_T \right)_V$$

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

- Generalized Susceptibilities - Quantifies how much a variable changes when a general force is applied

- Differential integral energy w.r.t another parameter $T = \left(\frac{\partial U}{\partial S}\right)_V, Q = -\left(\frac{\partial U}{\partial V}\right)_S$

- Examples: Isobaric Expansivity, $\beta_p = \frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$ [Fractional Change in Volume.]
- Adiabatic Expansivity, $\beta_S = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_S$ [with a change in pressure.]
- Isothermal Compressiblity, $K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$ [fractional change in V. w.r.t. pressure.]
- Adiabatic Compressiblity, $K_S = -\frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_S$ [with application of pressure.]

General Susceptibilities.

- To understand the work done by dielectric, $\vec{E} \cdot \vec{p}$ consider changing \vec{E}

- Interaction Energy: $d(\vec{p} \cdot \vec{E}) = -\vec{p} \cdot d\vec{E} - \vec{E} \cdot d\vec{p}$

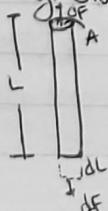
- There is also energy stored in the dipole

- $\vec{p} = q\vec{a}$, charge length by da .

- Work done $f_{SL} = qEda = Edp = \vec{E} \cdot d\vec{p}$

- Analogous Arguments can be made for the dipole.

- Eg. Elastic Rod in D.



- Stress: $\sigma = \frac{F}{A}$, Strain: $\epsilon = \frac{dl}{L}$

- Isothermal Young's Modulus: $E_T = \frac{\sigma}{\epsilon} = \frac{F}{A} = \frac{L}{d} \left(\frac{\partial F}{\partial L}\right)_T$

- Linear Expansivity of Constant Tension: $\alpha_F = \frac{1}{L} \left(\frac{\partial L}{\partial T}\right)_F$

- α_F is positive in most materials except rubber

Eg Elastic Rod Cont.

- $dU = TS - f dx$ (instead of $-pdV$).

- Recall Helmholtz function $\rightarrow f = U - TS$; $df = dU - TdS - SdT$.

- if $dL = dU - TS \rightarrow df = -SdT + pdV = \left(\frac{\partial f}{\partial T}\right)_V dT + \left(\frac{\partial f}{\partial V}\right)_T dV$

$$\therefore S = -\left(\frac{\partial f}{\partial T}\right)_V, \quad \gamma = \left(\frac{\partial f}{\partial V}\right)_T$$

- Recall for a gas $\rightarrow df = -SdT - pdV$ from which we derived $\left(\frac{\partial f}{\partial T}\right)_V = \left(\frac{\partial S}{\partial T}\right)_V$.

- Thus for the elastic rod, have Maxwell equation relationship.

$$\left(\frac{\partial f}{\partial T}\right)_L = \left(\frac{\partial S}{\partial L}\right)_T \quad (\star)$$

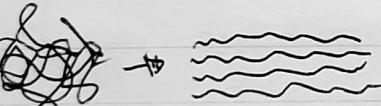
- By reciprocal theorem: $\left(\frac{\partial V}{\partial T}\right)_L = -\left(\frac{\partial L}{\partial T}\right)_V \left(\frac{\partial V}{\partial L}\right)_T$.

- Sub (\star) into (\star) :

$$-\left(\frac{\partial S}{\partial L}\right)_T = \left(\frac{\partial L}{\partial T}\right)_V \left(\frac{\partial V}{\partial L}\right)_T = \{L\alpha_T\} \{A/E_T\} = A\alpha_T E_T$$

- Stretching the rod results in an increase in entropy; i.e. $dF > 0$.
by a decrease in $\alpha_T < 0$.

-  (most materials) stretched lattice
more distorted

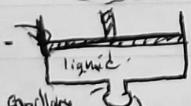
-  (rubber) rubber carbon stretched
chains more order.

- $dQ = TdS = TA E_T dL$ (isothermal)

Eg. Surface Tension

- Producing liquid surfaces costs energy (bonds must be broken). To minimize this, a droplet is formed, if possible.

-  To change the area of a surface costs $dW = \gamma dA$, where γ is the surface tension



Piston moves down, doing work on the liquid
 $dW = f dx = pdV$.

Radius increases to $r+dr$, change in A.

$$dA = 4\pi(r+dr)^2 - 4\pi r^2 \approx 8\pi r dr.$$

Work done to increase size of droplet.

$$dW = \gamma dA = 8\pi \gamma r dr - pdV = p(4\pi r^2 dr)$$

$$\Rightarrow p = \frac{2\gamma}{r} \quad (\text{difference in liquid pressure and atmospheric})$$

• Eg Surface Tension Cont.

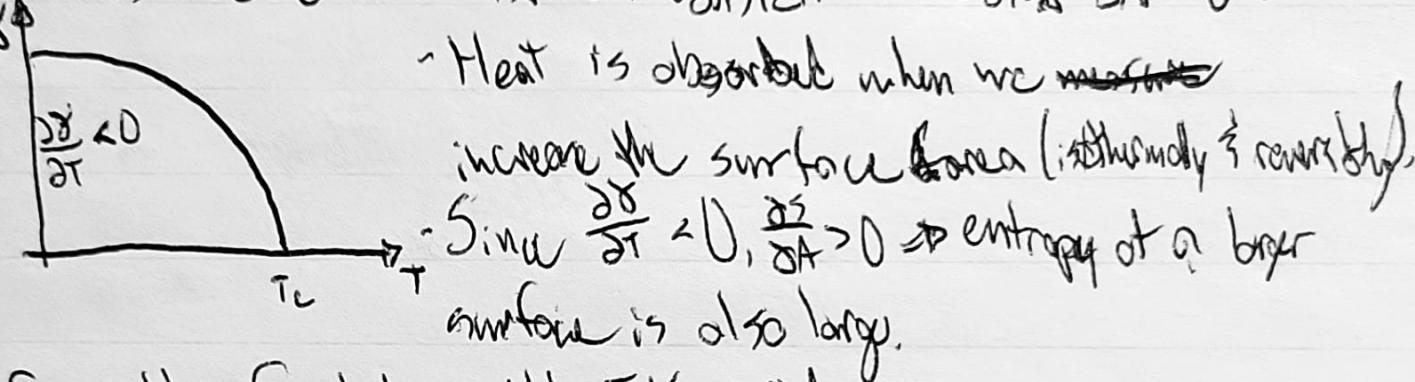
- Apply first law of thermodynamics.

$$dU = TdS + \gamma dA, \quad dF = -SdT + \gamma dA \quad (\text{Helmholtz})$$

- Maxwell relation: $-\left(\frac{\partial \gamma}{\partial T}\right)_A = \left(\frac{\partial S}{\partial A}\right)_T$

- Heat isotherm: $\Delta Q = TAS = T\left(\frac{\partial S}{\partial A}\right)_T dA = -T\left(\frac{\partial \gamma}{\partial T}\right)_A dA > 0$.

