Physics 415 Lecture Note \ All In One

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Statistical Mechanics (preview)

- In stat. mech., we will be interested in the laws governing the behavior of "macroscopic" systems:

  macroscopic = composed of many constituent particles (atoms, molecules, etc...)

  typical # $\sim 10^{23}$ particles.

- In principle, if "microscopic" laws are known, then prop.'s of system of large # of particles can be deduced by solving the μ-scopic eqn.'s: (μ = micro.)

Ex: Classical system of N particles:

$$\begin{cases} m_i \ddot{\vec{r}}_i = \vec{F}_i(\vec{r}_1, \dots, \vec{r}_N) & i = 1, \dots, N \quad \left(\dot{} \equiv \frac{d}{dt}, \ \ddot{} \equiv \frac{d^2}{dt^2}, \text{ etc.} \right) \\ + \text{ initial conditions } \vec{r}_i(t=0) \ \& \ \vec{v}_i(t=0). & (= 6 \times N \ \#'s) \end{cases}$$

$\Rightarrow$ knowledge of state of system at any time t.

- However, for macro N, this is <u>not</u> feasible.

Even <u>if</u> we could solve the equations of motion (EOM), simply recording ~~specifying~~ all 6N initial conditions (w/ $N \sim 10^{23}$) is not practical.

Indeed, knowing the state of each particle is not even very ~~idea~~ useful or interesting info. When the # of particles is that large, we'd rather have info. about the macro. (or "average") prop.'s of the system.

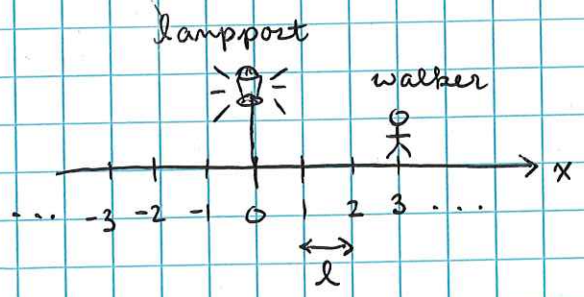
Thus, in stat. mech. we will abandon such μ-scopic determinism in favor of a <u>statistical</u>, or probabilistic, description. We will find that, precisely b/c of the large # of particles involved, new laws & types of regularities will appear that govern macro. behavior.

Ex: notions like "entropy" & "temperature" will emerge, that have no analog in particle mech. & are purely of statistical nature.

<u>Probability</u>.

- Since stat. notions will be important for understanding macro. systems, we'll spend some time reviewing basics of probability. This will be mostly <u>math</u> (not physics).
- Illustrate important ideas through an important example:

<u>1D random walk</u> (a good starting point for understanding a variety of phenomena).



- walker starts from lamppost at $x=0$, taking random steps of length l at regular intervals.

- Each step is indep. of the last. prob p to step to the right & prob. $q = 1-p$ to step to the left.

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Q: After taking N steps, what is prob. the walker is at a position $x = m\ell$ (m = integer) ?

[For another ex. of a 1D random walk, see "probability board" demo at Ingersoll museum]

- want to calculate prob. $P_N(m)$ that walker is at position $x = m\ell$ after N ~~steps~~. steps. Note $-N \le m \le N$.

$$\left.\begin{array}{l} n_1 = \#\text{ of steps right} \\ n_2 = \text{"} \qquad\qquad \text{" left} \end{array}\right\} \quad N = n_1 + n_2 \,, \quad m = n_1 - n_2 .$$

- prob. that walker takes n_1 steps right & n_2 steps left:

$$\underbrace{(p \times p \times \ldots \times p)}_{n_1 \text{ times}} \times \underbrace{(q \times q \times \ldots \times q)}_{n_2 \text{ times}} = p^{n_1} q^{n_2}$$

Of course, there are many different ways in which walker could take n_1 steps right & n_2 steps left

Ex: $n_1 = 2$, $n_1 = 1$ $\quad$ ($N = 3$, $m = 1$)

$$\left.\begin{array}{ll} a) & \rightarrow \ \rightarrow \ \leftarrow \\ b) & \rightarrow \ \leftarrow \ \rightarrow \\ c) & \leftarrow \ \rightarrow \ \rightarrow \end{array}\right\} \text{ 3 ways.}$$

In general, # of ways $= \binom{N}{n_1} = \dfrac{N!}{n_1!\,(N-n_1)!} = \dfrac{N!}{n_1!\,n_2!}$

[check above ex.: $n_1 = 2$, $n_1 = 1$ $\rightarrow$ $\dfrac{3!}{2!\,1!} = 3$ ✓]

$$\Rightarrow P_N(n_1) = \frac{N!}{n_1!\,n_2!}\, p^{n_1} q^{n_2} \qquad \text{"binomial distb.'n"} \qquad (*).$$

or, using $n_1 = \frac{N+m}{2}$ & $n_2 = \frac{N-m}{2}$:

$$P_N(m) = \frac{N!}{[(N+m)/2]! \times [(N-m)/2]!} \times p^{\frac{N+m}{2}} (1-p)^{\frac{N-m}{2}}$$

~~a binomial distb'n~~

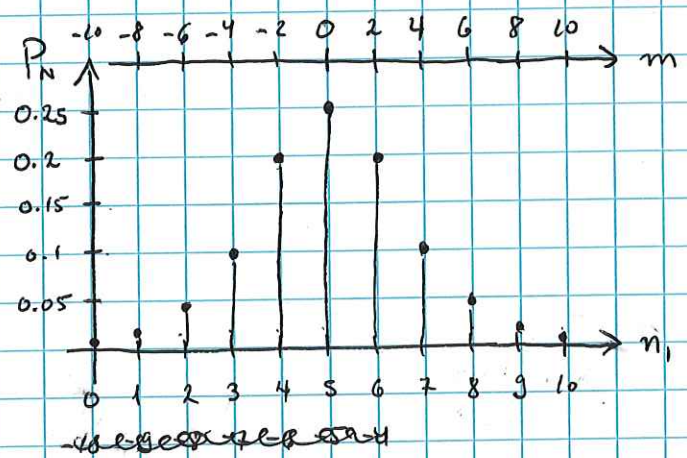
Recall binomial thm.: $(p+q)^N = \sum_{n=0}^{N} \frac{N!}{n!\,(N-n)!}\, p^N q^{N-m}$ c.f. $(*)$

hence the name "binomial distb.'n"

Ex: $p = q = 1/2 \rightarrow P_N(n_1) = \frac{N!}{n_1!\,n_2!} (1/2)^N$

N=10:

n_1	P_N
0	$\simeq 0.001$
1	$\simeq 0.01$
2	$\simeq 0.044$
3	$\simeq 0.12$
4	$\simeq 0.21$
5	$\simeq 0.25$



→ after N=10 steps, prob. is largest for particle to be near origin (m=0). prob. to be far from origin is small

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General notions:

- <u>mean</u>: Let x = random variable, taking N possible values $x_1, x_2, \ldots, x_N$ w/ associated probabilities $P(x_1), P(x_2), \ldots, P(x_N)$ $\left(0 \leq P(x_i) \leq 1 \;\&\; \sum_{i=1}^{N} P(x_i) = 1 \right)$.

  → "mean" (average) of x: $\bar{x} \equiv \sum_{i=1}^{N} P(x_i) x_i$.

  For $f(x)$: $\overline{f(x)} = \sum_{i=1}^{N} P(x_i) f(x_i)$

- <u>variance</u>: Suppose we want to know how much measurements of x "fluctuate" about mean value $\bar{x}$:

  → "variance" (second moment, dispersion)

  $$\equiv \overline{(x-\bar{x})^2} \equiv \sum_{i=1}^{N} P(x_i)\,(x_i - \bar{x})^2$$

  square since fluct. can have either sign.

  note: $\overline{(x-\bar{x})^2} = \overline{x^2} - \overline{2x\bar{x}} + \bar{x}^2 = \overline{x^2} - \bar{x}^2$

  We also define the root-mean square (RMS) deviation:

  $$\Delta x_{rms} = \sqrt{\overline{x^2} - \bar{x}^2}.$$

<u>Ex</u>: In section you will show that, for the binomial distbn.:

$$\begin{cases} \text{avg. \# of steps to the right} = \bar{n}_1 = N \times p \\ \qquad = (\text{total \# of steps}) \times (\text{prob. of step right}). \\ \text{dispersion} = \overline{n_1^2} - \bar{n}_1^2 = N \times pq, \quad \Delta n_{1,rms} = \sqrt{N} \times \sqrt{pq}. \end{cases}$$

→ the relative width is $\dfrac{\Delta n_{1,rms}}{\bar{n}_1} = \sqrt{\dfrac{q}{p}} \times \dfrac{1}{\sqrt{N}} \xrightarrow[N \gg 1]{} 0$ distbn sharply peaked when $N \gg 1$.

Summary

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- Binomial distb'n: $P_N(n) = \frac{N!}{n!\,(N-n)!}\, p^n (1-p)^{N-n}$ $\quad (q = 1-p)$

  → likelihood that event w/ prob. p occurs ~~occurs~~ n times in N trials.

  mean: $\bar{n} = Np$

  variance: $\overline{n^2} - \bar{n}^2 = Npq$

  $\frac{\Delta n_{rms}}{\bar{n}} = \sqrt{\frac{q}{p}}\,\frac{1}{\sqrt{N}}$ (relative width).

- Important regime to understand is $N \gg 1$. Convenient to work w/ $\ln P_N = \ln N! - \ln n! - \ln (N-n)! + n \ln p + (N-n) \ln q$.

- For $N \gg 1$, we use "Stirling's formula":

$$N! \simeq \sqrt{2\pi N}\, N^N e^{-N} \qquad (N \gg 1)$$

(see Reif App. A.6 for derivation).

$$\ln N! = N \ln N - N + \tfrac{1}{2} \ln 2\pi N.$$

$$\Rightarrow \ln P_N \simeq \left[N \ln N - N + \tfrac{1}{2} \ln 2\pi N\right] - \left[n \ln n - n + \tfrac{1}{2} \ln 2\pi n\right]$$

$$- \left[(N-n)\ln(N-n) - (N-n) + \tfrac{1}{2} \ln 2\pi (N-n)\right] + n \ln p + (N-n) \ln q.$$

$$= \frac{1}{2} \ln\left[\frac{N}{2\pi n (N-n)}\right] - N f(n/N)$$

w/ $f(x) = \left[x \ln x + (1-x)\ln(1-x)\right] - \left[x \ln p + (1-x) \ln q\right]$.

$$\Rightarrow P_N \simeq \sqrt{\frac{N}{2\pi n (N-n)}}\; e^{-N f(n/N)}. \qquad (\text{for } N \gg 1)$$

For N large, P_N will be sharply peaked near its max at $n = \tilde{n}$.

→ seek an approx. for P_N near ~~the~~ $n = \tilde{n}$.

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near $\tilde{n}$, we may treat $f(x)$ as a continuous fn. of x

$\Rightarrow$ determine ~~the~~ $\tilde{n}$ by the condition $f' = \frac{df}{dx} = 0$.

$$\rightarrow \quad f' = \ln\left(\frac{q}{p}\frac{\tilde{n}}{N-\tilde{n}}\right) = 0$$

$$\Rightarrow \tilde{n} = Np.$$

(maximize $e^{-Nf(x)}$ by minimizing $f(x)$)

now expand about $\tilde{n}$, $(\tilde{x} = \tilde{n}/N)$:

$$f(x) \simeq f(\tilde{x}) + \cancel{f'(\tilde{x})}^{\,0}(x-\tilde{x}) + \frac{1}{2} f''(\tilde{x})(x-\tilde{x})^2$$

$$\begin{cases} f(\tilde{x}) = 0 \\ f''(\tilde{x}) = \dfrac{1}{\tilde{x}(1-\tilde{x})} = \dfrac{1}{pq} \end{cases}$$

$$\Rightarrow P_N(n) \simeq \sqrt{\frac{N}{2\pi n(N-n)}}\; e^{-\frac{N}{2} f''(\tilde{x})(x-\tilde{x})^2}$$

$$= \sqrt{\frac{N}{2\pi n(N-n)}}\; e^{-\frac{(n-Np)^2}{2Npq}}.$$

Finally, b/c the exponential factor is sharply peaked at $n=\tilde{n}$, we may approx. n by $\tilde{n} = Np$ in the prefactor:

$$\boxed{P_N(n) \simeq \frac{1}{\sqrt{2\pi N pq}}\, e^{-\frac{(n-Np)^2}{2Npq}}} \qquad (N \gg 1)$$

$\rightarrow$ approx. to binomial distb.'n for $N \gg 1$ is a "Gaussian distb.'n"

(this result is an example of the "central limit theorem")

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· Can also verify that the Gaussian distb.'n is properly normalized:

$$\sum_{n=0}^{N} P_N(n) \simeq \int_{-\infty}^{+\infty} dn \; P_N(n)$$

$$= \int_{-\infty}^{+\infty} dn \; \frac{1}{\sqrt{2\pi N pq}} \, e^{-\frac{(n-Np)^2}{2Npq}}$$

see Section 1 for Gaussian integrals

$$= 1$$

· we may also write the final result as:

$$P_N(n) \simeq \frac{1}{\sqrt{2\pi\sigma^2}} \, e^{-\frac{(n-\mu)^2}{2\sigma^2}}$$

$\mu = Np$ = mean of binomial distb.'n

$\sigma^2 = Npq$ = variance " ".

<u>Probability distb.'n w/ multiple variables</u>:

· Consider two random variables u & v (the generalization to >2 random var.'s is straightforward), which can assume possible values:

$$\begin{cases} u_i & i = 1, 2, \ldots, M \\ v_j & j = 1, 2, \ldots, N \end{cases}$$

→ $P(u_i, v_j)$ = prob. that $u = u_i$ & $v = v_j$.

normalization:

$$\sum_{i=1}^{M} \sum_{j=1}^{N} P(u_i, v_j) = 1$$

"unconditional" prob. distbn.'s

$$\begin{cases} P_u(u_i) = \sum_{j=1}^{N} P(u_i, v_j) = \text{prob. } u = u_i, \text{ irrespective of } v \\ P_v(v_j) = \sum_{i=1}^{N} P(u_i, v_j) = \text{prob. } v = v_j, \text{ irrespective of } u. \end{cases}$$

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· Important special case is when prob. that one var. assumes a certain value is independent of the value assumed by the other var.

→ "statistically independent"

or "uncorrelated" variables.

In this case, we have:

$$P(u_i, v_j) = P_u(u_i)\, P_v(v_j)$$ (statistically indep. var.'s u & v).

· Calculate mean values according to:

$$\overline{F(u,v)} = \sum_{i=1}^{M} \sum_{j=1}^{N} P(u_i, v_j)\, F(u_i, v_j)$$

· A special case is the mean of a product $f(u) \times g(v)$ when u & v are statistically indep.:

$$\overline{f(u)\, g(v)} = \sum_{ij} P(u_i, v_j)\, f(u_i)\, g(v_j)$$

stat. indep u & v

$$= \sum_{ij} P_u(u_i)\, P_v(v_j)\, f(u_i)\, g(v_j)$$

$$= \left[\sum_{i=1}^{M} P_u(u_i)\, f(u_i) \right] \times \left[\sum_{j=1}^{N} P_v(v_j)\, g(v_j) \right]$$

$$= \overline{f(u)} \times \overline{g(v)}$$

$$\Rightarrow \quad \overline{f(u)\, g(v)} = \overline{f(u)} \times \overline{g(v)}$$ if u & v are stat. indep.

(not true in general!)

average "factorizer"

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Continuous probability distbn.'s.

- we will often encounter "continuous" prob. distbn.'s, where a random variable x can assume a continuous range of values $a_1 < x < a_2$.

Ex: Gaussian distb.'n: $p(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$, $-\infty < x < +\infty$.

- In the case of a cont. distb.'n, does not make sense to consider the prob. of x taking any particular value (which would be vanishingly small). Rather, we consider prob. that rand. var. lies in a range btwn. x & $x+dx$. (dx = small)

$\rightarrow$ $p(x)dx$ = prob. to find rand. var. in range $(x, x+dx)$

$p(x)$ = "probability density".

- For cont. prob. distbn.'s:

normalization: $\int_{a_1}^{a_2} dx\, p(x) = 1.$

mean: $\overline{f(x)} = \int_{a_1}^{a_2} dx\, p(x) f(x)$

c.f. $\sum_{i=1}^{N} P(x_i) = 1$

$\overline{f(x)} = \sum_{i=1}^{N} P(x_i) f(x_i)$

- Examples of important cont. prob. distbn.'s:
  - $p(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(x-\mu)^2/2\sigma^2}$ (Gaussian)
  - $p(x) = \delta(x - x_0)$ (Dirac δ-distb.'n).
  - $p(x) = \frac{1}{\pi} \frac{\gamma}{\gamma^2 + (x-x_0)^2}$ (Lorentzian)

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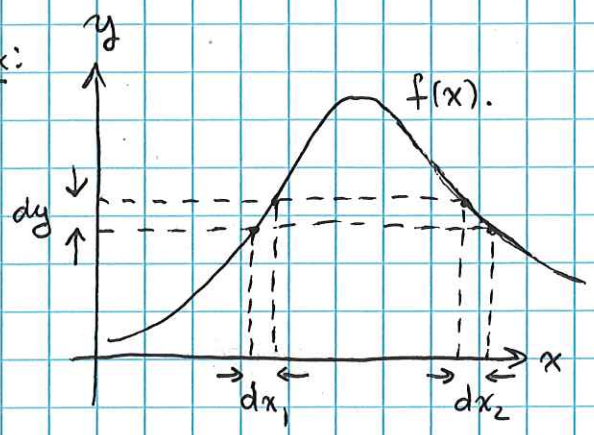
· For cont. prob. distbn's, important to know how to pass from rand. var. x to another rand. var. $y=f(x)$.

That is, given distb'n $p(x)$, what is distb.'n of $y=f(x)$?

→ call this distb.'n $\tilde{p}(y)$.