- $\gamma \uparrow$
 Heat is absorbed when we ~~increase~~ increase the surface area (irreversibly).



- Since $\frac{\partial \gamma}{\partial T} < 0, \frac{\partial S}{\partial A} > 0 \Rightarrow$ entropy of a larger surface is also large.

- From the First Law $dU = TdS + \gamma dA$.

$$\begin{aligned} -\left(\frac{\partial U}{\partial A}\right)_T &= T\left(\frac{\partial S}{\partial A}\right)_T + \gamma \\ &= -T\left(\frac{\partial \gamma}{\partial T}\right)_A + \gamma \end{aligned}$$

usually negative.

heat flows into the system.
 γ is energy going into surface to break bonds.

CONTINUATION FROM MISSED LECTURES.

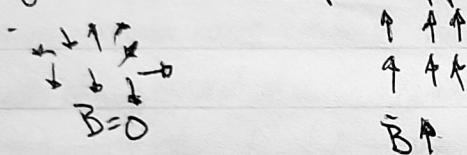
- $dU = TdS + dW$

.	X	X	dW
Fluid	-P	V	$-pdV$
Elastic	F	L	FdL
Film	Y	A	YdA
Magnetic Dipole \vec{B}	\vec{m}		$m\vec{B}$

Paramagnetism

- Lattice of non-interacting magnetic moments

- Paramagnetism occurs upon application of magnetic field \rightarrow moments align



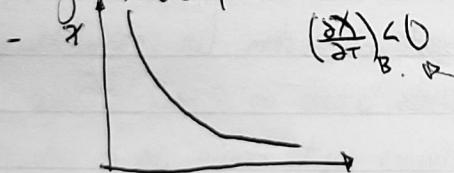
- First law: $dU = TdS - \frac{\partial U}{\partial B} dB$ | $B = \mu_0(H+M)$ ← magnetic susceptibility.

magnetic moment, $m = MV$
magnetization

$$\chi = \lim_{H \rightarrow 0} \frac{M}{H}, \text{ so } \frac{\partial M}{\partial B} = \mu_0 \chi$$

- For most paramagnets, $\chi \gg 1$

- Paramagnets obey Curie's law $\chi \propto \frac{1}{T}$.



- Example 1: Isothermal Magnetization

$$F = U - TS.$$

$$dF = \cancel{dU} - \cancel{TS} - SdT = -m dB - SdT$$

$$\text{By which one obtains: } \left(\frac{\partial S}{\partial B}\right)_T = + \left(\frac{\partial m}{\partial T}\right)_B \text{ negative.}$$

$$= \frac{V\beta}{\mu_0} \left(\frac{\partial M}{\partial T}\right)_B$$

$$\left(\frac{\partial S}{\partial V}\right)_T = - \left(\frac{\partial P}{\partial T}\right)_V$$

Entropy decreases upon increase in B (more ordered system)

$$\Delta Q = T \Delta S = T \left(\frac{\partial S}{\partial B}\right)_T \Delta B = T A B V \frac{\beta}{\mu_0} \left(\frac{\partial M}{\partial T}\right)_B \text{ negative} (\Delta Q \text{ is neg., heat emitted by sample})$$

• Example 2: Adiabatic Demagnetisation (Adiabatically decreasing field).

Changes T with adiabatic change in B .

$$\left(\frac{\partial T}{\partial B}\right)_S = - \left(\frac{\partial T}{\partial S}\right)_B \left(\frac{\partial S}{\partial B}\right)_T$$

Defn: $C_B = T \left(\frac{\partial S}{\partial T}\right)_B$ \leftarrow heat capacity at constant B

$$\left(\frac{\partial T}{\partial B}\right)_S = - \frac{1}{C_B} \frac{\nu_B}{\mu_0} \left(\frac{\partial S}{\partial T}\right)_S > 0$$

Thus one can cool ~~cool~~ a sample by reducing the magnetic field ~~by~~ keeping it at constant entropy (slowly/reversibly).

(Can be useful to cool sample to a few mK!)

Third Law of Thermodynamics

- Statement of 3rd Law \Rightarrow near absolute zero creations in system in internal equilibrium take place with ~~other~~ no change

~~state~~ - Nernst. $\Delta S \rightarrow 0$ as $T \rightarrow 0$

\Rightarrow Entropy of such system is ~~more~~ at absolute zero and can be taken to be zero from $S \rightarrow 0$, as $T \rightarrow 0$

Recall: $S = k_B \ln \Omega$, if $S=0$, implies Ω^2 such that the ground state is non-degenerate

\Rightarrow Contribution to entropy of a system by each aspect of system (in internal thermodynamics eqn). tends to zero as $f \rightarrow 0$. - Simon. e.g. e^+ s, nucleons, nuclear spins. Allows one to focus on a subsystem without worrying about entropy of other system.

• Consequences of Third Law.

- (1) Heat capacities tend to 0, as $T \rightarrow 0$.

$$C = T \left(\frac{\partial S}{\partial T}\right), \text{ note: } \frac{d \ln T}{dT} = \frac{1}{T} \Rightarrow T = \frac{dT}{d \ln T} \Rightarrow C = \left(\frac{\partial S}{\partial \ln T}\right)$$

- (2) Thermo Expansion Stays

$$\beta_p = \frac{1}{T} \left(\frac{\partial V}{\partial T}\right)_p = - \frac{1}{T} \left(\frac{\partial S}{\partial p}\right),$$

Maxwell relation.