Ex:



$$\tilde{p}(y)\,dy = p(x_1)\,dx_1 + p(x_2)\,dx_2$$

In words: y will be in range $(y, y+dy)$ if x is in range (x_1, x_1+dx_1) or (x_2, x_2+dx_2)

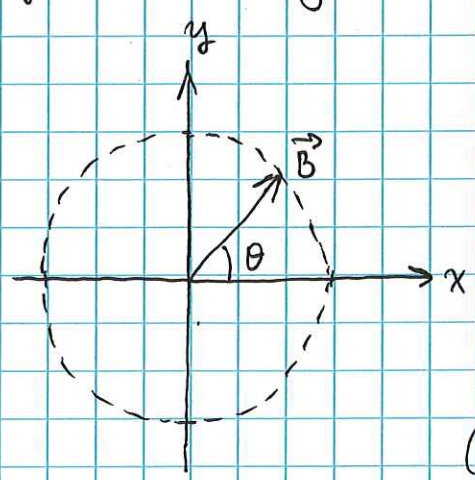
(here $y=f(x_1)=f(x_2)$)

→ rewrite the above as: $\tilde{p}(y) = p(x_1)\left|\frac{dx}{df}\right|_{x=x_1} + p(x_2)\left|\frac{dx}{df}\right|_{x=x_2}$

· In general, there may be a single or many pt.'s x_i s.t. $y=f(x_i)$

$$\Rightarrow \tilde{p}(y) = \sum_i p(x_i)\left|\frac{dx}{df}\right|_{x=x_i}, \quad y=f(x_i)$$

Ex: 2D vector $\vec{B}$ w/ fixed length $B=|\vec{B}|$, equally likely to point in any direction:

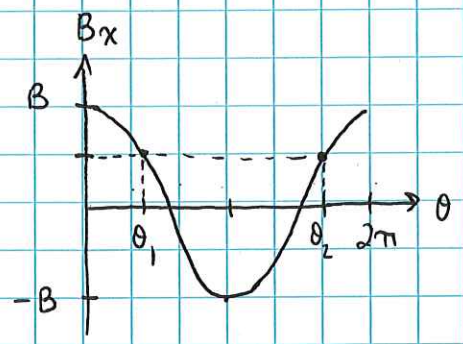


$$p(\theta)\,d\theta = \frac{d\theta}{2\pi}, \quad 0 \le \theta < 2\pi.$$

· x-comp. of $\vec{B}$ is $B_x(\theta) = B\cos\theta$.

→ Q: what is $\tilde{p}(B_x)$?

($\tilde{p}(B_x)\,dB_x$ = prob. to find x-comp. in range (B_x, B_x+dB_x))



Note: $-B \le B_x \le B$ 01/24/25

→ for given value of B_x there are two angles θ_1 & $\theta_2 = 2\pi - \theta_1$:

(i.e., $B_x = B\cos\theta_1 = B\cos\theta_2$.)

→ according to the general formula:

$$\tilde{p}(B_x) = p(\theta_1)\left|\frac{d\theta}{dB_x}\right|_{\theta=\theta_1} + p(\theta_2)\left|\frac{d\theta}{dB_x}\right|_{\theta=\theta_2}.$$

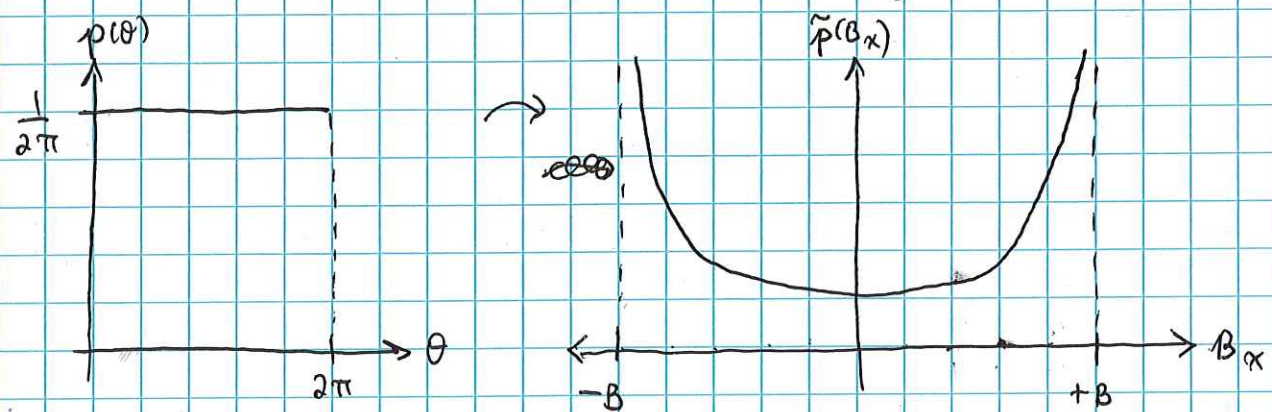
$$B_x = B\cos\theta \Rightarrow \frac{dB_x}{d\theta} = -B\sin\theta$$

& $B\cos\theta_1 = B_x \Rightarrow \left|\frac{dB_x}{d\theta}\right|_{\theta=\theta_1} = B\sqrt{1-\cos^2\theta_1} = \sqrt{B^2 - B_x^2}$.

& we also have $\left|\frac{dB_x}{d\theta}\right|_{\theta=\theta_2} = \sqrt{B^2 - B_x^2}$.

Using $p(\theta) = \frac{1}{2\pi}$, we find:

$$\tilde{p}(B_x) = 2 \times \frac{1}{2\pi}\frac{1}{\sqrt{B^2 - B_x^2}} = \begin{cases} \frac{1}{\pi}\frac{1}{\sqrt{B^2 - B_x^2}} & -B \le B_x \le B \\ 0 & \text{else.} \end{cases}$$



(uniform distb.'n)

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Statistical description of system of particles.

- Use statistical ideas to go from μ-scopic laws $\rightarrow$ macroscopic properties.
- While μ-scopic world is governed by quantum mech. (QM), it is often useful to consider classical description as well. We'll therefore go back & forth btwn. QM & CM, starting now CM.

- Consider a mechanical system w/ s DOF & associated coord.'s $(q_1, q_2, \ldots, q_s)$
  (degrees of freedom)

  Ex: N particles in 3D $\longrightarrow$ $s = 3N$ w/ coord.'s $(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N)$.
- The state of the system at any time t is completely determined by its coord.'s $q_i(t)$ $(i=1,\ldots,s)$ & momenta $p_i(t)$ $(i=1,\ldots,s)$.

  $\rightarrow$ $\{q_1(t), q_2(t), \ldots, q_s(t), p_1(t), p_2(t), \ldots, p_s(t)\}$ specifies the "microstate" (μ-state) of the system.

[We need q's & p's to specify state of system b/c equations of motion (EOM) of CM are second-order in time derivatives, & thus require 2 initial conditions for each DOF]

- Each μ-state specifies a point in $2s$-dimensional "phase space" of the mech. system.

  coord.'s on phase space $= (q_1, \ldots, q_s, p_1, \ldots, p_s)$.

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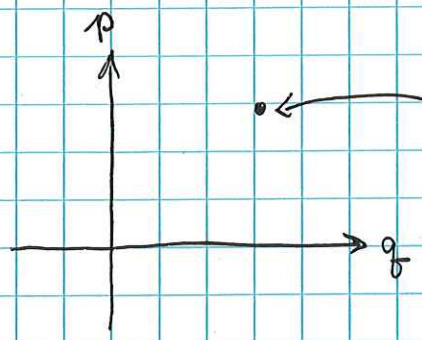
<u>Ex</u>: For $s=1$ DOF, dim. of phase-space $= 2$



pt. in phase space specifies a μ-state of the system.

(phase space)

- Pt.'s in phase space evolve according to "Hamilton's eqn.'s":

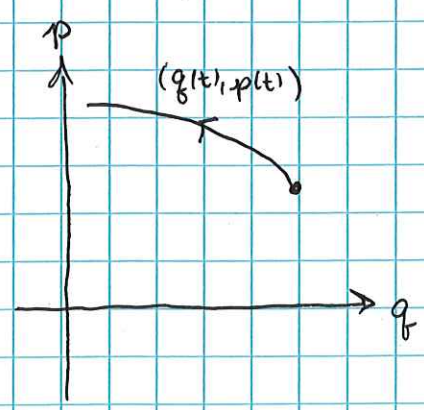
$$\begin{cases} \dot{q}_i = \dfrac{\partial H}{\partial p_i} \\ \dot{p}_i = -\dfrac{\partial H}{\partial q_i} \end{cases} \qquad i = 1, \ldots, s$$

$\rightarrow$ system of $2s$ coupled ODE's.

$H(q, p)$ = "Hamiltonian function".

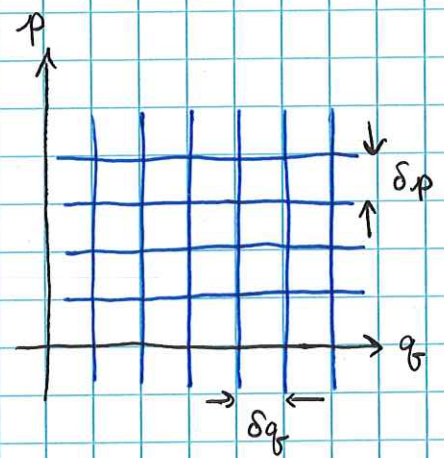
(can usually be expressed as energy of mech. system, written in terms of coord.'s q & momenta p).

- ~~as $q_i(t)$ & $p_i(t)$~~
- time evolution of $q_i(t)$ & $p_i(t)$ according to Hamilton's eqn.'s traces out an orbit in phase space.



($s=1$ DOF)

· In order to ~~[illegible]~~ "count" all possible μ-states, we discretize phase space into cells



(s=1 DOF)

→ $\delta q\,\delta p = h_0$ = small phase space "area"!

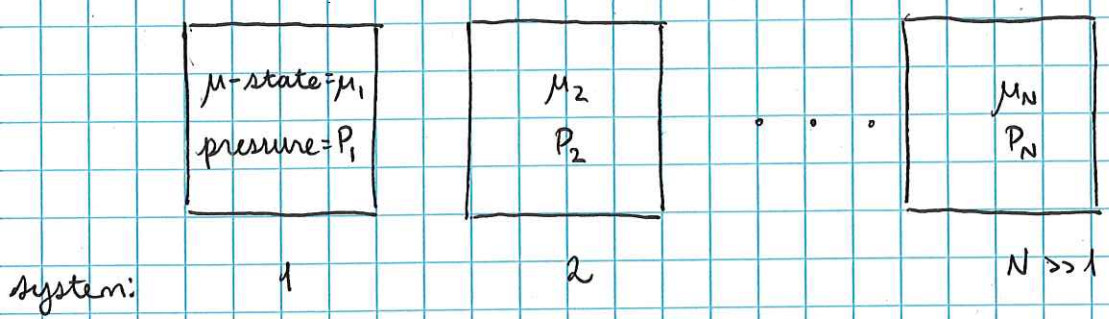
→ μ-state specified by a phase space cell.

· For s>1 DOF, similarly divide phase space into cells w/ "volume" = $\delta q_1 \delta q_2 \ldots \delta q_s\, \delta p_1 \delta p_2 \ldots \delta p_s = h_0^s$. w/ μ-state again specified by a phase space cell.

· Having specified the μ-states in the classical case (the phase space cells), we now turn to the statistical approach of analyzing a many DOF system.

· Recall our motivation: If we could specify all 2s initial conditions (say, for $N \sim 10^{23}$ particles) & time evolve Hamilton's eqn.'s, the state would be deterministic. However, this approach is neither practical nor useful. Instead, we seek statistical info. regarding macro. state of all particles

· To apply statistical/probabilistic concepts, we consider <u>not</u> a single isolated system, but rather an "ensemble" of a very large # of identical systems. In general, system in the ensemble will be in different μ-states.



→ since each system is in a different μ-state, each system will be characterized by a different macro. parameters.

<u>Ex</u>: pressure of system $1 = P_1$, pressure of system $2 = P_2$, etc...

→ <u>Q</u>: what is distb.'n of macro. parameter (e.g., pressure)?

· Before addressing this question, note that we can often place general constraints on allowed μ-states. For example, the total energy E, volume V, & # of particles N may be fixed, so that only those μ-states compatible w/ those fixed values are "accessible" states".

· To answer question above, we need to know prob. $p(\mu_i)$ to find system in μ-state μ_i.

→ to make progress, we will assume the system is in "equilibrium".

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- Equilibrium here means the prob. $p(\mu_i)$ is independent of time. This implies all macro. param.'s also time-indep.

→ <u>Fundamental postulate</u>: An isolated system in equilibrium is equally likely to be in any of its accessible states.

(In classical case: all accessible phase space cells are equally likely).

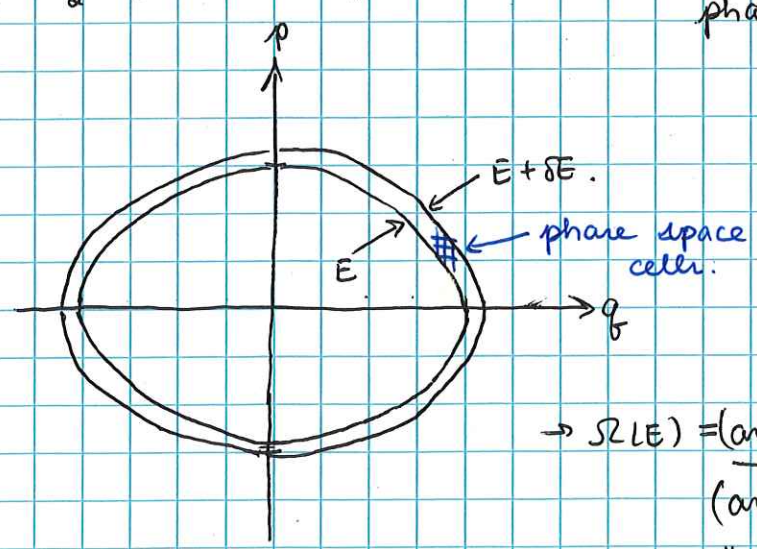
- Formulate mathematically as follows: Consider an isolated system w/ volume V, ~~coas~~ consisting of N particles, w/ fixed energy known to lie in some range $(E, E+\delta E)$.

Let $\Omega(E)$ = total # of μ-states in this range. Then ~~per~~ prob. $p(\mu_i)$ of ~~a~~ a μ-state μ_i ~~is~~ is:

$$p(\mu_i) = \begin{cases} \frac{1}{\Omega(E)}, & \mu_i = \text{accessible} \\ 0 & \text{else.} \end{cases}$$

<u>Ex</u>: (1D harmonic oscillator).

$H(q,p) = \frac{p^2}{2m} + \frac{1}{2}kq^2$; $H(q,p) = E = \text{const.}$ defines an ellipse in phase space.



$$\rightarrow \Omega(E) = \frac{(\text{area of annular region btwn } E+\delta E \text{ \& } E)}{(\text{area of phase space cell})}$$

= # of accessible states.

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· Using the fundamental postulate, we may now calculate probabilities & averages of interest

→ Suppose we want to know prob. of system having some value of macro. param. $y = y_k$ (e.g., that the pressure P has some particular value P_k).

· Let $\Omega(E; y_k)$ = # of accessible states for which y assumes the value y_k (there will in general be a subset of all accessible states).

$$\Rightarrow \text{prob } y = y_k = p(y_k) = \frac{\Omega(E; y_k)}{\Omega(E)}.$$

To find mean value of the parameter y:

$$\bar{y} = \sum_k p(y_k)\, y_k = \sum_k \frac{\Omega(E; y_k)}{\Omega(E)}\, y_k$$

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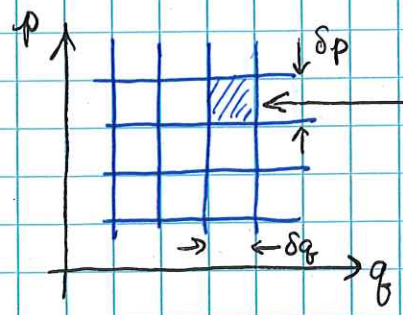
Summary.

· Stat. description of systems of particles (classical)



μ-state ↔ phase space cell.

· Fundamental postulate: Isolated, equil. system equally like to be in any of its accessible states.

= μ-state compatible w/ given constraints (e.g. energy ∈ (E, E+δE)).

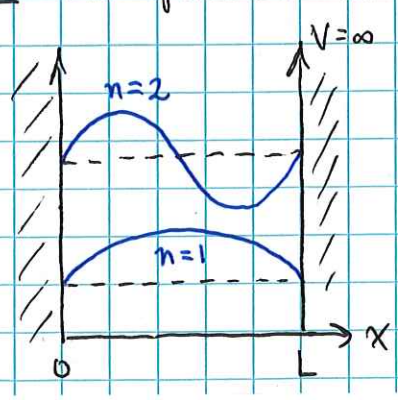
· $\Omega(E)$ = # of accessible states. ⇒ $p(\mu\text{-state}) = \frac{1}{\Omega(E)}$.

· In QM, main difference from classical approach is in identification of μ-states.

· In QM, state of a system is described by a wave fn. Ψ.

Such a quantum state may be specified by a set of "quantum numbers".

Ex: (1D particle in a box).



· Schrödinger eqn: $-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi = E\psi$, $\psi(x=0)=\psi(x=L)=0$.

$$\left.\begin{aligned} &\rightarrow \psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right) \\ &E_n = \frac{\hbar^2\pi^2 n^2}{2mL^2} \end{aligned}\right\} n = 1, 2, 3, \ldots$$

n = "quantum #" specifying the state.

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Ex: (1D harmonic oscillator).

Sch. eqn.: $\left(\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}kx^2\right)\psi = E\psi$

$\rightarrow$ allowed energies $E_n = (n+\frac{1}{2})\hbar\omega$, $n = 0, 1, 2, \ldots$

$\omega = \sqrt{k/m}$.

n = quantum #.

For a system of N decoupled oscillators, quant. state specified by N quantum #'s: $\{n_1, n_2, \ldots, n_N\}$ w/ $n_i = 0, 1, 2, \ldots$

Ex: (spin-$\frac{1}{2}$).

Consider spin-$\frac{1}{2}$ particle, fixed in space ($\Rightarrow$ no translational DOF).

$\rightarrow$ quant. state specified by projection m of spin along some axis (say $\hat{z}$).

m = quantum # & can take values $= \pm\frac{1}{2}$.

For N spin-$\frac{1}{2}$ particles ~~fixed~~ fixed in space, quant. state specified by N quant. #'s $\{m_1, m_2, \ldots, m_N\}$, $m_i = \pm 1/2$.

In QM, the fundamental postulate is unchanged:

If $\Omega(E)$ = # of quant. states w/ energy E (or # of states w/ energy in the range $(E, E+\delta E)$), then prob. that system is in any particular μ-state $= \frac{1}{\Omega(E)}$.

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Ex: Consider three spin-$\frac{1}{2}$ particles in equil., in an external magnetic field H ($\neq$ Hamiltonian!). The energy of each spin $= \begin{cases} -\mu H & \text{if } m = +1/2 \\ +\mu H & \text{if } m = -1/2. \end{cases}$

$\rightarrow$ μ-states specified by $\{m_1, m_2, m_3\}$ & there are $2^3 = 8$ such states.

Now suppose the total energy is known to $= -\mu H$.

$\Rightarrow$ the <u>accessible</u> states are $\underbrace{\{+\tfrac{1}{2}, +\tfrac{1}{2}, -\tfrac{1}{2}\}, \{+\tfrac{1}{2}, -\tfrac{1}{2}, +\tfrac{1}{2}\}, \{-\tfrac{1}{2}, +\tfrac{1}{2}, +\tfrac{1}{2}\}}_{\text{3 accessible states}}$

$\Rightarrow \Omega(E) = 3.$

Q: what is prob. that first spin has $m_1 = +\frac{1}{2}$?

$$\left.\begin{array}{l} \Omega(E; m_1 = +\tfrac{1}{2}) = 2 \\ \Omega(E) = 3 \end{array}\right\} \Rightarrow p(m_1 = +\tfrac{1}{2}) = \frac{2}{3}$$

Note $p(m_1 = -\frac{1}{2}) = \frac{1}{3}$.

what is mean value of the moment $\overline{\mu_z}$ of this spin?

$$\overline{\mu_z} = \frac{2}{3} \times (+\mu) + \frac{1}{3} \times (-\mu) = \frac{1}{3}\mu.$$

• ~~We now investigate~~

<u>Density of States</u>.

• The # of accessible states $\Omega(E)$ plays a central role in stat. phys. We now examine its behavior when the # of DOF becomes large

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- $\Omega(E)$ = # of accessible states w/ energy $\in (E, E+\delta E)$.

$\Rightarrow$ $\Omega(E)$ depends on the energy "width" δE.

$\rightarrow$ useful to write $\Omega(E) = \omega(E)\,\delta E$

$\omega(E)$ = "density of states" (DOS)

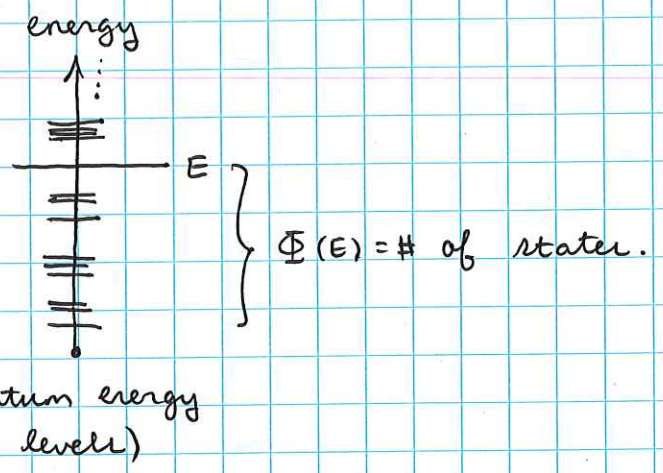
= # of states per unit energy

$\rightarrow$ $\omega(E)$ is indep. of δE.

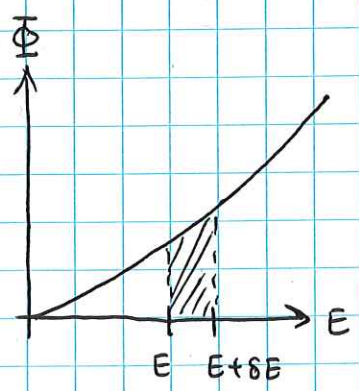
Another way to think about $\omega(E)$:

Let $\Phi(E)$ = # of states w/ energy $\leq E$.

Ex:



(when # of particles is large, energy levels are very dense & we ~~is~~ treat $\Phi(E)$ as a smooth fn. of E.)



$$\Omega(E) = \Phi(E+\delta E) - \Phi(E) \quad \text{δE = small}$$

$$\simeq \frac{\partial \Phi}{\partial E}\,\delta E$$

$$\Rightarrow \quad \omega(E) = \frac{\partial \Phi}{\partial E}$$

Q: How does $\Omega(E)$ (& $\omega(E)$) depend on E & # of particles N in a macro. system.

Ex: (Classical monatomic ideal gas).

"monatomic" $\Rightarrow$ particles have no internal DOF.

"ideal gas" $\Rightarrow$ neglect interaction btwn. atoms.

- Consider monatomic gas enclosed in vol. V. The Hamiltonian is:

$$H(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N, \vec{p}_1, \vec{p}_2, \ldots, \vec{p}_N) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}, \quad i = \text{particle label.}$$

$$(q \to \vec{x}_i)$$

& energy of system $(E, E+\delta E)$.

$$\Rightarrow \quad E \leq \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} \leq E + \delta E. \qquad (*)$$

$\rightarrow$ $\Omega(E) \propto$ vol. of phase space contained btwn. energies $(E, E+\delta E)$

$$\propto \int d^3\vec{x}_1\, d^3\vec{x}_2 \ldots d^3\vec{x}_N\, d^3\vec{p}_1\, d^3\vec{p}_2 \ldots d^3\vec{p}_N \qquad (d^3\vec{x}_i = dx_i\, dy_i\, dz_i)$$

$$E \leq \sum_i \frac{\vec{p}_i^{\,2}}{2m} \leq E + \delta E \leftarrow \text{integration region}$$

- To evaluate the integral note that the inequality $(*)$ defining the phase space region is indep of coord.'s $\vec{x}_i$

$$\Rightarrow \quad \int d^3\vec{x}_i = V = \text{vol.}$$

$$\Rightarrow \quad \Omega(E) \propto V^N \underbrace{\int_{E \leq \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} \leq E + \delta E.} d^3\vec{p}_1\, d^3\vec{p}_2 \ldots d^3\vec{p}_N}$$

int. over region btwn. 3N-dim spheres $\sum_i \frac{\vec{p}_i^{\,2}}{2m} = E + \delta E$ & $\sum_i \frac{\vec{p}_i^{\,2}}{2m} = E$.

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$$\Rightarrow \int_{E \le \sum_i \frac{\vec{p}_i^{\,2}}{2m} < E+\delta E} d^3\vec{p}_1\, d^3\vec{p}_2 \cdots d^3\vec{p}_N \propto \left[2m(E+\delta E)\right]^{\frac{3N}{2}} - \left[2mE\right]^{\frac{3N}{2}}$$

$\hookrightarrow$ δE = small

$$\propto E^{\frac{3N}{2}-1}\,\delta E.$$

when $N \gg 1$, we then have:

$$\begin{cases} \Omega(E) \propto V^N E^{\frac{3N}{2}} \delta E \\ \omega(E) \propto V^N E^{\frac{3N}{2}} \end{cases}$$

$\rightarrow$ when $N \gg 1$ ($\sim 10^{23}$) $\Omega(E)$ ($\&$ $\omega(E)$) are extremely rapidly increasing fn.'s of energy E $\&$ are exponentially increasing fn.'s of # of particles N.

- This representative of the general situation.

In general: $\omega(E) \sim E^{aN}$, where a = # of order 1.

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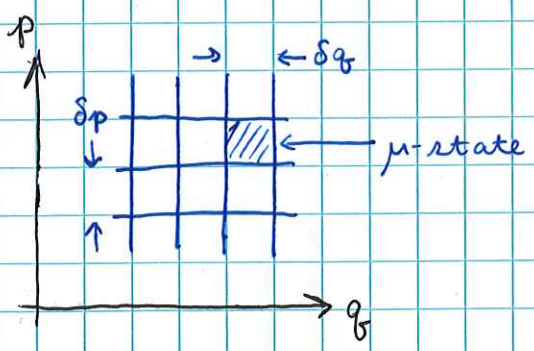
Summary.

- Stat. description of system of particles



(classical)

quant. μ-state $\psi_{n_1 n_2 \ldots n_f}$

specified by f quantum #'s

$\{n_1, n_2, \ldots, n_f\}$

(quantum).

- $\Omega(E)$ = # of accessible states $\sim E^{aN}$, N = # of particles, $a \sim 1$.
- Fundamental postulate: $\text{prob}(\mu\text{-state}) = \dfrac{1}{\Omega(E)}$.

Interaction btwn. macro. bodies.

- Consider macro. system in which Hamiltonian depends on external parameters $x_1, x_2, \ldots, x_n$: $H \doteq H(q, p; x_1, \ldots, x_n)$

(CM or QM).

Ex: $x = V$ = vol. or x = externally applied field ($\vec{E}, \vec{B}$, etc...)

$\Rightarrow$ $E = E(x_1, x_2, \ldots, x_n)$ (CM or QM)

→ energy = fn. of ext. param.'s.

→ "macrostate" of system is defined by specifying the values of all ext. param.'s + any other conditions specified on the system.

Ex: fixed vol. of system = V & tot. energy = E.

→ All member of stat. ensemble are prepared in accordance w/ specification of the macrostate. 01/31/25

Ex: all member have same vol. V & tot. energy E.

· For a given macrostate, system can be in any one of the very large # of accessible μ-states.

→ Data to specify macrostate << Data to specify μ-state.

· Now consider two macro. system A & B that can interact w/ each other, so that they can exchange energy (the total energy being conserved).

· Distinguish btwn. two types of interaction: "thermal" / "mechanical"

1) Thermal interaction: external param.'s fixed, so that energy levels do not change (use CM description here, but can also be done in classical case).

→ energy transfered from one system to the other.

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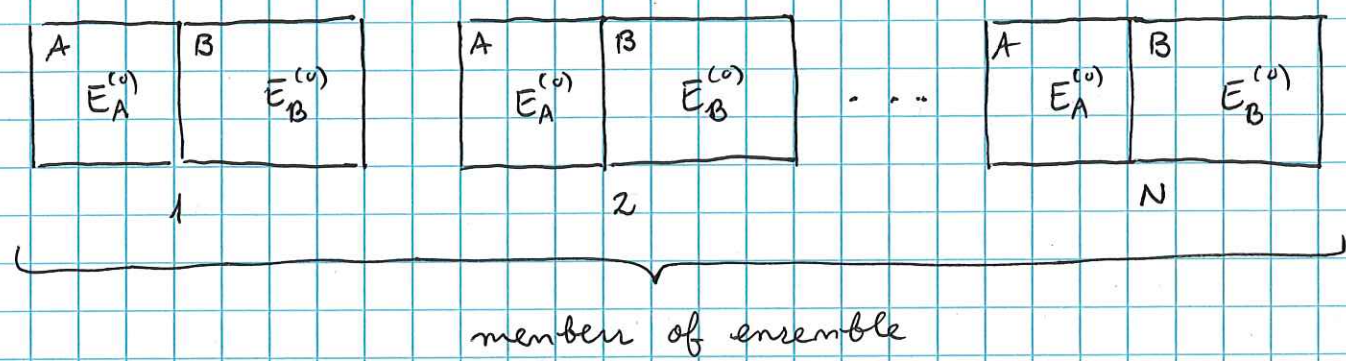
· In the stat. ensemble:

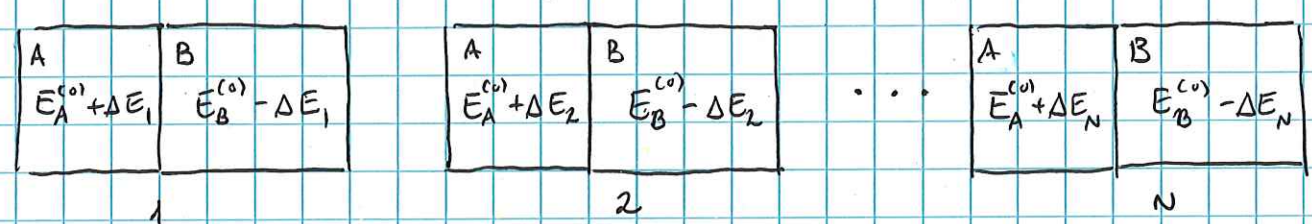
- when thermal int. is "turned off"



→ initially A has energy $E_A^{(0)}$ & B has energy $E_B^{(0)}$

w/ tot energy $= E_A^{(0)} + E_B^{(0)} = E = \text{const.}$

- with thermal int., after system has come to equil:



ΔE_i = energy transferred btwn. A & B for member "i" of ensemble

($\Delta E_i > 0$ or < 0)

⇒ distb.'n of ΔE_i & we consider the mean $\overline{\Delta E}$.

→ $Q \equiv \overline{\Delta E}$ = "heat" absorbed ($\overline{\Delta E} > 0$) or given off ($\overline{\Delta E} < 0$)

by system A. (heat absorbed by A = heat given off by B

& vice-versa).

[Later we'll see distb.'n of ΔE_i is very sharply peaked about the mean $\overline{\Delta E}$, so that stat. fluctuations will be entirely negligible. Same will be true for most macro. prop.'s]

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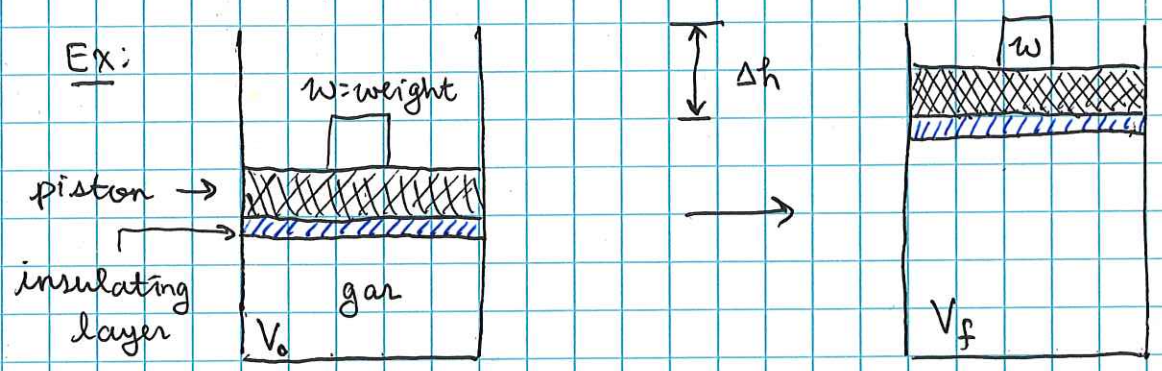
2) Mechanical interaction: Consider "thermally isolated" system ($\Rightarrow$ no thermal int. w/ other system). Two thermally isolated system may still interact through changes in their ext. param.'s $\rightarrow$ "mechanical interaction".

In this case, system exchange energy through "macroscopic work".

Ex:



initially compressed gas

gas expands, raising weight by amount Δh.

- system A = gas, system B = weight + piston.
  - $\rightarrow$ gas (A) does work raising weight + piston (B).
  - $\rightarrow$ change in ext param.'s $\leftrightarrow$ change in vol. ($V_0 \rightarrow V_f$) & change in height (Δh)
- In this situation, the work done by the gas (neglecting weight of piston) is simply $= w \times \Delta h$.

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· In the language of the stat. ensemble:

As param. x_α is varied, energy of ~~member~~ system in the ensemble changes by an amount $= \Delta_{x_\alpha} E_i$

member "i" of ensemble

Change due to variation of param. x_α

→ Consider again mean change $\Delta_{x_\alpha} \overline{E}$

· The quantity $\Delta_{x_\alpha} \overline{E}$ is the "macro. work" done <u>on</u> the system.

· We will more often use the quantity $W \equiv -\Delta_{x_\alpha} \overline{E}$ = macro. work done <u>by</u> the system.

<u>Ex</u>: In previous ex. of gas & weight + piston, $W = w \times \Delta h$.

work done by gas.

· In general, int. btwn. system ~~can~~ involves <u>both</u> a change in their ext. param.'s (mech. int.) & the system are not thermally isolated (thermal int.)

· As a result of such an int., mean energy of system will be changed by an amount $\Delta \overline{E}$. If $\Delta_x \overline{E}$ = increase of mean energy from macro. work, then we write:

$$\Delta \overline{E} \equiv \Delta_x \overline{E} + Q$$

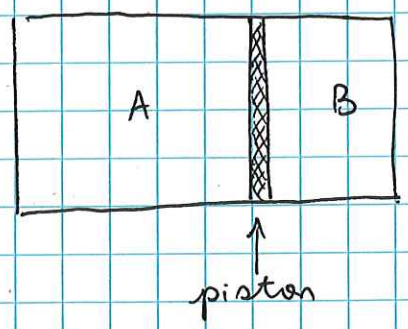
for the tot. change in energy. This relation <u>defines</u> the heat Q; i.e.,

$$Q \equiv \Delta \overline{E} - \Delta_x \overline{E} = \Delta \overline{E} + W$$

The heat Q measures mean energy change ~~does~~ not due 09/31/25

change in ext. param.'s (i.e., due to macro. work).

Ex:



· If piston is not insulating & is free to move, both mech. & thermal int. occur btwn. A & B.

· when the work done by the system is small (infinitesimal), w/ a correspondingly small change in mean energy $d\bar{E}$, we write:

$$\boxed{đQ \equiv d\bar{E} + đW}$$

$$\begin{cases} đW = \text{small work done by system.} \\ đQ = \text{small amount of heat absorbed by system.} \end{cases}$$

→ symbol ~~system~~ "đ" denotes an "inexact" differential. Unlike usual "d", "đ" does not indicate small change in the value of a function.

while $d\bar{E}$ = small difference btwn. values of mean energy $\bar{E}$, there is no meaning to "small difference btwn. works/heats"

Moreover, while a mean energy $\bar{E}$ of system is a well-defined quantity, there is no meaning to the "quantity of heat/work" of the system in a given state.

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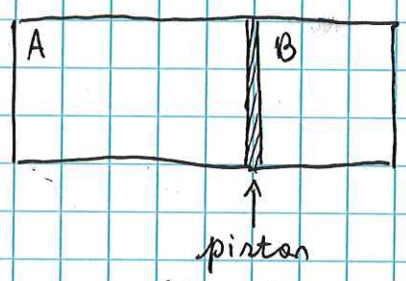
Summary

- macrostate of a system specified by

$$\begin{cases} (x_1, x_2, \ldots, x_n) = \text{fixed param.'s} \\ + \text{ addn'l conditions on system} \end{cases}$$

→ Ex: $x = V$ = vol. & energy E = const. is specified (closed system).

- interaction btwn. macro. systems



interaction = thermal (heat exchange Q)

+ mechanical (work W).

(really ensemble of such systems)

→ interaction ⇒ change in mean energy $\bar{E}$ of A (say)

→ decompose $đQ = dE + đW$;

$$\begin{cases} d\bar{E} = \text{small change in } \bar{E} \\ đQ = \text{small/infinitesimal heat absorbed} \\ đW = \text{" " work done by A.} \end{cases}$$

Exact vs inexact differentials (math)

→ Explain difference btwn. "d" & "đ".

- Consider a fn. $F(x,y)$ of two var's x & y. Small change

$x \to x + dx$, $y \to y + dy$: $F(x,y) \to F(x+dx, y+dy)$

& $dF = F(x+dx, y+dy) - F(x,y)$

$= A(x,y)\,dx + B(x,y)\,dy$ w/ $A = \frac{\partial F}{\partial x}$ & $B = \frac{\partial F}{\partial y}$.

"exact differential."

• In going from initial pt. (x_i, y_i) to final pt. (x_f, y_f), 02/03/25

the net change in F is:

$$\Delta F = F(x_f, y_f) - F(x_i, y_i)$$
$$= \int_i^f dF$$
$$= \underbrace{\int_i^f (A\,dx + B\,dy)}.$$

$\Rightarrow$ integral is <u>independent</u> of path in (xy)-plane btwn. (x_i, y_i) & (x_f, y_f).

• we may also consider infinitesimal quantities:

$$\tilde{A}(x,y)\,dx + \tilde{B}(x,y)\,dy \neq \text{differential of any fn.}$$

that is, there is <u>no</u> fn. G s.t.

$$G(x+dx, y+dy) - G(x,y) = \tilde{A}(x,y)\,dx + \tilde{B}(x,y)\,dy \quad \times$$

Thus we write such infinitesimals as $đG = \tilde{A}\,dx + \tilde{B}\,dy$.