$T \rightarrow 0$
 In $T \rightarrow 0$, remains non-zero
 $S \rightarrow 0$
 $\Delta S \neq 0$
 $C \rightarrow 0$
 $T \rightarrow 0$ @ $\partial \ln T / \partial T$
 $\beta_p \rightarrow 0$.

-③ Gases will no longer be "ideal" as $T \rightarrow 0$

Recall: $C_p - C_V = R$ & $C_V = \frac{3}{2}R$. but above we saw

$C_p \approx C_V \approx 0$ as $T \rightarrow 0$, i.e. results of ideal gas no longer hold

-④ Curie's Law Breaks down ($\chi \propto \frac{1}{T}$)

From example on isothermal magnetization

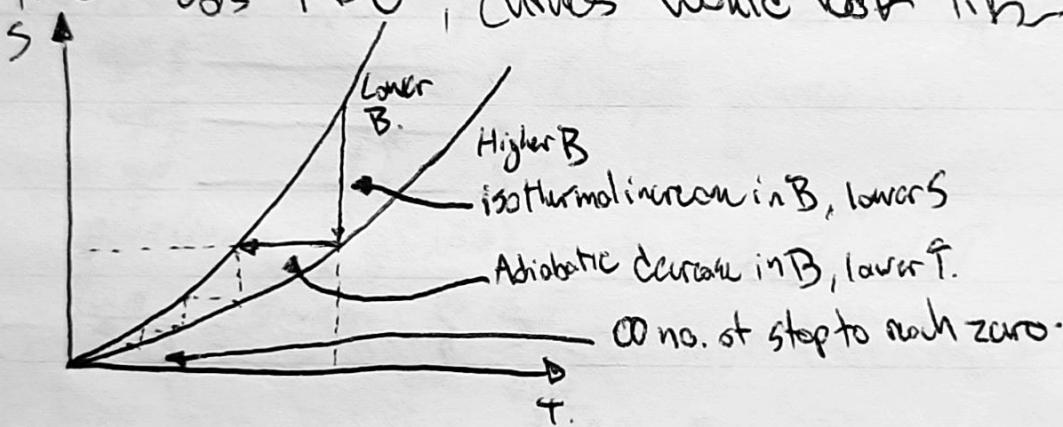
$$\left(\frac{\partial S}{\partial T}\right)_B = \left(\frac{\partial m}{\partial T}\right)_B = \frac{\sqrt{B}}{M_0} \left(\frac{\partial M}{\partial T}\right)_B$$

Since $S \rightarrow 0$ as $T \rightarrow 0$ $\left(\frac{\partial S}{\partial T}\right)_T \rightarrow 0$ as $T \rightarrow 0$ i.e. $\chi \equiv \text{constant}$.

-⑤ It is impossible to cool to $T=0$ in a finite no. of steps.

Plot S as a function of T for two different values of a parameter (e.g. B).

If $S \rightarrow 0$ as $T \rightarrow 0$, curves would look like



If S did not approach zero (some constant) as $T \rightarrow 0$, it would take a finite no. of steps.

Partition Function.

• Recall: $Z = \sum_{\alpha} e^{-\beta E_{\alpha}}$ (single particle) ($\beta = \frac{1}{k_B T}$)
 ↑
 possible states Energy of states.

- A two-level system has two possible energy levels

$$Z = e^{-\beta E_1} + e^{-\beta E_2}$$

assume $E_2 - E_1 = \Delta$

$$Z = \frac{(e^{-\beta \frac{\Delta}{2}} + e^{\beta \frac{\Delta}{2}})}{2}$$

$$\cosh x = \frac{e^x + e^{-x}}{2}$$

$$Z = 2 \cosh\left(\frac{\beta \Delta}{2}\right)$$

- Single Harmonic Oscillator [SHO]

Energy levels are given by $E_n = (n + \frac{1}{2})\hbar\omega$

i.e. evenly spaced

$$E_2 - \frac{\hbar\omega}{2}, \quad E_1 - \frac{\hbar\omega}{2}, \quad E_0 - \frac{\hbar\omega}{2}$$

Partition function: $Z = \sum_{\alpha} e^{-\beta E_{\alpha}} = \sum_{n=0}^{\infty} e^{-(n+\frac{1}{2})\hbar\omega\beta}$

$$= e^{-\frac{\hbar\omega\beta}{2}} \sum_{n=0}^{\infty} e^{-n\hbar\omega\beta} = e^{-\frac{\hbar\omega\beta}{2}} \frac{1}{1 - e^{-\hbar\omega\beta}}$$

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

- Similarly for an N -level system with $E_n = n\hbar\omega$

$$Z = \sum_{\alpha} e^{-\beta E_{\alpha}} = \sum_{n=0}^{N-1} e^{-n\hbar\omega} =$$

$$Z = \frac{1 - e^{-N\hbar\omega}}{1 - e^{-\hbar\omega}}$$

- Rotational Leds. ($E_J = (J+1)\hbar \frac{\pi^2}{2I}$)

for $J=2$, $m_J = -2, -1, 0, 1, 2$.

$$Z = \sum_{\alpha} e^{-\beta E_{\alpha}} = \sum_{J=0}^{\infty} (2J+1) e^{-\frac{\beta \hbar^2 J(J+1)}{2I}}$$

angular momentum number
 $J=0, 1, \dots, I = \text{rotational inertia}$

$$\sum_{n=0}^{\infty} r^n = \frac{a}{1-r}$$

$$\sum_{n=0}^{N-1} r^n = \frac{a(1-r^N)}{1-r}$$

Thermodynamic Functions

- Internal energy $\rightarrow U = \sum_i p_i E_i = \sum_i \frac{E_i e^{-\beta E_i}}{Z}$, $Z = \sum_i e^{-\beta E_i}$, $\beta = \frac{1}{k_B T}$
- Note $\frac{\partial Z}{\partial \beta} = \sum_i (-E_i) e^{-\beta E_i}$
- $\therefore U = -\frac{1}{2} \frac{\partial Z}{\partial \beta^2} = -\frac{d \ln Z}{d \beta}$
- $\frac{\partial \beta}{\partial T} = \frac{1}{k_B} \left(-\frac{1}{T^2} \right) \Rightarrow d\beta = -\frac{1}{k_B T^2} dT$
- So $U = -\frac{d \ln Z}{-\frac{\partial T}{k_B T^2}} = k_B T \frac{Z}{T} \frac{d \ln Z}{dT}$

- Entropy $S = k_B (\beta U + \ln Z)$. See tutorial 8.