In contrast to an exact differential, the integral

$$\int_i^f đG = \int_i^f (\tilde{A}\,dx + \tilde{B}\,dy)$$

<u>is</u> dependent on path in (xy)-plane btwn. initial & final pt.'s.

• Return to physics: $đQ = d\bar{E} + đW$

$\rightarrow$ $d\bar{E}$ = difference btwn. mean ~~energy~~ energies $\rightarrow$ exact differential.

$\Rightarrow$ if system from initial macrostate i to final macrostate f:

$$\Delta\bar{E} = \bar{E}_f - \bar{E}_i = \int_i^f d\bar{E}$$ = indep. of path (or process) to go from $i \rightarrow f$.

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· ch contrast, $W_{if} = \int_i^f đW$ & $Q_{if} = \int_i^f đQ$ do, in general, depend on the process.

· Special cases: thermally isolated system ($Q=0$)

$\Rightarrow đW = -d\bar{E}$ & $W_{if} = -\Delta\bar{E}$ depends only on energy difference & is path (process) independent

& if ext. param/s held fixed ($W=0$)

$\Rightarrow đQ = d\bar{E}$ & Q_{if} = indep. of process.

<u>Quasi-static processes</u>.

· quasi-static process = system A interacts w/ system B (heat exch + work) sufficiently <u>slowly</u> s.t. A remains in equil. throughout the process.

[How slowly depends on μ-scopic "relaxation time" τ = time for system to attain equil. if perturbed (come back to this)]

· For concreteness, consider CM (same works in QM). & let

x = ext. param (not coord!) (e.g.; x = vol. V).

→ Hamiltonian $H = H(q, p; x)$, $q = (q_1, q_2, \ldots q_s)$, $p = (p_1, p_2, \ldots, p_s)$

when x changes in time, $x \to x(t)$ (e.g., slow change in vol. of system)

we have:

$$\frac{d}{dt} H(q,p;x) = \frac{\partial H}{\partial q}\dot{q} + \frac{\partial H}{\partial p}\dot{p} + \frac{\partial H}{\partial x}\dot{x} \quad \& \quad \dot{q} = \frac{\partial H}{\partial p}, \quad \dot{p} = -\frac{\partial H}{\partial q}$$

$$= \cancel{\frac{\partial H}{\partial q}\frac{\partial H}{\partial p}} - \cancel{\frac{\partial H}{\partial p}\frac{\partial H}{\partial q}} + \frac{\partial H}{\partial x}\dot{x} \qquad \text{(Hamilton's eqn.'s)}$$

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$$\Rightarrow \frac{dH}{dt} = \frac{\partial H}{\partial x}\frac{dx}{dt}.$$

→ identifying H w/ the tot. energy, $E = H(q, p; x)$, we write:

$$\frac{dE}{dt} = \frac{\partial H}{\partial x}\frac{dx}{dt}.$$

⇒ in small time dt, change in energy (due to t-variation of x) is:

$$dE = \frac{\partial H}{\partial x}\frac{dx}{dt}\,dt. \quad (*).$$

• in a quasi-static process, at each time t the system is in equil.

⇒ average $(*)$ over equil. ensemble w/ value of x at time t

& identify left-hand side w/ macro. work $đW$ done by system:

$$đW = -\overline{\frac{\partial H}{\partial x}}\frac{dx}{dt}\,dt$$

no avg. since x is just a given fn. of t.

or $đW = \mathcal{X}\,dx$, $\mathcal{X} \equiv \overline{-\frac{\partial H}{\partial x}}$ = "generalized force"

(c.f. mechanics $W = F\Delta x$)

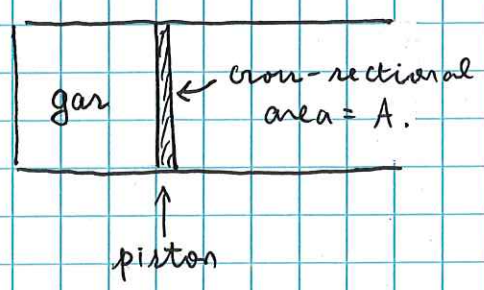
• w/ multiple ext. param.'s $(x_1, x_2, \ldots, x_n)$:

$$đW = \sum_{\alpha=1}^{n} \mathcal{X}_\alpha\,dx_\alpha, \quad \mathcal{X}_\alpha = \overline{-\frac{\partial H}{\partial x_\alpha}}$$ = generalized force conjugate to x_α.

---

important example: ext. param. $x = V$ (volume).

Ex:



$F = pA$ = force on piston, p = pressure

→ displacement of piston by amount ds:

⇒ work done by gas $= F \times ds = pA\,ds = p\,dV$.

w/ $dV = A\,ds$ = change in vol.

02/03/25

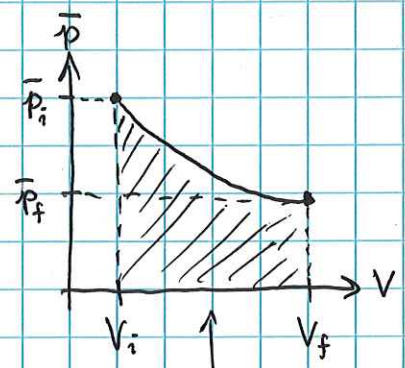
· If change in vol. dV is <u>quasi-static</u>, then throughout the process system is in equil. (at each vol. V) & we can compute <u>mean</u> work $đW = \bar{p}\, dV$.

→ $\bar{p}$ = mean pressure at particular value of vol. V., $\bar{p} = \bar{p}(V)$.

⇒ when system vol. changes from $V_i \to V_f$ quasi-statically, we have:

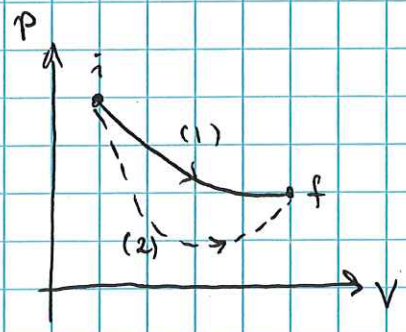
$$W_{if} = \int_{V_i}^{V_f} đW = \int_{V_i}^{V_f} dV\ \bar{p}(V).$$

· Since $\bar{p} = \bar{p}(V)$, we can graph:



W_{if} = area under curve.

· Since $đW$ = ~~isoexact~~ $\bar{p}\, dV$ = inexact differential, the work will, in general, depend on the process:



$W_{if}^{(1)} \neq W_{if}^{(2)}$

(Note that area under curves (1) & (2) are different).

02/03/25

Approach to equilibrium.

- Return briefly to notion of "equilibrium".

→ Recall: For a given macrostate (determined, e.g., by fixed vol. V & conserved tot energy E), there are very many accessible μ-states ($\# = \Omega(E)$).

→ equilibrium: prob. to find system in any μ-state, $p(\mu)$, is t-independent (⇒ macro. param.'s t-indep.).

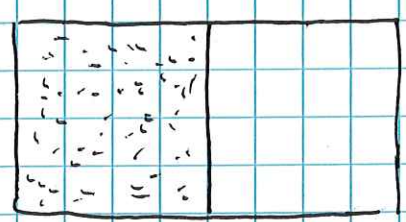
→ postulate: isolated system in equil. equally likely to be in any accessible μ-state.

Q: what if isolated system not equally likely to be in any μ-state?

→ by postulate above, cannot be equil. situation

⇒ system evolves in t.

Ex: gas confined to $\frac{1}{2}$ of box:



→ immediately after partition is removed, system not equally likely to be in any accessible state, since $\frac{1}{2}$ of container is empty.

→ experience tells us this situation will not last for long. System will evolve w/ t & after a relatively short time density of particles will be uniform over the box.

02/03/25

- In general, if at some time t system is only in subset of accessible states, we anticipate t-evolution toward distb.'n in which <u>all</u> accessible μ-states are equally likely.
- Similarly, if we perturb ~~any~~ an equil. system & drive it out of equil, we expect system will eventually return to equil once perturbation has been "turned off".

→ time scale associated w/ attainment of equil. is the "relaxation time" τ.

↑ value of τ varies significantly btwn. different systems.

(A proof of the above statements regarding approach to equil. are contained in Boltzmann's ~~other~~ H-theorem — see Reif App. A.12).

02/05/25

Statistical thermodynamics.

→ connect stat. mech. w/ general prop.'s of macro systems.

introduce important (purely statistical) notions of entropy & temperature.

Recall: isolated system w/ energy $\in (E, E+\delta E)$.

& $\Omega(E)$ = # of accessible μ-states.

→ postulate: in equil., prob. (μ-state) $= \dfrac{1}{\Omega(E)}$.

↑ prob. distb'n of μ-states is t-indep.

Thermal interaction btwn. macro systems:

1	2
E_1	E_2
$\Omega_1(E_1)$	$\Omega_2(E_2)$

· systems 1 & 2 can exchange energy through heat transfer (no work, for now).

→ Combined sys. 1 + 2 is isolated ⇒ tot. energy $\underbrace{E = E_1 + E_2}$ = const.

assume int. btwn. 1 & 2 weak enough that energy is additive.

· now, E = fixed, but E_1 & E_2 will vary. In stat. ensemble, there will be a distb.'n of E_1 & E_2 (s.t. $E_2 = E - E_1$).

⇒ # of accessible states of combined system is:

$$\Omega(E) = \sum_{E_1} \Omega_1(E_1)\,\Omega_2(E-E_1).$$

↑ sum over all possible energies of system 1.

02/05/25

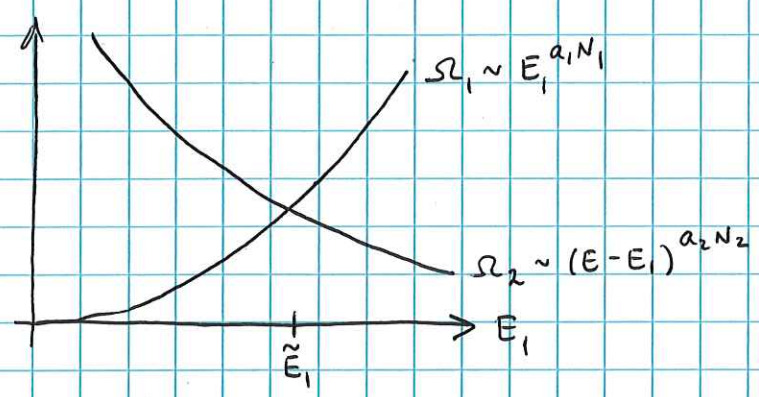
& prob. that sys. 1 has energy $= E_1$ is:

$$P_1(E_1) = \frac{\Omega_1(E_1) \times \Omega_2(E-E_1)}{\Omega(E)}$$

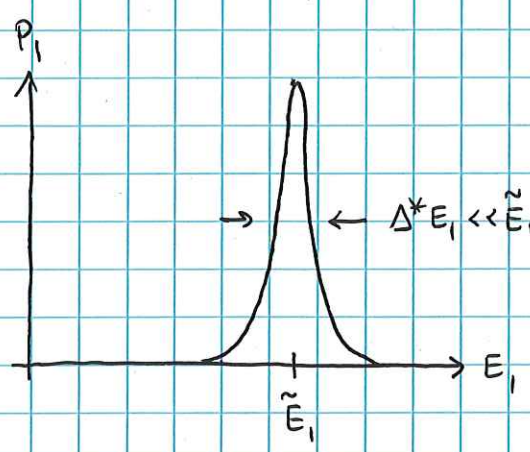
· now investigate how $P_1(E_1)$ behaves in a macro. system.

→ recall $\Omega(E) \sim E^{aN}$, $N = \#$ of particles & $a \sim 1$ (e.g. $a = \frac{3}{2}$, ideal gas)

schematically:



⇒



· prob. narrowly peaked near $E_1 = \tilde{E}_1$, s.t "width" $\Delta^* E_1 \ll \tilde{E}_1$ (come back to this).

→ look for most probable value $E_1 = \tilde{E}_1$, i.e., max. of $P_1(E_1)$:

$$\frac{\partial}{\partial E_1} P_1(E_1) = \frac{1}{\Omega(E)}\left[\left(\frac{\partial \Omega_1}{\partial E_1}\right)\Omega_2 - \Omega_1\left(\frac{\partial \Omega_2}{\partial E_2}\right)\right] = 0.$$

$$\Rightarrow \frac{1}{\Omega_1}\left(\frac{\partial \Omega_1}{\partial E_1}\right) = \frac{1}{\Omega_2}\left(\frac{\partial \Omega_2}{\partial E_2}\right)$$

$$\text{or} \quad \frac{\partial}{\partial E_1} \ln \Omega_1 \Big|_{E_1 = \tilde{E}_1} = \frac{\partial}{\partial E_2} \ln \Omega_2 \Big|_{E_2 = E - \tilde{E}_1} \qquad (*).$$

→ determines $\tilde{E}_1$, where $P_1 = \max.$

02/05/25

We define the "entropy" $\boxed{S \equiv \ln \Omega}$, so that (*) is:

$$\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2} \rightarrow \text{eqn. determining value } \tilde{E}_1$$

where $P_1(E_1)$ is max.

& note that condition of max. prob. can be written:

$$\underbrace{S_1 + S_2}_{\text{"total entropy"}} = \max \qquad \left(\text{since } \ln P_1 = S_1 + S_2 - \underbrace{\ln \Omega}_{= \text{const.}}\right)$$

$\Rightarrow$ Condition of max prob. = condition of max. total entropy.

- The quantity $\frac{\partial S}{\partial E}$ is a prop. of separate subsystems 1 & 2

& we define: $\boxed{\frac{1}{T} \equiv \frac{\partial S}{\partial E}}$ $\qquad [T] = \text{energy}$

$T =$ "temperature" (or "absolute temp.").

so $\frac{\partial S_1}{\partial E_1} = \frac{\partial S_2}{\partial E_2} \Rightarrow T_1 = T_2$.

Q: How do we identify $T = 1/(\partial S/\partial E)$ w/ the familiar notion of temp?

$\rightarrow$ come back to this. For now, we'll show that quantity T behaves qualitatively as you'd expect for the temperature. To see this, we'll consider how system 1 & 2 approach equil.

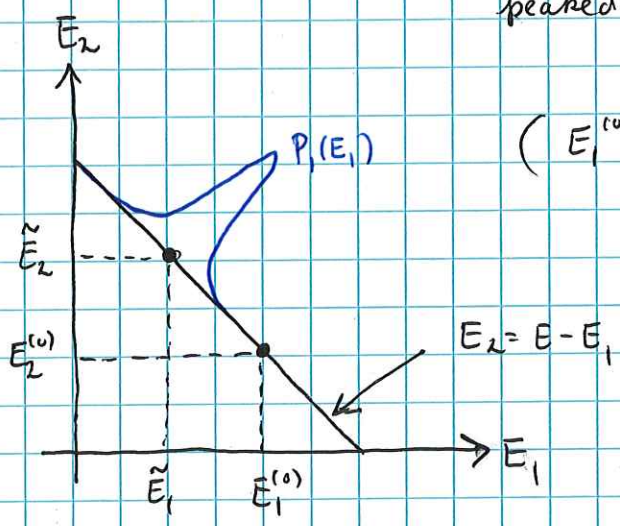
- Consider initial situation where 1 & 2 are thermally isolated (no heat transfer) w/ respective energies $E_1^{(0)}$ & $E_2^{(0)}$, as well as resp. temp.'s $T_1^{(0)}$ & $T_2^{(0)}$.
- now suppose insulating barrier removed, so that energy can be exchanged btwn. 1 & 2 (heat transfer).

→ we expect the mean values of the energies to then evolve in t toward the most probable state:

$$\begin{cases} \overline{E_1^{(0)}} = E_1^{(0)} \longrightarrow \overline{E}_1 = \tilde{E}_1 = \text{most prob. energy.} \\ \overline{E_2^{(0)}} = E_2^{(0)} \longrightarrow \overline{E}_2 = \tilde{E}_2 = E - \tilde{E}_1 \end{cases}$$

(here we use that $P_1(E_1)$ sharply peaked to set $\overline{E}_{1,2} = \tilde{E}_{1,2}$).

$$\left(E_1^{(0)} + E_2^{(0)} = \tilde{E}_1 + \tilde{E}_2 = E = \text{const.} \right)$$



In terms of entropy $S = \ln \Omega$:

$$\frac{dS}{dt} = \frac{dS_1}{dt} + \frac{dS_2}{dt}$$

$$= \left(\frac{\partial S_1}{\partial E_1}\right)\frac{dE_1}{dt} + \left(\frac{\partial S_2}{\partial E_2}\right)\frac{dE_2}{dt} \quad E_2 = E - E_1$$

$$= \left[\left(\frac{\partial S}{\partial E_1}\right) - \left(\frac{\partial S_2}{\partial E_2}\right)\right]\frac{dE_1}{dt}$$

$$\Rightarrow \quad \frac{dS}{dt} = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\frac{dE_1}{dt} \geq 0$$

S increases until mean energies $\bar{E}_1 = \tilde{E}_1$ & $\bar{E}_2 = \tilde{E}_2$ are attained.

$\Rightarrow$ If $T_2^{(0)} > T_1^{(0)}$, then $\frac{dE_1}{dt} > 0$ (so that $\frac{dS}{dt} > 0$) & $\frac{dE_2}{dt} < 0$.

Thus energy of sys. 1 increases, while that of sys. 2 decreases; i.e. energy passes (heat is transferred) from sys. at higher T to that at lower T.

- Some addn.'l prop.'s of T:
  - since we expect in general $\Omega(E) \sim E^{aN}$, we have $\frac{\partial \ln \Omega}{\partial E} > 0$

    $\Rightarrow T = \frac{1}{\partial \ln \Omega / \partial E} > 0$; i.e. temp. is positive

  - again using $\Omega(E) \sim E^{aN}$; $\ln \Omega \simeq aN \ln E$

$$\Rightarrow \frac{\partial \ln \Omega}{\partial E} \sim \frac{aN}{E}$$

$$\Rightarrow T = \left.\frac{1}{\partial \ln \Omega / \partial E}\right|_{E=\bar{E}} \sim \frac{\bar{E}}{aN}.$$

$\Rightarrow T \sim \bar{E}/N$; i.e., T (roughly) measures mean energy per degree of freedom (or particle).

$\Rightarrow$ for sys. in thermal contact, cond.'n $T_1 = T_2$ is therefore (roughly) the statement that tot. energy shared btwn. systems s.t. mean energy per DOF is the same for both systems.

02/05/25

<u>note on units</u>: We have defined T w/ units of energy & $s = \ln \Omega$ is dimensionless. Often, temp. measured in degrees Kelvin. Conversion factor is Boltzmann's const: $k_B \simeq 1.38 \times 10^{-6}$ erg./deg.

$$\Rightarrow \quad T_{energy} = k_B \times T_{degree}$$

If T measured in deg., factor of k_B also included in def.'n of entropy: $S = k_B \ln \Omega$.

→ We'll measure T in energy units & keep S dimensionless. To convert, make the substitution:

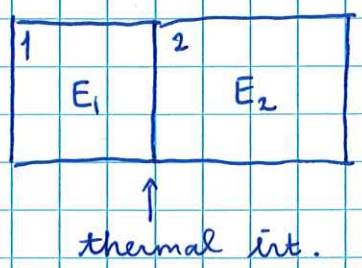
$$T \to k_B T \quad \& \quad S \to S/k_B .$$

02/07/25

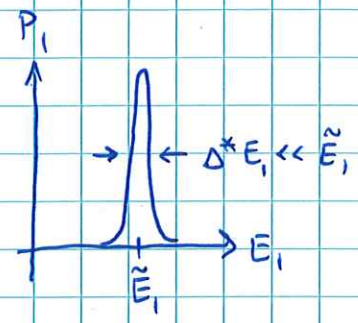
Summary.

- $\Omega(E)$ = # accessible states w/ energy $\in (E, E+\delta E)$.
- "entropy" $S = \ln \Omega$
- "temperature" T : $\frac{1}{T} = \frac{\partial S}{\partial E}$

} fn.'s of macrostate of system.



- $E_1 + E_2 = E = \text{const}$.
- $P_1(E_1)$ sharply peaked at $E_1 = \tilde{E}_1$



- $P_1 = \max \Rightarrow S_1 + S_2 = \max$.

$\Rightarrow T_1 = T_2$. → most probable state has temp.'s of sys. 1 & 2 equal.

- If, initially, $E_1 = E_1^{(0)} \neq \tilde{E}_1$ & $E_2 = E_2^{(0)} \neq \tilde{E}_2$:

$$\Delta S_1 + \Delta S_2 = \left[S_1(\tilde{E}_1) - S_1(E_1^{(0)})\right] + \left[S_2(\tilde{E}_2) - S_2(E_2^{(0)})\right] \geq 0.$$

- Tying up loose ends:
- Dependence of entropy S on energy range δE:

write $\Omega(E) = \omega(E)\,\delta E$, $\omega(E)$ = DOS, indep. of range δE.

$\Rightarrow S = \ln \Omega = \ln(\omega\,\delta E)$ (entropy depends on δE).

If we choose a different subdivision $\delta E'$:

$$S' = \ln(\omega\,\delta E') \Rightarrow S - S' = \ln(\delta E/\delta E').$$

Since $\Omega \sim E^{aN}$, we see $S = \ln \Omega \sim N$; i.e., S scales w/ # of DOF.

$\Rightarrow \ln(\delta E/\delta E') \ll S, S'$; e.g., even if $\delta E' \sim N\,\delta E \rightarrow \ln(\delta E'/\delta E) \sim \ln N \ll N$

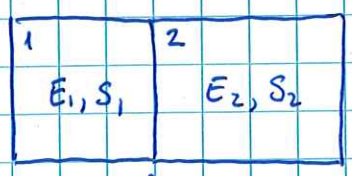
$\Rightarrow S = S'$ for $N \gg 1$

02/07/25

Note that T is indep of δE:

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{\partial}{\partial E}\left[\ln \omega + \ln \delta E\right) = \frac{\partial}{\partial E} \ln \omega(E)$$

· Next, demonstrate <u>additivity</u> prop. of entropy:



(thermal int.)

$E = E_1 + E_2 = \text{const.}$

· For combined sys. 1 + 2:

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

& let $S = \ln \Omega$, $S_1 = \ln \Omega_1$, $S_2 = \ln \Omega_2$.

→ as we have discussed, prob. $P_1(E_1)$ sharply peaked for $E_1 \simeq \tilde{E}_1$

$$\Rightarrow \quad \Omega(E) \simeq \sum_{\substack{(\tilde{E}_1 - \Delta^* E_1) \\ \leq E_1 \leq (\tilde{E}_1 + \Delta^* E_1)}} \Omega_1(E_1)\,\Omega_2(E - E_1)$$

$$\simeq \underbrace{\left[\frac{\Omega_1(\tilde{E}_1)\,\Omega_2(E - \tilde{E}_1)}{\delta E}\right]}_{= \text{DOS at } E_1 = \tilde{E}_1} \times \Delta^* E_1 .$$

$$\Rightarrow \quad S = \ln \Omega = \ln \Omega_1(\tilde{E}_1) + \ln \Omega_2(\tilde{E}_2) + \ln\left(\Delta^* E_1 / \delta E_1\right)$$

$$= \underbrace{S_1 + S_2}_{\sim N = \#\text{ of DOF.}} + \underbrace{\ln\left(\Delta^* E_1 / \delta E_1\right)}_{\text{b/c of } \ln\text{, this term will always be negligible compared to } S_1 + S_2\ (\sim N).}$$

$$\Rightarrow \quad S = S_1 + S_2 \qquad (N \gg 1)$$

i.e., the entropy of int. macro. system = sum of individual entropies.

→ this is similar to the tot. energy $E = E_1 + E_2$.

02/07/25

· Now study sharpness of prob. distb.'n $P_1(E_1) = \dfrac{\Omega_1(E_1)\,\Omega_2(E-E_1)}{\Omega(E)}$.

$\rightarrow \ln P_1 = \ln\Omega_1 + \ln\Omega_2 - \ln\Omega$.

to analyze P_1 near its max. $(\tilde{E}_1)$, write $E_1 = \tilde{E}_1 + \eta$ & expand in η:

$$\Rightarrow \ln\Omega_1(\tilde{E}_1+\eta) = \ln\Omega_1(\tilde{E}_1) + \underbrace{\left(\frac{\partial \ln\Omega_1}{\partial E_1}\right)_{\tilde{E}_1}}_{\frac{1}{T_1}}\eta + \frac{1}{2}\underbrace{\left(\frac{\partial^2 \ln\Omega_1}{\partial E_1^2}\right)}_{\equiv -\lambda_1}\eta^2 + \dots$$

& $$\ln\Omega_2(\underbrace{\tilde{E}_2-\eta}_{=E-\tilde{E}_1}) = \ln\Omega_2(\tilde{E}_2) - \frac{1}{T_2}\eta - \frac{1}{2}\lambda_2\eta^2$$

$$\Rightarrow \ln P_1 \simeq \underbrace{\ln\left[\frac{\Omega_1(\tilde{E}_1)\,\Omega_2(E-\tilde{E}_1)}{\Omega(E)}\right]}_{P_1(\tilde{E}_1)} + \underbrace{\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}_{=0 \text{ when } E_1=\tilde{E}_1 \,\&\, E_2=\tilde{E}_2}\eta - \frac{1}{2}\lambda\eta^2, \quad \lambda \equiv \lambda_1+\lambda_2$$

$$\Rightarrow P_1(E_1) \simeq P_1(\tilde{E}_1)\,e^{-\frac{1}{2}\lambda\eta^2} \quad (\lambda>0, \text{ since } \tilde{E}_1 = \text{max.})$$

or $$P_1(E_1) \simeq P_1(\tilde{E}_1)\,e^{-(E_1-\tilde{E}_1)^2/2(\Delta^* E)^2}$$

$\Delta^* E \equiv \lambda^{-1/2}$ = "width" of distb.'n.

prob. distb.'n = Gaussian $(\Rightarrow \bar{E}_1 = \tilde{E}_1)$.

when $|E_1-\tilde{E}_1| > \Delta^* E$, prob. is negligible.

· To estimate $\Delta^* E$, suppose $\lambda_1 \gg \lambda_2$, so $\Delta^* E \simeq \lambda_1^{-1/2}$ & $\lambda_1 = -\left.\dfrac{\partial^2 \ln\Omega_1}{\partial E_1^2}\right|_{\tilde{E}_1}$

Using our estimate $\Omega(E) \sim E^{aN}$: $\left.\dfrac{\partial^2 \ln\Omega_1}{\partial E_1^2}\right|_{\tilde{E}_1} \sim \dfrac{aN}{\tilde{E}_1^2}$

$$\Rightarrow \Delta^* E \sim \frac{\tilde{E}_1}{\sqrt{N}} \quad \text{or} \quad \frac{\Delta^* E}{\tilde{E}_1} \sim \frac{1}{\sqrt{N}}$$

$\Rightarrow$ relative width goes down $\sim 1/\sqrt{N}$; i.e.,

fluctuations about the max. (= mean) are

utterly negligible when N = macroscopic ($\sim 10^{23}$).

~~→ Thus, even though our μ-scopic description~~

→ This behavior is generic among macro. quantities (energy, pressure, etc...) – that is, they are equal to their most probable (= mean) values.

→ Thus, even though our μ-scopic description is statistical, the stat. fluct. are so insignificant that predictions are essentially <u>deterministic</u>.

Also note: $\lambda = -\frac{\partial}{\partial E}\frac{\partial \ln \Omega}{\partial E} = -\frac{\partial}{\partial E}\frac{1}{T} = \frac{1}{T^2}\frac{\partial T}{\partial E} \geq 0.$

$$\Rightarrow \frac{\partial T}{\partial E} \geq 0.$$

→ i.e., temp. of a sys. is an increasing fn. of its energy.

02/07/25

· Entropy leads to concept of "reversible" & "irreversible" processes.

→ for systems in thermal contact, tot. entropy increases:

if $S_1^{(0)} = \ln \Omega_1(E_1^{(0)})$ & $S_2^{(0)} = \ln \Omega_2(E_2^{(0)})$ initially & if,

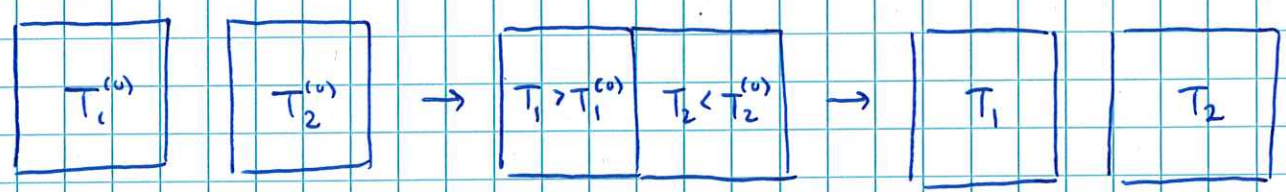
in the final equil. state $S_1 = \ln \Omega_1(\tilde{E}_1)$ & $S_2 = \ln \Omega_2(\tilde{E}_2)$, then:

$$S_1 + S_2 \geq S_1^{(0)} + S_2^{(0)} \quad \text{or} \quad \Delta S_1 + \Delta S_2 \geq 0$$

→ In general, when a constraint on a closed/isolated system is removed (in this case, E-conservation for 1 & 2) entropy can only <u>increase</u>

→ A process is "irreversible" if tot. entropy of isolated system increases $\Delta S > 0$.

<u>Ex:</u>



$S^{(0)} = S_1^{(0)} + S_2^{(0)}$

suppose $T_2^{(0)} > T_1^{(0)}$

$T_1 = T_2$

(thermal int.)

$S_f = S_1 + S_2 > S_1^{(0)} + S_2^{(0)}$

→ A process is "reversible" if tot. entropy of isolated system is const. $\Delta S = 0$ (examples later).

02/10/25

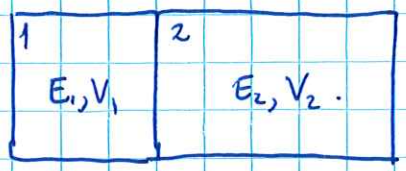
Summary.

- $\Omega(E)$ = # of accessible states w/ energy $\in (E, E+\delta E)$.
- $S = \ln \Omega$ (entropy),
- $\frac{1}{T} = \frac{\partial S}{\partial E}$ (T = temperature).
- Interacting systems 1 & 2: total entropy $S = S_1 + S_2$ (additivity).

  & in equil.: $T_1 = T_2$.
- Irreversible process: tot. entropy of isolated system increases $\Delta S > 0$.

  Reversible process: " " const. $\Delta S = 0$.

General interaction btwn. macro. bodies:



$$\begin{cases} E = E_1 + E_2 = \text{Const.} \\ V = V_1 + V_2 = \text{Const.} \end{cases}$$

- In general, sys. 1 & 2 interact by exchanging heat & doing work on each other.

  (e.g., change vol.)

→ sys. 1: energy E_1 & vol. V_1 $\Rightarrow$ $\Omega_1 = \Omega_1(E_1, V_1)$ & $S_1 = \ln \Omega_1 = S_1(E_1, V_1)$

sys. 2: energy E_2 & vol. V_2 $\Rightarrow$ $\Omega_2 = \Omega_2(E_2, V_2)$ & $S_2 = \ln \Omega_2 = S_2(E_2, V_2)$

[More generally, $V \to (x_1, x_2, \dots, x_n)$ = external param.'s. For simplicity, consider single param. $x = V$, but all results easily generalize]

→ We have seen that, in equil., distb.'n for E_1 is sharply peaked about $E_1 = \tilde{E}_1$ ($= \bar{E}_1$). Similarly, distb.'n of V_1 will be sharply peaked about $V_1 = \tilde{V}_1$ ($= \bar{V}_1$)

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[As we have argued, fluct. of macro. observables about their most probable (= mean) values are entirely negligible in equil. Thus, we will omit averaging symbol when referring to macro. quantities (e.g., $\bar{E} \to E$, $\bar{p} \to p$, etc...)]

- Also, since $S = S(E, V)$, we should make our def.'n of temp. T more precise:

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial E}\right)_V$$

partial derivative taken at fixed vol. V.

[If $V \to (x_1, x_2, \ldots, x_n)$, then $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{x_1 x_2 \ldots x_n}$]

- Just as w/ purely thermal int., equil. state when work is included is also characterized by max. tot. entropy $S = S_1 + S_2$ (most probable state).

$$\to dS = dS_1 + dS_2 \qquad S_1 = S_1(E_1, V_1) \;\&\; S_2 = S_2(E_2, V_2)$$

$$= \left(\frac{\partial S_1}{\partial E_1}\right)_{V_1} dE_1 + \left(\frac{\partial S_1}{\partial V_1}\right)_{E_1} dV_1 + \left(\frac{\partial S_2}{\partial E_2}\right)_{V_2} dE_2 + \left(\frac{\partial S_2}{\partial V_2}\right)_{E_2} dV_2 \qquad dE_2 = -dE_1,\; dV_2 = -dV_1$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE_1 + \left[\left(\frac{\partial S_1}{\partial V_1}\right)_{E_1} - \left(\frac{\partial S_2}{\partial V_2}\right)_{E_2}\right] dV_1$$

max. entropy $\Rightarrow dS = 0$, & coeff.'s of dE_1 & $dV_1 = 0$.

$\Rightarrow T_1 = T_2$ thermal equil., as before.

$\left(\frac{\partial S_1}{\partial V_1}\right)_{E_1} = \left(\frac{\partial S_2}{\partial V_2}\right)_{E_2}$ new cond.'n.

→ Q: what is interpretation of $\left(\frac{\partial S}{\partial V}\right)_E$?

To find interpretation for $\left(\frac{\partial S}{\partial V}\right)_E$, consider doing quasi-static reversible work on a system:

$$\begin{cases} E \to E - p\,dV & \text{(change in energy due to quasi-stat. work} = -p\,dV\text{)}. \\ dS = 0 & \text{(reversible process)}. \end{cases}$$

$$\Rightarrow S(E,V) \to S(E - p\,dV, V + dV) = S(E,V) + \underbrace{\left(\frac{\partial S}{\partial E}\right)_V (-p\,dV) + \left(\frac{\partial S}{\partial V}\right)_E dV}_{=0,\ \text{since } dS=0}$$

$$\Rightarrow \left[\frac{p}{T} - \left(\frac{\partial S}{\partial V}\right)_E\right] dV = 0$$

$$\Rightarrow \left(\frac{\partial S}{\partial V}\right)_E = \frac{p}{T}$$

~~Thus~~ We may thus write:

$$dS = \left(\frac{\partial S}{\partial E}\right)_V dE + \left(\frac{\partial S}{\partial V}\right)_E dV \qquad (S = S(E,V))$$

$$\Rightarrow dS = \frac{dE}{T} + \frac{p}{T} dV$$

or $\boxed{dE = T\,dS - p\,dV}$ (*) ← important eqn. in stat. mech. (& thermo.) provides relation btwn. differentials of macro. quantities in equil. state.

Ex: (Ideal gas) To illustrate utility of the above result, consider ideal monatomic gas. Recall: $\Omega(E) = B V^N E^{\frac{3N}{2}}$, $N = \#$ particles

$$\Rightarrow S = \ln \Omega = N \ln V + \frac{3N}{2} \ln E + \text{const.}$$

& $p = T\left(\frac{\partial S}{\partial V}\right)_E \Rightarrow p = \frac{NT}{V}$ or $pV = NT$ ← ideal gas law!

The relation $pV = NT$ is ex. of an "eqn. of state", which is a relation connecting quantities characterizing a macro. state.

We also have: $\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V \Rightarrow E = \frac{3}{2}NT$ (mean energy of ideal gas).

- There is another important application of the result (*):

Consider change in (mean) energy dE, due to infinitesimal heat absorbed $đQ$ & work done $đW$:

$$\cancel{đQ = dE} \quad dE = đQ - đW.$$

In the special case of a quasi-static process, we have shown that $đW = pdV \Rightarrow dE = đQ - pdV$.

→ comparing to (*) $\Rightarrow$ $T\,dS = đQ$

$$\text{or} \quad \boxed{dS = \frac{đQ}{T}} \quad (**).$$

→ relation btwn. change in entropy & heat absorbed in a quasi-stat. process.

- For special case of quasi-stat. process in thermally isolated system ($đQ = 0$), we have $dS = 0$.

$\Rightarrow S = \text{const.}$ if quasi-stat. work done on a thermally isolated system

($\Rightarrow$ process is reversible).

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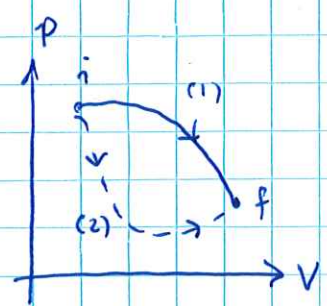
Eq. (**) is also notable b/c it relates the inexact differential $đQ$ to the exact differential dS (since S is a fn. only of macro. state; i.e., $S = S(E, V)$).

In particular, btwn. any initial state (i) & final state (f):

$$\Delta S = S_f - S_i = \int_i^f dS = \int_{\text{equil.}} \frac{đQ}{T}$$

↳ int. for any quasi-stat. process, in which sys. taken through sequence of (near) equil. states.

Ex:



$$\int_{(1)} đQ \neq \int_{(2)} đQ$$

but $\displaystyle\int_{(1)} \frac{đQ}{T} = \int_{(2)} \frac{đQ}{T} = S_f - S_i$.

Finally, return to initial problem of equil. btwn. sys. 1 & 2:

$$T_1 = T_2 \qquad \text{thermal equil.}$$

$$\& \quad \left(\frac{\partial S_1}{\partial V_1}\right)_{E_1} = \left(\frac{\partial S_2}{\partial V_2}\right)_{E_2} \Rightarrow \frac{p_1}{T_1} = \frac{p_2}{T_2}$$

Setting $T_1 = T_2$ in second eqn. $\Rightarrow p_1 = p_2$ "mechanical equil."