- With $\beta = \frac{1}{k_B T} \Rightarrow (S = \frac{U}{T} + k_B \ln Z)$

- Helmholtz function $F = U - TS = U - (U + k_B T \ln Z)$.

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

$$\frac{-F}{k_B T} = \ln Z$$

$$- \beta F = k_B T \Rightarrow Z = e^{-\beta F}$$

Example: Show that at high temp such that $k_B T \gg \hbar \omega$, the partition function for the SHO is approx $Z \approx e^{-\beta \hbar \omega}$ and calculate U, C, F and S at high

$$Z = \frac{e^{-\frac{\beta \hbar \omega}{2}}}{1 - e^{-\beta \hbar \omega}}, e^{-\frac{\beta \hbar \omega}{2}} = e^{\frac{\beta \hbar \omega}{2}} \approx 1 - \frac{\hbar \omega}{2k_B T} \approx 1 - \frac{1}{e^{\beta \hbar \omega}}$$

$$e^{\beta \hbar \omega} = e^{-\beta \hbar \omega}$$

$$Z \approx \frac{1}{1 - (1 - e^{-\beta \hbar \omega})} \approx \frac{1}{e^{-\beta \hbar \omega}}$$

$$U = \frac{1}{V} \ln Z = -\beta \hbar \omega (-\beta \hbar \omega + \frac{1}{e^{\beta \hbar \omega}})$$

$$\begin{aligned} & \text{2DOF} \\ & \frac{1}{2} m^2 + \frac{1}{2} k_1^2 \end{aligned}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{1}{\beta^2} (k_B T) = k_B$$

$$F = -k_B T \ln Z - k_B T \ln \left(\frac{k_B T}{m \hbar \omega} \right)$$

$$S = \frac{U}{T} + k_B \ln Z = \frac{k_B}{T} + k_B \ln \left(\frac{k_B T}{m \hbar \omega} \right) = k_B \left[1 + \ln \left(\frac{k_B T}{m \hbar \omega} \right) \right]$$

• Some Observations:

- ① If $k_B T \ll \hbar \omega$: $E_1 - E_0$, system will sit in the lowest level.

- ② For a finite-level system $\nexists k_B T \gg E_n - E_0$, each level will be occupied with approx. equal prob.

- ③ If there are an infinite "ladder" of levels and $k_B T \gg \hbar \omega$; $E_{j+1} - E_j$ then $U = \langle E \rangle \approx \alpha T$ i.e. SHO, $U = k_B T$ at high.

Combining Partition Functions

- Consider system with energy levels given by $E_{\text{tot}} = E_i^{(a)} + E_j^{(b)}$, where $E_i^{(a)}$ is the i^{th} level of contribution (a), and contribution (b) is $E_j^{(b)}$ is the j^{th} level of contribution (b), independent of contribution (b).

Then partition function is:

$$Z = \sum_i \sum_j e^{-\beta(E_i^{(a)} + E_j^{(b)})}$$

$$= \sum_i e^{-\beta E_i^{(a)}} \sum_j e^{-\beta E_j^{(b)}}$$

$$= Z_a Z_b$$

- Partition functions of independent contributions multiply

- $\ln Z = \ln Z_a + \ln Z_b$, for functions which depend on $\ln Z$, the independent contributions add.

- Ex. Diatomic molecule with both vibrational & rotational DOF

$$Z = Z_{\text{vib}} Z_{\text{rot}} = \underbrace{\frac{e^{-\beta E_{\text{vib}}}}{1 - e^{-\beta E_{\text{vib}}}}}_{\text{vib. } Z_{\text{vib}}} \cdot \underbrace{\frac{1}{j} \sum_j (2j+1) e^{-\beta E_{\text{rot}} j(j+1)}}_{\text{rot. } Z_{\text{rot}}}$$

- Ex. Paramagnet. (Spin $\rightarrow \frac{1}{2}$). Place spin $\frac{1}{2}$ particle in a magnetic field along z. Can exist in two eigenstates \rightarrow
- $\rightarrow \uparrow$ (L is parallel to B) , L is angular momentum. ~~is it?~~
- $\rightarrow \downarrow$ (L is anti-parallel to B).

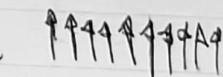
$$E = -\vec{m} \cdot \vec{B} = -(-\mu_B) B = \mu_B B$$

$$E = -\vec{m} \cdot \vec{B} = -(+\mu_B) B = -\mu_B B$$

- Single-particle partition function $Z_1' \xrightarrow{\text{cash time baby}}$

$$Z_1' = e^{\beta \mu_B B} + e^{-\beta \mu_B B} = \frac{2}{2} (e^{\beta \mu_B B} + e^{-\beta \mu_B B}) = 2 \cosh(\beta \mu_B B)$$

- A spin $\frac{1}{2}$ paramagnet is an assembly of N such particles (assumed non-interacting).

- Lowest energy state is when all moments align with field 
however, there is one such state out all microstates so it is very unlikely.

- Less energetically-favourable is a state with half parallel, half anti-parallel

- There are many such states \rightarrow much more likely.

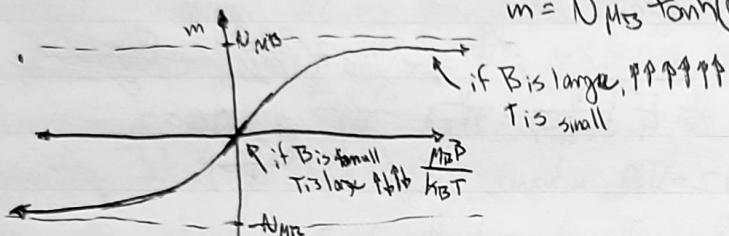
- This interplay between N and entropy, $S = k_B \ln \Omega$, is encoded in the Helmholtz function ($F = U - TS$).

- $F = U - TS$ - S becomes more important as T increases
 - U becomes more important as T decreases.
- Because they are non-interacting, N -particle partition function is: $Z_N = Z_1 \cdot Z_1 \cdot Z_1 \cdots = Z_1^N$
- $F = -k_B T \ln Z_N$
 $= -k_B T \ln Z_1^N = -k_B N T \ln Z_1$
 $= -k_B N T \ln(2 \cosh(\beta \mu_B \beta))$
- $\delta F = -SdT - \mu d\delta$ ~ from previous

$$\delta F = \left(\frac{\partial F}{\partial T}\right)_B dT - \left(\frac{\partial F}{\partial \delta}\right)_T d\delta$$

$$\therefore m = -\left(\frac{\partial F}{\partial \delta}\right)_T = -\frac{\partial}{\partial \delta} \left[-N k_B T \ln \left(2 \cosh(\beta \mu_B \beta) \right) \right]$$
 $= N k_B T \frac{2 \sinh(\beta \mu_B \beta)}{2 \cosh(\beta \mu_B \beta)} \frac{\partial \cosh(\beta \mu_B \beta)}{\partial \beta}$
 $= N k_B T \frac{\sinh(\beta \mu_B \beta)}{\cosh(\beta \mu_B \beta)} \frac{\partial \cosh(\beta \mu_B \beta)}{\partial \beta}$
 $= N k_B T \tanh(\beta \mu_B \beta) \beta \mu_B$

$$m = N \mu_B \tanh(\beta \mu_B \beta)$$



$$\therefore M = \frac{m}{V} = \frac{N}{V} \mu_B \tanh(\beta \mu_B \beta)$$

in limit of small B ,

$$M \approx \frac{N}{V} \mu_B \beta \frac{1}{\cosh^2 \beta}$$

$$\propto = \frac{N \mu_B}{B} = \frac{\mu_B N}{B} \frac{1}{\sqrt{1 + \mu_B^2 B^2}} = \frac{\mu_0 \mu_B^2}{V} N \frac{1}{k_B T}. \text{ i.e. } \propto \neq \propto (Curie's \text{ law})$$

for small $x \rightarrow \tanh x \approx x$

Statistical Mechanics of an Ideal Gas

- Density of state - Number of states in an energy or momentum interval
- Consider a box, $V = L \cdot L \cdot L$ filled with gas molecules. Assume zero probability to find molecules outside. Solutions are that of 3D-particles in a box.

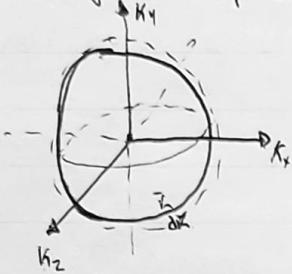
$$4 = \left(\frac{2\pi}{3}\right)^{\frac{3}{2}} \sin(k_x a) \sin(k_y a) \sin(k_z a)$$

$$k_x = \frac{p_x}{\hbar}, \quad \vec{k} = (k_x, k_y, k_z).$$

- k must be zero at boundaries of box. Gives rise to quantization of k_i : $k_i = (k_x, k_y, k_z) = \frac{\pi}{L} (n_x, n_y, n_z)$, positive integers.

- Points in k -space are separated by $\frac{\pi}{L}$

- Each point occupies volume: $dV_{\text{state}} = \left(\frac{\pi L^3}{L}\right)^3$



Since n_x, n_y, n_z must be positive integers allowed points in k -space, occupy an extent of a sphere.

Consider number of points that lie in spherical $\sim \frac{1}{8}^{\text{th}}$ -shell between $\vec{k} + d\vec{k}, dV = (4\pi k^2) d\vec{k}$.

- Define $g(k)$ as the density of states. Then number of allowed states within dV is:

$$g(k) dk \approx \frac{dV}{dV_{\text{state}}} = \frac{\frac{1}{8} \pi k^2 dk}{\left(\frac{\pi L^3}{L}\right)^3} = \frac{3k^2 dk}{2\pi^2 L^3} = \frac{V k^2 dk}{2\pi^2}$$

- To obtain partition function for ideal gas:

$$\begin{aligned} Z_1 &= \sum_k e^{-\beta E_k} \Rightarrow \text{integral} \Rightarrow Z_1 = \int e^{-\beta E_k} g(k) dk \\ Z_1 &= \int_0^\infty e^{-\beta E_k} \frac{V k^2 dk}{2\pi^2} = \frac{V}{2\pi^2} \int_0^\infty k^2 e^{-\beta E_k} dk \\ &= \frac{V}{2\pi^2} \frac{1}{4} \sqrt{\frac{\pi}{\frac{E_k}{k_B T}}} = \frac{V}{2\pi^2} \frac{\sqrt{\frac{\pi}{m^2 (k_B T)^2}}}{\frac{1}{2}} = V N Q = Z_1. \end{aligned}$$

$$\Leftrightarrow Z_1 = V N_Q \text{ where } N_Q = \frac{1}{h^3} \left(\frac{k_B T m}{2\pi} \right)^{\frac{3}{2}} \rightarrow \text{quantum concentration}$$

- Also define Thermal wavelength $\lambda_{\text{th}} = n_Q^{-\frac{1}{3}}$

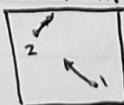
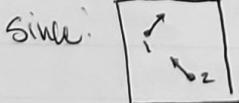
$$\lambda_{\text{th}} = \frac{n}{\sqrt{2\pi m k_B T}}$$

Distinguishability.

- Consider system of 2 non-interacting distinguishable particles. Total Energy is $E_1 + E_2$

$$\begin{aligned} Z &= \sum_{\text{all}} \sum_{\text{all}} e^{-\beta E_1} e^{-\beta E_2} \\ &= \sum_{E_1} e^{-\beta E_1} \sum_{E_2} e^{-\beta E_2} = \cancel{Z_1 Z_2} \quad (*) \end{aligned}$$

- Next assume particles are indistinguishable, then $(*)$ will overcount number of states since independent contribution multiply



interchanging 2 particles leaves system in same state.