→ Thus, in equil., sys. 1 & 2 have equal temp.'s & the pressure is balanced.

⌈ Note: mech. equil. (equality of pressures) reached much more rapidly than equality of temp.'s ⌋

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Summary.

- $\Omega(E)$ = # accessible w/ energy $\in (E, E+\delta E)$
- $S = \ln \Omega$, $\begin{cases} 1/T = (\partial S/\partial E)_V. \\ p/T = (\partial S/\partial V)_E \end{cases}$ (for $S = S(E,V)$).

  $\rightarrow dE = TdS - pdV.$
- equil. conditions: (sys. 1 & 2) $\begin{cases} T_1 = T_2 \\ p_1/T_1 = p_2/T_2 \end{cases}$ (follow from max. tot. entropy).
- Quasi-stat. process: $dS = \frac{đQ}{T}$.

Comments on entropy:

- In QM, if E & ext. param.'s (e.g. vol. V) are specified, then Ω & hence S are completely determined.
- Same is not true in CM. Recall: In CM, we introduce phase space cells $\delta q \delta p$ of undetermined size $\delta q \delta p = h_0$

$\Rightarrow$ for s DOF: $\Omega = \dfrac{(\text{vol. of accessible phase-space})}{(\text{vol of phase space cell})}$

$$= \frac{1}{h_0^s} \int dq_1 \ldots dq_s \, dp_1 \ldots dp_s$$

int over accessible region $E \leq H(q,p) \leq E+\delta E$.

$$\Rightarrow S = \ln \Omega = \ln\left(\int dq_1 \ldots dp_s\right) - s \ln h_0.$$

arbitrary additive const. that depends on cell size.

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Note: const. drops out when considering entropy <u>differences</u>

$\Rightarrow \Delta S$ well-defined in CM.

→ the arbitrary cell size is ultimately fixed by QM.

taking "classical limit" of quant. stat. mech., one finds:

$$h_0 \to h = \text{Planck's const.} \quad (h = 2\pi\hbar).$$

⌈ The result is essentially a consequence of Heisenberg's uncertainty principle $\Delta q \Delta p \gtrsim \hbar$, which (roughly) tells us how precisely we can simultaneously determine particle's position & momentum in QM. ⌋

• Another comment concerns behavior as $E \to E_0$, E_0 = QM gnd. state energy

As $E \to E_0$, $\Omega(E) \longrightarrow \Omega(E_0) = \begin{cases} 1, & \text{unique QM gnd. state.} \\ g, & \text{"degenerate" gnd. state, } g = \# \text{ of deg. states.} \end{cases}$

$$\Rightarrow S = \ln\Omega \to S(E_0) = \ln\Omega(E_0) = \begin{cases} 0, & \text{unique gnd. state} \\ \ln g, & \text{deg. " "} \end{cases}$$

Now, we have shown earlier that $\frac{\partial T}{\partial E} > 0$.

$\Rightarrow T$ is a monotonically increasing fn. of E; i.e., as

$T \to 0$, $E \to E_0$.

$$\Rightarrow S \to 0 \ (\text{or } \ln g) \text{ as } T \to 0.$$

→ this is a result of QM, where quant. states are naturally discrete. No analog in CM (& counterexamples easy to construct, as we'll see later).

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- Our development thus far regarding stat. mech. can be summarized in a set of "macroscopic laws" (or thermodynamic laws).

→ Laws of thermodynamics:

(0) If sys. A is in thermal equil. w/ sys. C & if sys. B is in thermal equil. w/ system C, then A is in thermal equil. w/ B.

→ immediately follows from $T_A = T_C$, $T_B = T_C \Rightarrow T_A = T_B$

(equil. cond.'s deduced from stat. mech.)

(1) Macrostate of sys. characterized by energy E. Change in E due to int. w/ other systems is:

$$\Delta E = -W + Q$$ ← this eqn. defines heat Q

work done by system

heat absorbed

→ this decomposition of ΔE ~~for~~ follows from stat. considerations of sys.'s in thermal contact (Q) that can also do work (W).

(2) Equilib. macrostate characterized by a fn. S = "entropy" s.t.

(i) ~~As~~ For process in which isolated sys. goes from one macro-state to another $\Delta S \geq 0$.

(ii) If system is not isolated & undergoes ~~is~~ a quasi-stat. process: $dS = \frac{đQ}{T}$.

→ (i) + (ii) follow from stat. def.'n of S.

(3) as $T \to 0$, $S \to S_0$ w/ S_0 = indep. of all ~~exte~~ param.'s of the system.

→ follows from QM + stat. defn. of S.

· The thermo. laws (0)–(3) are purely macro. statements. Historically, laws of thermo. identified <u>before</u> the development of stat. mech. (Carnot, Clapeyron, Kelvin, Joule, ...) However, we now see that these laws are simple corollaries of fund. postulate of stat. mech & identification of entropy $S = \ln \Omega$.

· Next major topic = application of macro. thermo. — i.e., of the thermo. laws — in some important examples. Although we have seen that laws are <u>consequences</u> of μ-scopic <u>stat. mech.</u>, we will, for now, mostly adopt a macroscopic viewpoint.

· Focus primarily on system w/ macro-state determined by single ext. param. = vol. V. & energy E. (really mean values, but b/c of insignificant stat. fluct.'s, we don't emphasize this distinction in macro. approach).

→ Given E & V, other macro. param.'s determined:

entropy $S = S(E,V)$, temp. $T = T(E,V)$, pressure $p = p(E,V)$.

In ~~some~~ many cases, E & V are not the most convenient indep. var.'s & we may want to use other macro. param.'s as indep. var.'s: e.g., $(T, V) \to S = S(T,V)$, $E = E(T,V)$, $p = p(T,V)$

or (E, p), etc...

Response fn.'s:

~~Often, we probe macro systems by varying some thermo. var. (e.g., T) & C&~~

- A common way of characterizing macro. sys. is to measure how thermo. var.'s (e.g., T or V) changes due to external perturbation → "response fn.". Some important ex.'s are:
  - Heat capacities: change in T due to added heat $đQ$.

$$\to đQ\Big|_x = C_x\, dT, \quad C_x = \text{"heat capacity"}.$$

x = param. kept const. when heat added.

$$\to đQ\Big|_V = C_V\, dT. \quad (\text{heat added at const. vol.})$$

$$đQ\Big|_p = C_p\, dT \quad (\text{" " pressure}).$$

$$\to đQ\Big|_V = dE + đW\Big|_V = dE\Big|_V + \cancel{p\,dV\Big|_V}^{\,0} \underset{E=E(T,V)}{=} \left(\frac{\partial E}{\partial T}\right)_V dT \Rightarrow C_V = \left(\frac{\partial E}{\partial T}\right)_V.$$

$$đQ\Big|_p = dE + đW\Big|_p = dE\Big|_p + p\,dV\Big|_p \underset{\substack{E=E(T,p)\\ V=V(T,p)}}{=} \left[\left(\frac{\partial E}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p\right] dT$$

$$\Rightarrow C_p = \left(\frac{\partial E}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p.$$

- other response fn.'s include; e.g.:

compressibility $\kappa_T = -\frac{1}{V}\left.\frac{\partial V}{\partial p}\right|_T$ (change in vol. under pressure)

"isothermal" = fixed T

~~expansivity~~
expansivity: $\alpha_p = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_p$ (change in vol. w.r.t. change in T).

In discussing macro. thermo., we will also distinguish btwn. "extensive" quantities & "intensive" quantities.

- Extensive quantities are prop. to system size. (vol., # of particles)

Ex: ~~volume~~ vol. V, tot. energy E, entropy S, ... (additive quantities).

- Intensive quantities are indep. of sys. size.

Ex: pressure p, temp T, ...

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Summary.

- Equilib. macro. system: $dE = TdS - pdV$, $E = E(S,V)$.
- First law of thermo: $dE = đQ - đW$

$$\rightarrow \left.\begin{aligned} đW &= pdV \\ đQ &= TdS \end{aligned}\right\} \text{quasi-stat. process.}$$

- Heat capacity: $đQ|_x = C_x\, dT$, C_x = "heat capacity".

heat added w/ param. x = const.

$$\rightarrow C_x = T\left(\frac{\partial S}{\partial T}\right)_x \Rightarrow S(x,T_2) = S(x,T_1) + \int_{T_1}^{T_2} dT\, \frac{C_x(T)}{T}.$$

→ mear. $C_x(T)$ to determine changes in S (at fixed x).

Ideal gas:

- Ideal gas = gas in which interactions btwn. particles so weak they can be neglected

  → limit (usually) achieved in dilute gases, where particles almost always far apart, so int. forces are small.

- Ideal gas eqn. of state: $pV = NT$ (T in energy units).

  or $pV = Nk_BT$ (T in degrees).

writing $N = \nu N_A$, ν = # moles & $N_A = 6.02\times10^{23}\ \text{mol}^{-1}$

$$\rightarrow pV = \nu RT, \quad R = N_A k_B = \text{"gas const."}$$

⌈ Derived eqn. of state from $\Omega(E,V)$ for (monatomic) ideal gas ⌋

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- Earlier, we showed $E = E(T) = \frac{3}{2} N k_B T$, starting from μ-scopic considerations. As a first application of macro. thermo. we rederive result that $E = E(T)$ – i.e., indep. of V – from purely macro. consideration

- Take as our indep. var.'s (T, V) ($\Rightarrow E = E(T,V)$, in general).

$$\Rightarrow \quad dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV.$$

$$\& \quad dE = T\,dS - p\,dV \qquad \text{(fundamental relation)}.$$

$$= T\left[\left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV\right] - p\,dV \qquad S = S(T,V)$$

$$= \underbrace{T\left(\frac{\partial S}{\partial T}\right)_V}_{\left(\frac{\partial E}{\partial T}\right)_V} dT + \underbrace{T\left[\left(\frac{\partial S}{\partial V}\right)_T - \frac{p}{T}\right]}_{\left(\frac{\partial E}{\partial V}\right)_T} dV$$

- equality of mixed partials $\Rightarrow$ $\left.\frac{\partial}{\partial V}\right|_T \left(\frac{\partial E}{\partial T}\right)_V = \left.\frac{\partial}{\partial T}\right|_V \left(\frac{\partial E}{\partial V}\right)_T$

$$\Rightarrow \quad T\,\frac{\partial^2 S}{\partial V \partial T} = \left.\frac{\partial}{\partial T}\right|_V \left\{T\left[\left(\frac{\partial S}{\partial V}\right)_T - \frac{p}{T}\right]\right\}$$

$$T\,\cancel{\frac{\partial^2 S}{\partial V \partial T}} = \underbrace{\left[\left(\frac{\partial S}{\partial V}\right)_T - \frac{p}{T}\right]}_{\frac{1}{T}\left(\frac{\partial E}{\partial V}\right)_T} + T\left[\cancel{\frac{\partial^2 S}{\partial T \partial V}} - \left.\frac{\partial}{\partial T}\right|_V \left(\frac{p}{T}\right)\right]$$

$$\Rightarrow \quad \left(\frac{\partial E}{\partial V}\right)_T = T^2 \left.\frac{\partial}{\partial T}\right|_V \left(\frac{p}{T}\right) \qquad \text{(general result)}$$

ideal gas $\frac{p}{T} = \frac{\nu R}{V}$

$$= 0. \qquad \Rightarrow \left.\frac{\partial}{\partial T}\right|_V \frac{p}{T} = 0.$$

$\Rightarrow E(T,V) =$ indep of V; i.e. $E = E(T)$ ✓

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Heat capacity / specific heat of ideal gas

$đQ|_x = C_x\, dT$, define $c_x = \frac{C_x}{\nu}$ = "specific heat"

↑ heat capacity per mole.

→ C_x = extensive, c_x = intensive

· const. V: $đQ|_V = C_V\, dT = \nu c_V\, dT$

→ first law: $đQ|_V = dE|_V + đW|_V$ ↳ $đW|_V = p\,dV|_V = 0$.

$= dE|_V$ ↳ $E = E(T, V)$

$= \left(\frac{\partial E}{\partial T}\right)_V dT.$

$\Rightarrow c_V = \frac{1}{\nu}\left(\frac{\partial E}{\partial T}\right)_V$ (general result)

note: $c_V > 0$, since $\frac{\partial E}{\partial T} > 0$ (proved earlier).

→ for ideal gas: $E = E(T) \Rightarrow dE = \left(\frac{\partial E}{\partial T}\right)_V dT$

$\Rightarrow dE = \nu c_V\, dT$ (ideal gas).

· const. p: $đQ|_p = \nu c_p\, dT$, $đQ|_p = dE|_p + p\,dV|_p$ ↳ ideal gas $dE = \nu c_V\, dT$

$= \nu c_V\, dT + p\,dV|_p$ ↳ $dV|_p = \frac{1}{p}\nu R\, dT$

$= \nu c_V\, dT + \nu R\, dT$ (eqn. of state)

$= \nu (c_V + R)\, dT.$

$\Rightarrow c_p = c_V + R.$ (ideal gas).

note: $c_p > c_V$ – some added heat goes into work

- This is as much as we can say about c_V / c_p from macro. theory. (We also know $c_V = c_V(T)$ is indep. of V, since E indep. of V). To say more, we resort to μ-<u>r</u>copic approach.

→ Recall: <u>monatomic</u> ideal gas has $\Omega(E) = B V^N E^{3N/2}$

($N = \#$ particles)

$$\Rightarrow S = \ln \Omega = N \ln V + \frac{3N}{2} \ln E + \text{const.}$$

now, $T^{-1} = \left(\frac{\partial S}{\partial E}\right)_V = \frac{3N}{2E} \Rightarrow E = \frac{3}{2} N T$

or $E = \frac{3}{2} \nu R T$ (T in degrees).

using $c_V = \frac{1}{\nu}\left(\frac{\partial E}{\partial T}\right)_V \Rightarrow c_V = \frac{3}{2} R$ (indep. of T).

& $c_p = c_V + R = \frac{5}{2} R$.

$\Rightarrow \gamma \equiv c_p / c_V = 5/3$.

↳ can be measured from sound speed in gas.

In <u>polyatomic</u> gases, dep. on T a bit more complex (see below).

- Now investigate ideal gas subject to various processes.

→ For "isothermal" quasi-stat. expansion: $pV = \text{const.}$ ($\Rightarrow p \sim \frac{1}{V}$).

↑ const. T

→ For "adiabatic" expansion, gas will change energy (& change T) by doing work.

↑ no heat transfer

→ <u>Q</u>: what is relationship btwn. p & V for such a process?

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first law: $đQ = dE + đW \rightarrow 0 = dE + đW = dE + p\,dV$

ideal gas

$$0 = \nu c_V dT + p\,dV.$$

eqn. of state: $pV = \nu RT \Rightarrow p\,dV + V\,dp = \nu R\,dT$

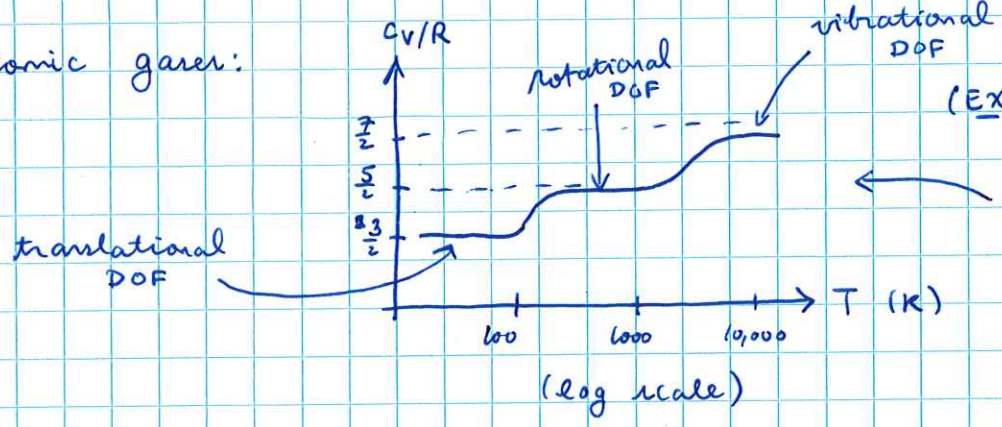
$$\Rightarrow 0 = \frac{c_V}{R}(p\,dV + V\,dp) + p\,dV.$$

$$= \underbrace{(c_V + R)}_{c_p} p\,dV + c_V V\,dp$$

$$\Rightarrow \gamma\, p\,dV + V\,dp = 0 \qquad (\gamma = c_p/c_V).$$

$$\text{or} \quad \gamma \frac{dV}{V} + \frac{dp}{p} = 0. \qquad (*)$$

For monatomic ideal gas, we showed c_V = const. (indep. of T). ch polyatomic gases:



(EX: H_2 molecule).

these "steps" are QM effects that we'll revisit later.

→ c_V = const. over broad ranges of T.

→ treating γ as const., we can integrate (*):

$$\Rightarrow \gamma \ln V + \ln p = \text{const.}$$

$$\text{or} \quad pV^\gamma = \text{const.} \quad (\text{equiv. } TV^{\gamma-1} = \text{const., using eqn. of state}).$$

→ in adiabatic process, $p \sim 1/V^\gamma$ varies more rapidly w/ V than for isothermal process, where $p \sim 1/V$ (since $\gamma > 1$)

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Summary.

- Fundamental equil. relation: $dE = TdS - pdV$.
- First law: $dE = đQ - đW$.
- Second law: in thermally isolated sys. $\Delta S \geq 0$ for any spontaneous process.
  $\rightarrow$ $S = \max.$ in equil.

Thermodynamic potentials.

- thermo var.'s: $\{E, S, T, V, p, \ldots\}$ (in general, there may be more, but, for simplicity, we focus on these).
- in a closed/isolated sys. vol. V is specified & energy $E = \text{const.}$
  $\Rightarrow$ (E, V) are natural "independent var.'s" & other quantities then determined in terms of these; $S = S(E,V)$, etc...

  We may equiv. take (S, V) as indep. var.'s & $E = E(S,V)$.

  T & p then determined by fundamental rel.'n $dE = TdS - pdV$

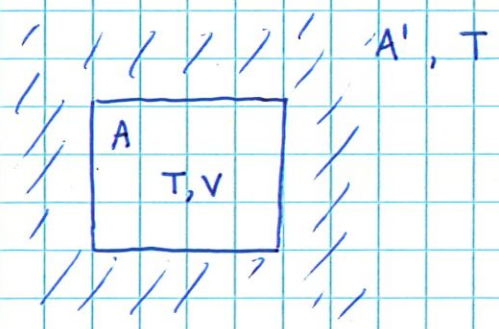
$$\Rightarrow \quad T = \left(\frac{\partial E}{\partial S}\right)_V, \quad p = -\left(\frac{\partial E}{\partial V}\right)_S.$$

- in practice, would like to take as indep. var.'s those quantities we can experimentally control, like T & p (S & E hard to "control" experimentally).

~~Hel~~ Helmholtz free energy

02/17/25

· To put system at fixed (controllable) T, couple to heat bath



(sys. A immersed in larger sys. A')

· sys. A = sys. of interest

· A' = heat bath (a system much larger than A) that fixes temp T.