- Thus a more accurate result in this case would be $\rightarrow Z = \frac{1}{2} Z_1^2$

- This is not exact however, because states aren't always double counted ($\alpha_1 = \alpha_2$)
- However for many systems (eg ideal gas), the density is low enough that chance of both particle being in same state is negligible!

- This leads to double counting to be negligible.
- If we generalize to N particle system,
 $z = z_1 z_2 \dots z_N$ $\begin{matrix} \text{3 distinguishable} \\ \text{3 indistinguishable} \end{matrix}$
 $z = \frac{1}{N!} z_1^N$ $\begin{matrix} \text{number of ways particle can be interchanged.} \\ \text{number of molecules} \end{matrix}$

When is this approximation okay?

- When number of thermally accessible states \gg number of particles
- For ideal gas this means, $\frac{N}{V} \ll N_A$
number density of molecules \gg number density of states.

Hence can write $Z = \frac{1}{N!} \left(\frac{V}{\lambda_m^3} \right)^N$

- From figure 21.3 we see λ_{N_2} is 10^{-11} m^3 @ room T but typically λ is 10^{-9} m^3 (\approx , approximation is good).

Functions of State for the Ideal Gas

For Ideal Gas

$$Z = \frac{1}{N!} \left(\frac{V}{\lambda_m^3} \right)^N = \frac{1}{N!} V^N \left(\frac{12 \pi k_B T}{h} \right)^{3N}$$

$$z_1 = \text{const.} \cdot V^N \cdot T^{3N}$$

$$\text{Recall: } U = k_B T \frac{\partial \ln Z}{\partial T}$$

$$U = k_B T \frac{\partial \ln Z}{\partial T} = k_B T^2 \left[\left(\text{constant } N \ln V + \frac{3}{2} N \ln T \right) \right] = k_B T^2 [\ln T]_T = k_B T^3 \frac{1}{2} N \frac{1}{T} = \frac{3}{2} k_B T N = \frac{3}{2} N k_B T.$$

$$-C_V = \frac{\partial U}{\partial T} = \frac{3}{2} N k_B$$

$$-\ln z_1 = \ln(V!) + N \ln \left(\frac{V}{\lambda_m^3} \right) = -\ln(N!) + N \ln \left(\frac{V}{\lambda_m^3} \right)$$

$$= \cancel{N \ln N} - (N \ln N + N) + N \ln \left(\frac{V}{\lambda_m^3} \right)$$

$$= N \ln \left(\frac{V}{\lambda_m^3} \right) - \ln N + 1 = N \left[\ln \left(\frac{V}{\lambda_m^3 N} \right) \right]$$

$$\ln z_1 = N \ln \left(\frac{V}{\lambda_m^3 N} \right) \quad \text{sometimes seen as } N \ln \left(\frac{e}{\lambda_m^3 n} \right), \quad n = \frac{N}{V}$$

$$-F = -k_B T \ln z_1$$

$$= -k_B T N \ln \left(\frac{e}{\lambda_m^3 n} \right) = k_B T N \ln \left(\frac{n h m^3}{c} \right) = k_B T N [\ln(n \lambda_m^3) - 1].$$

$$F = V - TS \cancel{= \frac{1}{T} \ln z_1}$$

$$\Rightarrow S = \frac{U - F}{T} = \frac{3}{2} k_B T - \dots \Rightarrow -N k_B \left[\frac{3}{2} - \ln(n \lambda_m^3) \right] + \text{Sackur-Tetrode Equation}$$

• Can find:

$$- H = \frac{5}{2} N k_B T.$$

$$- G = N k_B T \ln(\pi \lambda_m^3).$$

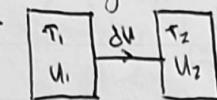
• In general (for ideal gas)

$$\begin{aligned} - Z_i &= Z_{\text{trans}} Z_{\text{int}} \rightarrow \\ &\quad \uparrow \quad \downarrow \quad \text{other energy} \\ &\quad \text{translational states} \quad \text{levels.} \\ - Z_i &= \frac{V}{h^3} Z_{\text{int}} \end{aligned}$$

The Chemical Potential.

- Chemical Potential denoted by μ
- Systems that exchange particles with their surroundings
 - Differences in chemical potential drive flow of particles.
 - Chemical Potential (μ) - amount internal energy changes by when 0 particle is added.
 - Modified 1st law: $dU = TdS - pdV + \mu dN \rightarrow \# \text{ of particles}$
 - $M = \left(\frac{\partial U}{\partial N}\right)_{S,V}$. ($S \& V$ are not always convenient constants).
 - so $F = U - TS \Rightarrow dF = dU - TdS - dTS = TdS - pdV + \mu dN - TS - dS$
 - $= -pdV - SdT + \mu dN \Rightarrow M = \left(\frac{\partial F}{\partial N}\right)_{T,V}$.
 - Further, $G = U + pV - TS \Rightarrow dG = dU + pdV + Vdp - SdT - dTS$.
 - $= TdS - pdV + \mu dN + pdV + Vdp - TdS - SdT$
 - $= Vdp - SdT + \mu dN \Rightarrow \mu = \left(\frac{\partial G}{\partial N}\right)_{P,T}$.
 - Let us find μ for an ideal gas.
 - $M = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \frac{1}{2} N [N k_B T \ln\left(\frac{N \lambda_m^3}{V e}\right)]_{T,V}$
 - $= k_B T \ln\left(\frac{N \lambda_m^3}{V e}\right) + N k_B T \frac{1}{2} \ln\left(\frac{N \lambda_m^3}{V e}\right)_{T,V}$
 - $= k_B T \left[\ln\left(\frac{N \lambda_m^3}{V e}\right) + \frac{N \lambda_m^3}{2V} \frac{1}{\lambda_m^3} \right]_{T,V}$
 - $= k_B T \ln\left(\frac{N \lambda_m^3}{V e}\right)$
 - $\mu = k_B T \ln\left(\frac{N \lambda_m^3}{V}\right)$
 - Comparing with $\mu = \frac{G}{N}$
 - From first law: $TdS = dU + pdV - \mu dN \rightarrow$ natural variable for entropy
 - $S \equiv S(U, V, N)$
 - $dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN$
 - Comparing: $\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}, \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N}, -\frac{\mu}{T} = \left(\frac{\partial S}{\partial N}\right)_{U,V}$

- Consider two systems, thermally isolated from surroundings but able to exchange heat with each other. (System 1 loses dU , System 2 gains dU).

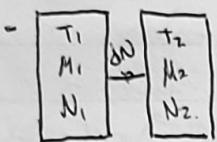


- Change in entropy $dS = \left(\frac{\partial S_1}{\partial U_1}\right)_{NN} dU_1 + \left(\frac{\partial S_2}{\partial U_2}\right)_{NN} dU_2$
 $dS = \left(\frac{\partial S_1}{\partial U_1}\right)_{NN} (dU) + \left(\frac{\partial S_2}{\partial U_2}\right)_{NN} (dU)$
 $= -\frac{1}{T_1} dU + \frac{1}{T_2} dU = dU(T_2 - T_1) \geq 0$

- If $T_1 > T_2$; $dU > 0$ energy flows from 1 \rightarrow 2.

- If $T_1 = T_2$; $dS = 0 \rightarrow$ equilibrium.

- Similarly Consider two systems isolated from surroundings but able to exchange particles with each other. (System 1 loses dN , System 2 gains dN)



- $dS = \left(\frac{\partial S_1}{\partial N_1}\right)_{UN} dN_1 + \left(\frac{\partial S_2}{\partial N_2}\right)_{UN} dN_2$
 $= \left(\frac{\partial S_1}{\partial M_1}\right)_{UN} (-dN) + \left(\frac{\partial S_2}{\partial M_2}\right)_{UN} dN$
 $= \frac{M_1}{T_1} dN - \frac{M_2}{T_2} dN$
 $= \left(\frac{M_1}{T_1} - \frac{M_2}{T_2}\right) dN \geq 0$.

- If $T_1 = T_2$, & $dN > 0$.

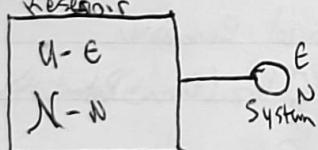
- If $M_1 > M_2$, particles flow from 1 \rightarrow 2; & if $M_2 > M_1$ particles flow from 2 \rightarrow 1 and $dN < 0$.

- If $M_1 = M_2$, $dS = 0 \rightarrow$ Equilibrium



Grand Partition Function

- Consider small system of energy E containing N particles connected to a reservoir of energy $U-E$ and $N-N$ particles.



$$U \geq E$$

$$N \geq N$$

$$x-a = U-E-U$$

$$x-N-x$$

- $S(U, V, N) \Rightarrow S(U-E, X-N) = S(U, N) + (-E)\left(\frac{\partial S}{\partial U}\right)_{NN} + (-N)\left(\frac{\partial S}{\partial N}\right)_{UN} + \dots$
 $S(U-E, X-N) = S(U, N) - \frac{E}{T} - N\left(-\frac{1}{T}\right) + \dots$
 $= S(U, N) - \frac{1}{T}(E - MN)$

- The probability that the system chooses a particular macrostate Ω is proportional to number of microstates Ω corresponding to that macrostate. ($S = k_B \ln \Omega \Rightarrow \Omega = e^{\frac{S}{k_B}}$).

Taylor Expansion:
 $f(x) = f(a) +$
 $(x-a)\left(\frac{\partial f}{\partial x}\right)_{x=a} + \dots$

$$- \sum = e^{\frac{f}{k_B}}$$

- $P(E, N) \propto e^{\frac{f}{k_B}(U - f - \mu N)}$ all of the microstates in the system giving up $N\delta N$ to the system

$$\begin{aligned} - P(E, N) &\propto e^{\frac{f}{k_B}(U - f - \mu N)} \\ &\propto \underbrace{e^{-\frac{f}{k_B}(U - f)}}_{\text{constant.}} e^{-\frac{E - \mu N}{k_B T}} \end{aligned}$$

Boltzmann
Distribution

$$- P(E, N) \propto e^{P(MN - E)} \quad \text{Note: if } \mu = 0 \Rightarrow P(E, N) \rightarrow P(E) \propto e^{-\frac{E}{k_B T}}$$

- The normalized probability is:

$$- P_i = \frac{e^{P(MN - E_i)}}{\sum_i e^{P(MN - E_i)}} = \frac{e^{P(MN - E_i)}}{Z}$$

- Z is the Grand Partition Function

$$- Z = \sum_i e^{P(MN - E_i)}$$

- The GPF can be used to derive thermodynamic functions

$$- N = \sum_i N_i P_i = k_B T \left(\frac{\partial \ln Z}{\partial \mu} \right)_B$$

$$U = \sum_i E_i P_i = - \left(\frac{\partial \ln Z}{\partial \beta} \right)_B + MN$$

$$S = -k_B \sum_i P_i \ln P_i = (U - MN + k_B T \ln Z)/T.$$

- E.g. N

$$\begin{aligned} - N &= \sum_i N_i P_i = \sum_i N_i \frac{e^{P(MN - E_i)}}{Z} = \frac{1}{Z} \sum_i N_i e^{P(MN - E_i)} \\ - \left(\frac{\partial P}{\partial \mu} \right)_B &\Rightarrow \frac{\partial}{\partial \mu} \sum_i N_i e^{P(MN - E_i)} \\ &= \sum_i \beta N_i e^{P(MN - E_i)} \end{aligned}$$

$$- N = \frac{1}{\beta} \frac{1}{Z} \left(\frac{\partial Z}{\partial \mu} \right)_B$$

$$= \frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial \mu} \right)_B = k_B T \left(\frac{\partial \ln Z}{\partial \mu} \right)_B$$

- Recall: Canonical Ensemble $Z = e^{-\beta U_0}$.