→ A + A' = closed sys, but A is not closed.

Q: what is work done by sys. A when T = const?

first law → $đW = đQ - dE$ (if A = closed, $đQ = 0$ & $đW = -dE$).

for a quasi-stat. process $đQ = TdS$ (S = entropy of sys. A).

$$\Rightarrow đW = -dE + TdS$$

T = const.

$$= -d\underbrace{(E - TS)}_{\equiv F}$$

"Helmholtz free energy".

$$\Rightarrow đW = -dF.$$

→ work done by sys. in quasi-stat. process at const. T = ~~change~~ decrease in F.

$F = F(T, V)$ is a fn. of state of sys. (so dF = exact differential).

Note: F is determined entirely by sys. A

To exhibit explicitly dep. of F on V & T, take dF: 02/17/25

$$dF = dE - TdS - SdT \quad \Rightarrow \quad dE = TdS - pdV$$

$$dF = -SdT - pdV$$

$$\Rightarrow \quad S = -\left(\frac{\partial F}{\partial T}\right)_V, \qquad p = -\left(\frac{\partial F}{\partial V}\right)_T.$$

$\Rightarrow$ from $F(T,V)$ can obtain S & p.

Also note: $E = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_V = -T^2\left(\frac{\partial}{\partial T}\frac{F}{T}\right)_V$.

The mathematical procedure we have used to pass from ~~the~~ the fn. $E = E(S,V)$ to $F = F(T,V)$ w/ $T = \left(\frac{\partial E}{\partial S}\right)_V$ is a "Legendre transform".

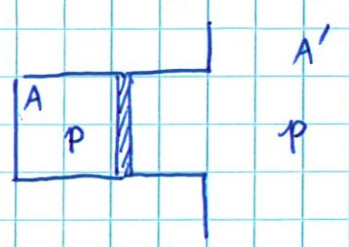
$= E(S,V) - TS$

You have performed a similar procedure in CM, when passing from the Lagrangian $L(q,\dot{q})$ to the Hamiltonian $H = H(q,p)$ w/ $p = \frac{\partial L}{\partial \dot{q}}$: $H(q,p) = p\dot{q} - L(q,\dot{q})$

$(\dot{q} \leftrightarrow S,\ p \leftrightarrow T,\ L \leftrightarrow E,\ -H \leftrightarrow F)$

<u>Enthalpy</u>

- Just as we considered sys. at fixed (controllable) T, we may consider a system at fixed p (as opposed to fixed V).



$A' \gg A$

02/17/25

For sys. at fixed V, $đQ = dE$ (first law).

For sys. at fixed p: $đQ = dE + đW$ ~~exclude pdV~~

quasi-stat. work.

$$= dE + pdV$$

$p = \text{const.}$

$$= d\underbrace{(E+pV)}_{\equiv \mathcal{H}}$$

"enthalpy"

$$\Rightarrow đQ = d\mathcal{H}.$$

→ ~~heat absorbed~~ for process at const. p, change in $\mathcal{H}$

= heat absorbed by sys.

Like F, $\mathcal{H} = \mathcal{H}(S, p)$ is a fn. of state of the sys.

$$\rightarrow d\mathcal{H} = dE + pdV + Vdp$$

$dE = TdS - pdV$

$$d\mathcal{H} = TdS + Vdp$$

$$\Rightarrow T = \left(\frac{\partial \mathcal{H}}{\partial S}\right)_p, \quad V = \left(\frac{\partial \mathcal{H}}{\partial p}\right)_S.$$

If sys. = thermally isolated, then $đQ = 0 \Rightarrow d\mathcal{H} = 0$

$\Rightarrow \mathcal{H} = \text{const.}$ (enthalpy conserved).

Heat capacity at const. p:

$$đQ\big|_p = C_p\, dT \Rightarrow d\mathcal{H} = C_p\, dT$$

$$\Rightarrow C_p = \left(\frac{\partial \mathcal{H}}{\partial T}\right)_p \quad \left(\text{c.f. } C_V = \left(\frac{\partial E}{\partial T}\right)_V\right).$$

$\mathcal{H} \leftrightarrow E$ for process at const. p.

Ex: (monatomic ideal gas) $pV = NT$. & $E = \frac{3}{2}NT$

$$\Rightarrow \mathcal{H} = E + pV = \frac{3}{2}NT + NT = \frac{5}{2}NT \Rightarrow C_p = \left(\frac{\partial \mathcal{H}}{\partial T}\right)_p = \frac{5}{2}N \quad ✓$$

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Gibbs free energy

- To describe sys. at const. (externally specified) T & p, we use "Gibbs free energy": $G = G(T,p) = E - TS + pV = \mathcal{H} - TS$.

$$\rightarrow dG = dE - TdS - SdT + pdV + Vdp. \quad \& \quad dE = TdS - pdV.$$

$$dG = -SdT + Vdp$$

$$\Rightarrow S = -\left(\frac{\partial G}{\partial T}\right)_p, \quad V = \left(\frac{\partial G}{\partial p}\right)_T.$$

$$\& \quad \mathcal{H} = G + TS = G - T\left(\frac{\partial G}{\partial T}\right)_p = -T^2\left(\frac{\partial}{\partial T}\frac{G}{T}\right)_p.$$

- From any of $E(S,V)$, $F(T,V)$, $\mathcal{H}(S,p)$, $G(T,p)$ we can obtain all thermo. quantities (S,T,p,V) by taking partial derivatives.

$\rightarrow$ $E, F, \mathcal{H}, G$ = "thermodynamic potentials".

- Thermo. dyn. potentials are also important b/c (as we show below) they are minimized in equil. (under certain conditions).
- For closed sys. $S = \max.$, & $\Delta S \geq 0$ tells us ~~the~~ sys. approaches equil., by increasing entropy, until attaining max. is equil.

$\rightarrow$ find analogous statements for sys. that can exchange heat w/, or do work on, their environments.

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Summary.

- Thermo. potentials:

	E	$E = E(S,V)$	$dE = TdS - pdV$
"enthalpy"	$\mathcal{H} = E + pV$	$\mathcal{H} = \mathcal{H}(S,p)$	$d\mathcal{H} = TdS + Vdp$
"Helmholtz free energy"	$F = E - TS$	$F = F(T,V)$	$dF = -SdT - pdV$
"Gibbs free energy"	$G = E - TS + pV$	$G = G(T,p)$	$dG = -SdT + Vdp.$

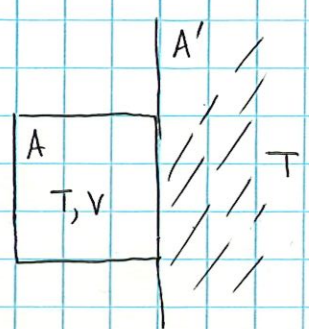
- Closed sys. in equil: $S = \max.$

$\rightarrow$ $\Delta S \geq 0$ tells us that sys. approaches equil. by increasing entropy.

Q: what about systems that are not closed; i.e., can exchange heat with, or do work on, their environment?

- Start w/ sys. A in contact w/ heat bath, so $T = \text{const.}$

Suppose also that vol. V of sys A = const. (& A does not do any other form of work):



$$\Delta S_{tot} = \underbrace{\Delta S}_{\text{sys. A}} + \underbrace{\Delta S'}_{\text{sys A}'} \geq 0$$

Q = heat absorbed by A.

$\rightarrow$ for heat bath $\Delta S' = -\dfrac{Q}{T}$

$$\Rightarrow \Delta S - \frac{Q}{T} \geq 0 \quad \text{or} \quad T\Delta S - Q \geq 0.$$

First law $\Rightarrow$ $\Delta E = Q - W$ (for system A) & we assume $W = 0$:

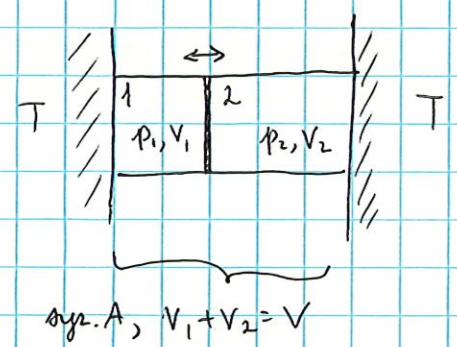
$$\Rightarrow \Delta E = Q$$

$$\Rightarrow T\Delta S - \Delta E \geq 0.$$

Since $F = E - TS$, we find $-\Delta F \geq 0$ or $\Delta F \leq 0$. 02/19/25

→ for sys. at fixed T, V, F decreases on approach to equil. in equil. $F = \min.$ (consequence of $S_{tot.} = \max$).

Ex:



equil. cond.'n $\delta F = 0$ ($F = \min.$)

$$\rightarrow \delta F = \left(\frac{\partial F}{\partial V_1}\right)_T \delta V_1 + \left(\frac{\partial F}{\partial V_2}\right)_T \delta V_2$$

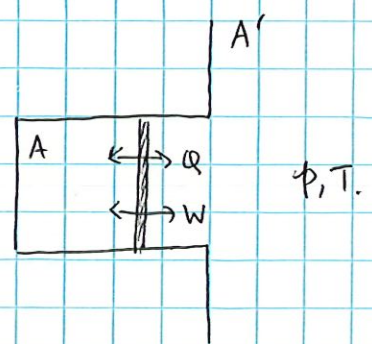
$\left(\frac{\partial F}{\partial V}\right)_T = -p$ & $\delta V_2 = -\delta V_1$

$$= (p_2 - p_1)\,\delta V_1$$

$$= 0$$

$\Rightarrow$ $p_1 = p_2$ in equil. ✓

A similar situation holds for Gibbs free energy G:



$$\Delta S_{tot} = \Delta S + \Delta S' \geq 0.$$

$$\Delta S' = -\frac{Q}{T} \Rightarrow T\Delta S - Q \geq 0$$

→ first law: $\Delta E = Q - W = Q - p\Delta V$ (sys. A)

(assume no other form of work & use $p = \text{const.}$)

$$\Rightarrow T\Delta S - (\Delta E + p\Delta V) \geq 0.$$

or $\Delta G \leq 0$ ($G = E - TS + pV$).

& $G = \min.$ at equil.

→ Gibbs free energy decreases on approach to equil. at fixed (T, p) & is min. at in equil.

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Maxwell relations

- Use thermo. potentials to derive some useful (& general) results for macro. sys.

- Start w/ fundamental rel.'n:

$$dE = TdS - pdV$$

$$\Rightarrow \quad T = \left(\frac{\partial E}{\partial S}\right)_V \quad \& \quad p = -\left(\frac{\partial E}{\partial V}\right)_S .$$

equality of mixed partials: $\dfrac{\partial^2 E}{\partial V \partial S} = \dfrac{\partial^2 E}{\partial S \partial V}$

$$\Rightarrow \quad \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \qquad (1)$$

- Helmholtz free energy:

$$dF = -SdT - pdV$$

$$\Rightarrow \quad \left(\frac{\partial F}{\partial T}\right)_V = -S \quad \& \quad \left(\frac{\partial F}{\partial V}\right)_T = -p$$

$$\frac{\partial^2 F}{\partial V \partial T} = \frac{\partial^2 F}{\partial T \partial V}$$

$$\Rightarrow \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \qquad (2)$$

- Enthalpy: $\quad d\mathcal{H} = TdS + Vdp$

$$\Rightarrow \quad \left(\frac{\partial \mathcal{H}}{\partial S}\right)_p = T \quad \& \quad \left(\frac{\partial \mathcal{H}}{\partial p}\right)_S = V \quad \Rightarrow \quad \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \qquad (3)$$

- Gibbs free energy: $\quad dG = -SdT + Vdp$

$$\Rightarrow \quad \left(\frac{\partial G}{\partial T}\right)_p = -S \quad \& \quad \left(\frac{\partial G}{\partial p}\right)_T = V \quad \Rightarrow \quad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \qquad (4).$$

→ Relations (1)-(4) are the "Maxwell relations" & are very useful in practice. The relations highlight fact that (T, S, p, V) are not all indep.

also note that the relations are not indep. (any one can be derived from any other by change of indep. var.'s).

→ see examples utilizing Maxwell reln.'s below.

<u>Specific heats</u>.

Q: what is general rel.'n btwn c_V (specific heat at V=const) & c_p (specific heat at p=const.)? (For ideal gas $c_p = c_V + R$).

→ useful in practice: easier to calculate at const. V but easier to measure at const. p.

$$\rightarrow \quad đQ|_V = C_V\, dT \qquad đQ|_p = C_p\, dT$$

$$đQ = T\,dS \quad \Rightarrow \quad C_V = T\left(\frac{\partial S}{\partial T}\right)_V \quad \& \quad C_p = T\left(\frac{\partial S}{\partial T}\right)_p .$$

· Start w/ indep. var.'s (T, p) (easiest to control in expt.)

$$\rightarrow \quad S = S(T,p) \quad \& \quad dS = \left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$$

$$= \frac{1}{T} C_p\, dT + \left(\frac{\partial S}{\partial p}\right)_T dp. \qquad \downarrow\ p = p(T,V)$$

$$= \frac{1}{T} C_p\, dT + \left(\frac{\partial S}{\partial p}\right)_T \left[\left(\frac{\partial p}{\partial T}\right)_V dT + \left(\frac{\partial p}{\partial V}\right)_T dV\right]$$

$$= \left[\frac{1}{T} C_p + \left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V\right] dT + \left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T dV$$

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$$\rightarrow \quad dS = \left[\frac{1}{T} C_p + \left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V\right] dT + \left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T dV.$$

viewing $S = S(V,T)$: $dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$

$$\Rightarrow \quad T\left(\frac{\partial S}{\partial T}\right)_V = C_p + \left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V$$

$$\Rightarrow \quad C_V = C_p + \left(\frac{\partial S}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V.$$

$\rightarrow$ relation btwn. C_V & C_p.

The derivatives $\left(\frac{\partial S}{\partial p}\right)_T$ & $\left(\frac{\partial p}{\partial T}\right)_V$ are not readily measured.

$\rightarrow$ use Maxwell relation: $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$ & $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$

$= -V\alpha$

(thermal expansion ~~coff~~ coeff.)

to simplify $\left(\frac{\partial p}{\partial T}\right)_V$ use: $V = V(T,p) \rightarrow dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp.$

$\Rightarrow$ if $V = \text{const}$; then $dV = 0$ & $dp = \left(\frac{\partial p}{\partial T}\right)_V dT.$

$$\Rightarrow \left(\frac{\partial p}{\partial T}\right)_V = \frac{-(\partial V/\partial T)_p}{(\partial V/\partial p)_T} = \frac{\alpha}{\kappa}$$

$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$ irothermal ~~compressibility~~ compressibility.

$$\Rightarrow C_V = C_p + T(-V\alpha)\left(\frac{\alpha}{\kappa}\right)$$

$$\Rightarrow C_p - C_V = VT\frac{\alpha^2}{\kappa}.$$

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Summary.

- ~~Maxwell~~ Fundamental rel.'n: $dE = T\,dS - p\,dV$.

- Maxwell reln.'s:

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

$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

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

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p.$$

- Heat capacity: $đQ\big|_x = C_x\,dT$, $\quad C_x = T\left(\frac{\partial S}{\partial T}\right)_x$.

- $C_p - C_V = VT\frac{\alpha^2}{\kappa}$, $\quad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ (thermal expansion coeff.)

$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$ (isothermal compressibility).

<u>Ex</u>: (ideal gas) $\quad pV = \nu RT$

$$\rightarrow \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V}\,\frac{\nu R}{p} = \frac{1}{T}.$$

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{V}\left(\frac{-\nu RT}{p^2}\right) = \frac{1}{p}$$

$$\Rightarrow C_p - C_V = VT \times \frac{(1/T^2)}{(1/p)} = \frac{pV}{T} = \nu R.$$

per mole: $c_p - c_V = R$ ✓.

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· Third law of thermo. also has interesting implications for specific heat (& other response fn.'s).

→ third law: $S \to 0$ as $T \to 0$.

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V \Rightarrow \text{as } T \to 0,\ C_V \to 0,\ \text{since } \left(\frac{\partial S}{\partial T}\right)_V = \text{finite as } T \to 0.$$

[alt: $S(T) - \cancel{S(T=0)}^{\,0} = \int_0^T dT' \, \frac{C_V(T')}{T'}$

→ for integral to converge at $T=0$, need $C_V \to 0$ as $T \to 0$]

Similarly follows that $C_p = 0$ at $T=0$.

Also have $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \underset{\text{Maxwell rel.'n}}{=} -\frac{1}{V}\left(\frac{\partial S}{\partial p}\right)_T \Rightarrow \alpha \to 0$ as $T \to 0$

(since $S(T=0) = 0$ for any p).

Note $\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$ is non-zero as $T \to 0$ (it is a mechanical quantity).

· In most cases, $S \to 0$ as a power: $S \sim T^n$ as $T \to 0$.

$$\Rightarrow C_p - C_V = VT\frac{\alpha^2}{\kappa} \underset{\alpha \sim \left(\frac{\partial S}{\partial p}\right)_T \sim T^n}{\sim} T^{2n+1} \Rightarrow \frac{C_p - C_V}{C_V} \sim T^{n+1} \to 0 \text{ as } T \to 0$$

i.e., difference of specific heats → 0 faster than specific heats themselves.

Note: Specific heats of ideal gas fail to satisfy prop.'s above. This is b/c, as $T \to 0$, QM effects become important (return to this later).

Entropy & internal energy:

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- Take (T, V) as indep. var.'s describing macro. system.

→ Q: what info. do we need to reconstruct $S(T,V)$ & $E(T,V)$?

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

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

$$= \frac{C_V}{T} dT + \left(\frac{\partial p}{\partial T}\right)_V dV.$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \quad \text{(Maxwell rel.'n)}$$

can be evaluated if eqn. of state $p = p(T,V)$ is known.

C_V is in general a fn. of T & V: $C_V = C_V(T,V)$.

In fact, dep. of C_V on V is determined by eqn. of state:

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \frac{\partial}{\partial V}\Big|_T \left[T\left(\frac{\partial S}{\partial T}\right)_V\right] = T\,\frac{\partial^2 S}{\partial V \partial T}$$

$$= T\,\frac{\partial^2 S}{\partial T \partial V}$$

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

Maxwell rel.'n $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$

$$= T\,\frac{\partial}{\partial T}\Big|_V \left(\frac{\partial p}{\partial T}\right)_V$$

$$\Rightarrow \left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_V.$$

determined by eqn. of state.