Similarly for Grand Canonical Ensemble:

$$Z = e^{-\beta \Phi_G}, \text{ where } \Phi_G = -k_B T \ln Z \text{ (Grand Potential),}$$

$$\text{from } \Phi_G = U - \mu N - TS$$

$$\Phi_G = U - \mu N - TS$$

$$\Phi_G = F - \mu N$$

It is differentiable with: $d\Phi_G = dF - \mu dN - N d\mu$.

- Recall $dF = -pdV - SdT + \mu dN$ (see previous notes)

$$\begin{aligned} d\Phi_G &= -pdV - SdT + \mu dN - \mu dN - N d\mu \\ &= -pdV - SdT - N d\mu \end{aligned}$$

$$\cdot S = -\left(\frac{\partial \ln P}{\partial T}\right)_{V, \mu}, P = -\left(\frac{\partial \ln G}{\partial V}\right)_{T, \mu}, N = -\left(\frac{\partial \ln F}{\partial \mu}\right)_{T, V}$$

• Example: ~~Carb~~ Carbon Monoxide Dissociation

- hemoglobin \rightarrow 4 absorption sites for O_2 . Each site has ~~one~~ Fe^{2+} ion, which can hold one O_2 molecule

- Simplify by cons. for one site only

- If O_2 is present, there are 2 possible states.

$$N_i = 0 \text{ (occupied)} \quad \text{with } E = 0$$

$$N_i = 1 \text{ (unoccupied)} \quad " \quad E = -0.7 \text{ eV}$$

$$\text{- Then } \sum_i e^{-E_i/(k_B T)} = e^{-(E_0 - 0)/(k_B T)}$$

$$= e^{(E_0 - 0)/(k_B T)} + e^{(E_0 + 0.7)/(k_B T)}$$

$$= 1 + e^{(E_0 + 0.7)/(k_B T)}$$

- In environment of lungs chemical potential is $\mu = -0.6 \text{ eV}$ at body temp 310 K .

$$\text{- Thus: } e^{\mu/(k_B T)} = e^{\frac{-0.6 \text{ eV} - (-0.7 \text{ eV})}{0.02612 \text{ eV}}}$$

$$K_B T = 0.02612 \text{ eV}$$

$$= 42.2$$

$$\text{- } P(\text{occupied by } O_2) = \frac{e^{-E_0/(k_B T)}}{1 + e^{-E_0/(k_B T)}} = 0.977$$

• Suppose there is carbon monoxide present, which can be adsorbed on the same site.

• for CO: $\mu_0 = -0.72 \text{ eV}$, $E_{CO} = -0.85 \text{ eV}$



$$E_0 = 0, \mu_0 = -0.6 \text{ eV} \quad E_{CO} = -0.85 \text{ eV}, \mu_{CO} = -0.72 \text{ eV}$$

$$\text{- } P(\text{occupied by } O_2) = \frac{e^{-E_0/(k_B T)}}{1 + e^{-E_0/(k_B T)} + e^{-E_{CO}/(k_B T)}} = 0.244$$

• Recall for ideal gases we have $G = \mu N$

- This is true in general

- Also, $G = U + PV - T\Delta S$

$$\text{- So; } \mu N = U + PV - TS.$$

$$-PV = U - TS$$

- If there is more than one type of particle we add

$$\Delta U = TS - PV + \sum_i \mu_i N_i$$

$$\Delta F = -PV - SdT + \sum_i \mu_i N_i$$

$$\Delta G = \cancel{TS} - PV - SdT + \sum_i \mu_i N_i$$

• for constant N

$$- dF = \sum_i \mu_i N_i$$

• for constant V

$$- dF = \sum_i \mu_i M_i$$

Particle Number Conservation Laws

- Consider system of particles is a box of constant VT , where particle number N is not conserved.
 - : i.e. Can create/destroy particles as long as energy/mass conservation ~~laws~~ holds.
 - Show consider that when VT is in constant equilibrium state is obtained by minimizing $F \rightarrow$ choose # of particles in each.
 - i.e. $\left(\frac{\partial F}{\partial N}\right)_{VT} = 0$
but $\mu = \left(\frac{\partial F}{\partial N}\right)_{VT}$ so $\mu = 0$ for a sys with no number ~~conservation~~ conservation law
 - Next consider a system where particle number is conserved.
 - electron belongs to a lepton class of particles, along with its antiparticle, positron, and corresponding neutrinos and anti-neutrinos
 - In such reactions involving these particles total electron family number (+1 for particle, -1 for antiparticle) must be conserved
 - $e^- + \bar{e}^+$ (total electron family number = $+1-1=0$) can annihilate and produce 2 photons or neutrino/antineutrino but not 2 neutrinos
 - So consider box of $N_- - \bar{e}^+$'s at $N_+ e^+$ conservation law fixed. $N = N_- + N_+$
 - Choose N to minimize F .
- $$\left(\frac{\partial F}{\partial N_-}\right)_{VT} = 0 \quad F = f(N_-, N_+)$$
- $$dF = \left(\frac{\partial F}{\partial N_-}\right)_{N_+} dN_- + \left(\frac{\partial F}{\partial N_+}\right)_{N_-} dN_+$$
- $$\frac{\partial F}{\partial N_-} = \left(\frac{\partial F}{\partial N_-}\right)_{N_+} + \left(\frac{\partial F}{\partial N_+}\right)_{N_-} \frac{dN_+}{dN_-}$$

$$-\left(\frac{\partial F}{\partial N}\right)_{VN} = \underbrace{\left(\frac{\partial F}{\partial N_-}\right)_{VN_+}}_{\text{chemical potential of } e^-} + \underbrace{\left(\frac{\partial F}{\partial N_+}\right)_N \cdot \frac{\partial N_+}{\partial N_-}}_{\text{chemical potential of positron.}} = 0.$$

$$= \mu_- + \mu_+ \underbrace{\frac{\partial N_+}{\partial N_-}}_N$$

to keep family number N constant; if I odd
on e^- I need to add positron

$$\Rightarrow \mu_- + \mu_+ = 0 \quad \leftarrow \text{for equilibrium state.}$$