⇒ if $C_V(T,V)$ is known at a single vol. $V = V_1$, we can obtain entire dep. on vol.:

$$C_V(T,V) = C_V(T,V_1) + \int_{V_1}^{V} \left(\frac{\partial C_V}{\partial V}\right)_T dV' = C_V(T,V_1) + \int_{V_1}^{V} T\left(\frac{\partial^2 p}{\partial T^2}\right)_V dV'$$

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Coming back to $dS = \frac{C_V}{T} dT + \left(\frac{\partial p}{\partial T}\right)_V dV$, we find that:

$S(T,V)$ can be ~~to~~ reconstructed from knowledge of eqn. of state $p(T,V)$ & $C_V(T,V)$ at a ~~singe~~ single vol. V. Explicitly:

$$S(T,V) - S(T_0,V_0) = [S(T,V) - S(T_0,V)] + [S(T_0,V) - S(T_0,V_0)]$$

reference state

$$= \int_{T_0}^{T} \frac{C_V(T',V)}{T'} dT' + \int_{V_0}^{V} \left(\frac{\partial p(T_0,V')}{\partial T}\right)_V dV'.$$

→ similarly reconstruct energy $E(T,V)$:

$$dE = TdS - p\,dV$$

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

$$= \left(\frac{\partial p}{\partial T}\right)_V \text{ (Maxwell)}$$

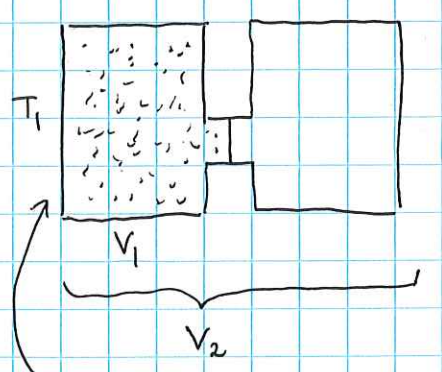
$$= C_V dT + \left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right] dV$$

$$\Rightarrow \left(\frac{\partial E}{\partial T}\right)_V = C_V \quad \& \quad \left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p$$

⇒ $E(T,V) - E(T_0,V_0)$ can again be obtained from integration, using knowledge of eqn. of state & $C_V(T)$.

· Now consider "free expansion" & "throttling" processes. These examples will illustrate some general methods in macro. thermo.

Free expansion:



· gas initially in equil. at temp T_1 & vol. V_1 is allowed to expand freely into evacuated chamber, s.t. total vol. $= V_2$. System is thermally isolated throughout.

→ Q: What is final temp. T_2, after system reaches equil.?

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→ sys. is thermally isolated ⇒ $Q=0$ (no heat flow).

→ sys. does no work ⇒ $W=0$.

first law $\Delta E = Q - W = 0$; i.e., no change in energy of the sys.

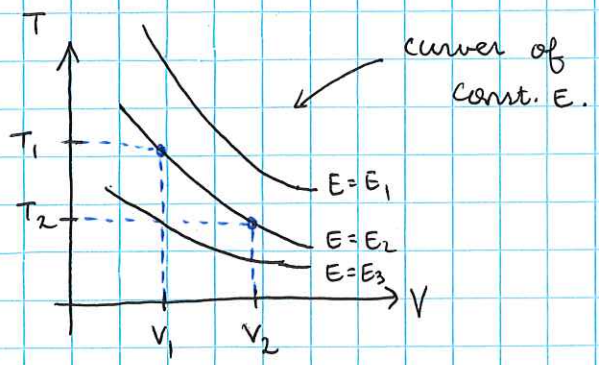
$$\Rightarrow E(T_1, V_1) = E(T_2, V_2) \quad \text{(initial } E = \text{final } E\text{)}.$$

→ implicit eqn. for T_2.

· For an <u>ideal gas</u>, $E = E(T)$ (indep. of V), & $E(T_1) = E(T_2) \Rightarrow T_1 = T_2$

⇒ for an ideal gas, no change of T in free expansion.

· In general, we need to know $E(T,V)$ to determine T_2.



→ although the actual expansion is <u>not</u> quasi-stat., the initial & final (equil.) states will lie on the same $E=$ const. curve.

To see how we could obtain T_2, consider temp. change due to a <u>small</u> change in vol.: $\left(\frac{\partial T}{\partial V}\right)_E$.

$$\rightarrow \quad dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV \overset{E=\text{const.}}{=} 0$$

$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_E = -\frac{(\partial E/\partial V)_T}{(\partial E/\partial T)_V} = -\frac{1}{C_V}\left(\frac{\partial E}{\partial V}\right)_T.$$

& we also have $\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial T}\right)_V - p$.

$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_E = -\frac{1}{C_V}\left[p - T\left(\frac{\partial S}{\partial V}\right)_T\right]$$

$$= \frac{1}{C_V}\left[p - T\left(\frac{\partial p}{\partial T}\right)_V\right]$$

Maxwell rel.'n $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$.

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In our analysis of specific heat, we have shown:

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{\alpha}{\kappa}, \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \quad \text{(expansion coeff.)}$$

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \quad \text{(compressibility)}$$

$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_E = \frac{1}{C_V}\left(p - \frac{T\alpha}{\kappa}\right).$$

⌈ For ideal gas, $\alpha = 1/T$ & $\kappa = 1/p$ $\Rightarrow$ $(\partial T/\partial V)_E = 0$ ✓ ⌋

→ for finite change ΔT, we integrate along the (fictitious) quasi-stat. path of $E = \text{const}$:

$$T_2 = T_1 + \int_{V_1}^{V_2} dV \left(\frac{\partial T}{\partial V}\right)_E .$$

- In principle, adiabatic free expansion could be used to cool (non-ideal) gases. In practice, effect is too weak to be useful.
- It is also of interest to calculate change in entropy $\Delta S = S_2 - S_1$ in the free expansion. First note that:

$$\left(\frac{\partial S}{\partial V}\right)_E = \frac{p}{T} > 0 \; ; \text{ i.e., entropy increases upon expansion (as it should)}$$

expansion occurs at fixed E.

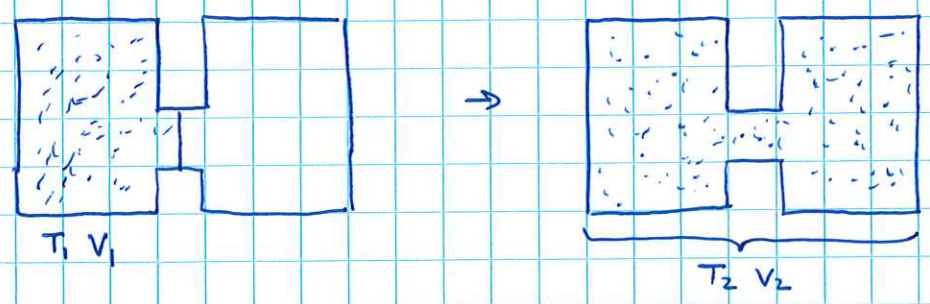
<u>Ex</u>: (ideal gas) $pV = NT \Rightarrow \left(\frac{\partial S}{\partial V}\right)_E = \frac{N}{V}$. Integrating along fictitious quasi-stat. path $V_1 \to V_2$ w/ $E = \text{const}$ gives:

$$S_2 = S_1 + \int_{V_1}^{V_2} dV \left(\frac{\partial S}{\partial V}\right)_E = S_1 + N\int_{V_1}^{V_2} \frac{dV}{V} \Rightarrow \Delta S = N \ln \frac{V_2}{V_1}$$

02/24/25

Summary.

Adiabatic free expansion:



$T_2 = ?$

$$Q = W = 0 \Rightarrow \Delta E = 0 \Rightarrow E_1 = E_2 \quad \text{or} \quad E(T_1, V_1) = E(T_2, V_2).$$

for ideal gas: $E = E(T) \Rightarrow T_1 = T_2$

in general: $$\left(\frac{\partial T}{\partial V}\right)_E = \frac{1}{C_V}\left[p - T\left(\frac{\partial p}{\partial T}\right)_V\right].$$

Change in S: $$\left(\frac{\partial S}{\partial V}\right)_E = \frac{p}{T} > 0$$ (entropy increases in free expansion).

Ex: (van der Waals gas)

- van der Waals eqn. of state: $\left(p + \frac{a}{v^2}\right)(v - b) = RT$, $v = V/\nu$ = molar vol.

(empirical eqn.)

reduction of gas pressure due to attractive interaction btwn. particles

reduction in vol. due to "size" of particles.

$$\rightarrow \left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{v-b} \quad \& \quad \left(\frac{\partial T}{\partial V}\right)_E = \frac{1}{C_V}\left[p - T\left(\frac{\partial p}{\partial T}\right)_V\right] = -\frac{a}{C_V v^2} = -\frac{a\nu^2}{C_V V^2}.$$

- It can be shown that C_V = const. for vdW gas (see end of notes).

$$\Rightarrow \Delta T = \int_{V_1}^{V_2} dV \left(\frac{\partial T}{\partial V}\right)_E = -\frac{a\nu^2}{C_V}\int_{V_1}^{V_2}\frac{dV}{V^2} = \frac{a\nu^2}{C_V}\left(\frac{1}{V_2} - \frac{1}{V_1}\right).$$

If $V_2 > V_1$ then $\Delta T < 0$; i.e., $T_2 < T_1$ & gas cools in free expansion.

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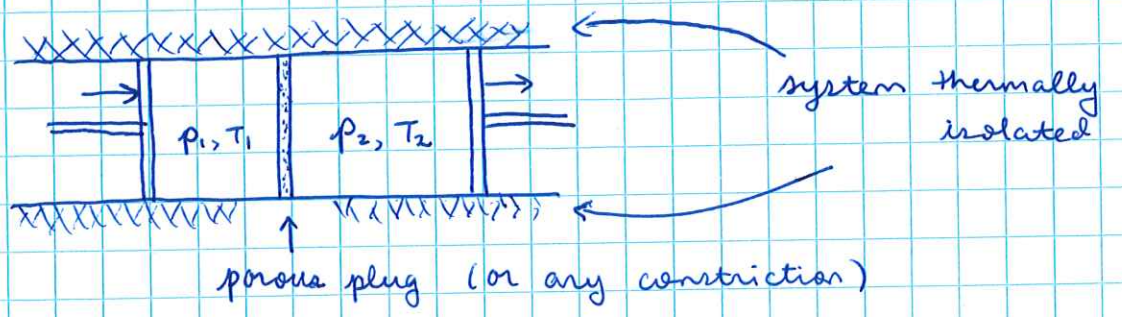
Joule-Thomson process:



→ gas/liquid ~~at~~ at const. pressure p_1 & temp. T_1 is steadily transferred to region w/ pressure p_2.

Q: what is ~~final~~ temp. T_2?

→ $\Delta E = E_2 - E_1 = E(T_2, p_2) - E(T_1, p_1)$.

& $W = p_2 V_2 - p_1 V_1$

$+p_2V_2$ = work done by gas in occupying vol. V_2 at pres. p_2

$+p_1V_1$ = work done on gas to move it out of vol. V_1 at pres. p_1.

$Q = 0 \Rightarrow \Delta E = -W \Rightarrow E_2 - E_1 = p_1V_1 - p_2V_2$

(first law)

$\Rightarrow E_2 + p_2V_2 = E_1 + p_1V_1$ ↓ $\mathcal{H} = E + pV$ (enthalpy).

$\Rightarrow \mathcal{H}_1 = \mathcal{H}_2$ → enthalpy conserved.

or $\mathcal{H}(T_1, p_1) = \mathcal{H}(T_2, p_2)$

(c.f. $E(T_1, p_1) = E(T_2, p_2)$ for free expansion).

- For ideal gas: $\mathcal{H} = E + pV = E(T) + \nu RT \Rightarrow \mathcal{H} = \mathcal{H}(T)$ for ideal gas.

& $\mathcal{H}(T_1) = \mathcal{H}(T_2) \Rightarrow T_1 = T_2$

→ no temp. change of ideal gas in Joule-Thomson process.

More generally, we may determine small change in T ~~due~~ due to small change in p at const. enthalpy $\mathcal{H}$ is the following way:

~~$d\mathcal{H} = TdS + Vdp$ (general relation).~~

~~for $d\mathcal{H} = 0$ ⇒ ($\mathcal{H}$ = const.)~~

$$d\mathcal{H} = \left(\frac{\partial \mathcal{H}}{\partial T}\right)_p dT + \left(\frac{\partial \mathcal{H}}{\partial p}\right)_T dp = 0 \quad \mathcal{H} = \text{const.}$$

$$\Rightarrow \left(\frac{\partial T}{\partial p}\right)_{\mathcal{H}} = \frac{-(\partial \mathcal{H}/\partial p)_T}{(\partial \mathcal{H}/\partial T)_p} \qquad \left(\frac{\partial \mathcal{H}}{\partial T}\right)_p = C_p.$$

$$= -\frac{1}{C_p}\left(\frac{\partial \mathcal{H}}{\partial p}\right)_T.$$

Now use the general rel.'n:

$$d\mathcal{H} = TdS + Vdp \qquad S = S(T,p)$$

$$= T\left(\frac{\partial S}{\partial T}\right)_p dT + \left[T\left(\frac{\partial S}{\partial p}\right)_T + V\right]dp.$$

$$= T\left(\frac{\partial S}{\partial T}\right)_p dT + \underbrace{\left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right]}_{=\left(\frac{\partial \mathcal{H}}{\partial p}\right)_T} dp$$

$$\Rightarrow \left(\frac{\partial T}{\partial p}\right)_{\mathcal{H}} = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right] \qquad \alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

$$= \frac{V}{C_p}(T\alpha - 1).$$

(expansion coeff.)

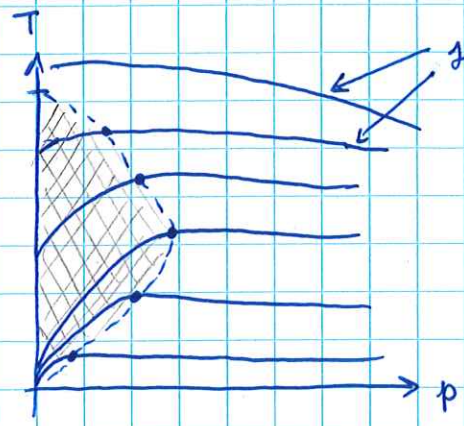
[For ideal gas, $\alpha = 1/T \Rightarrow (\partial T/\partial p)_{\mathcal{H}} = 0$ ✓]

Also note: $d\mathcal{H} = 0 \Rightarrow \left(\frac{\partial S}{\partial p}\right)_{\mathcal{H}} = -\frac{V}{T}$.

$$\Rightarrow \Delta S = \left(\frac{\partial S}{\partial p}\right)_{\mathcal{H}} \Delta p = -\frac{V}{T}\Delta p > 0 \text{ if } \Delta p < 0.$$

⇒ irreversible process, entropy increases.

Curves of const. enthalpy $\mathcal{H}$ generally ~~take~~ have the following qualitative form:



(✱ will do concrete ex. on homework using vdW gas)

• = pt.'s where $\left(\frac{\partial T}{\partial p}\right)_{\mathcal{H}} = 0$.

--- = "inversion curve". $\left(\frac{\partial T}{\partial p}\right)_{\mathcal{H}} = 0$.

→ hatched region has $\left(\frac{\partial T}{\partial p}\right)_{\mathcal{H}} > 0$. In this region, a small pressure drop will lead to a decrease in T. In this region of the (T, p) plane Joule-Thomson process is used to cool, or even liquefy, gases.

Outside the hatched region, gas ~~will be heated~~ warms up in the Joule-Thomson process.

The slope $\mu \equiv \left(\frac{\partial T}{\partial p}\right)_{\mathcal{H}}$ is called the "Joule-Thomson ~~coe~~ coefficient".

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Appendix: C_V for vdW gas.

→ vdW eqn. of state: $\left(p + \frac{a}{v^2}\right)(v - b) = RT$ $\quad v = V/\nu$ = molar vol.

→ fundamental rel.'n: $dE = T\,dS - p\,dV$ ↳ $S = S(T, V)$

$$= T\left(\frac{\partial S}{\partial T}\right)_V dT + \left[T\left(\frac{\partial S}{\partial V}\right)_T - p\right] dV$$

↳ Maxwell rel.'n $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$

$$= T\left(\frac{\partial S}{\partial T}\right)_V dT + \underbrace{\left[T\left(\frac{\partial p}{\partial T}\right)_V - p\right]}_{\left(\frac{\partial E}{\partial V}\right)_T} dV.$$

$$\Rightarrow \left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V - p \underset{\substack{\uparrow \\ \text{vdW eqn. of state.}}}{=} \frac{a}{v^2} = \frac{a\nu^2}{V^2}.$$

Integrating w.r.t V: $E(T, V) = f(T) - \frac{a\nu^2}{V}$. or $\varepsilon(T, v) = \frac{f(T)}{\nu} - \frac{a}{v}$.

w/ $E = \nu\varepsilon$ ↑ energy per mole.

$$\Rightarrow C_V = \left(\frac{\partial E}{\partial T}\right)_V = f'(T). \quad \& \quad c_V = \frac{f'(T)}{\nu}$$

→ to find $f(T)$, consider the dilute limit $v \to \infty$:

$$\varepsilon(T, v) = \frac{f(T)}{\nu} - \frac{a}{v} \xrightarrow[v \to \infty]{} \frac{f(T)}{\nu}$$

In the dilute limit, the gas becomes ideal: $\varepsilon(T, v \to \infty) = c_V T$. ↑ ideal gas c_V.

$$\Rightarrow \frac{f(T)}{\nu} = c_V T.$$

$$\Rightarrow c_V^{(vdW)} = c_V^{(\text{ideal gas})}$$

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Summary.

- First law: $\Delta E = Q - W$, Q = heat absorbed, W = work done by system.

  $dE = đQ - đW$ (differential form)

- Second law: $\Delta S_{tot} \geq 0 \rightarrow \begin{cases} \Delta S_{tot} > 0 & \text{"irreversible process".} \\ \Delta S_{tot} = 0 & \text{"reversible process"} \end{cases}$

- Heat bath/reservoir: $\Delta S = \frac{Q}{T}$, Q = heat absorbed by bath.

  $\rightarrow \Delta T = Q/C$ is negligible

  C: heat capacity of bath, assumed very large.

Heat engines & refrigerators.

- Heat engine = device that absorbs heat q & converts part of the energy to work w.

- In more detail: device (thermo. sys.) M takes through a cyclic process in which heat q_1 is absorbed from a ~~the~~ high-temp reservoir, converted to work w, & remaining heat q_2 dumped to a "heat sink" (lower-temp. reservoir).

→ we will see that the laws of thermo. ultimately ~~limited~~ limit the efficiency (to be defined below) of such a heat engine.

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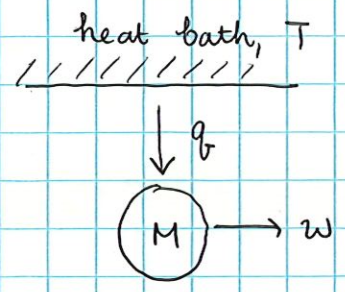
Now, a "perfect" engine would, in each cycle, convert all heat q into work w:



→ such a device would not be in conflict w/ first law of thermo.

$(q > 0 \ \& \ w > 0)$

Unfortunately, second law forbids such a machine:

$$\Delta S_{tot} = \Delta S_M + \Delta S_{heat\text{-}bath} \geq 0$$

→ after cycle, $\Delta S_M = 0$ (comes back to initial state) & $\Delta S_{heat\text{-}bath} = -\frac{q}{T}$

$$\Rightarrow \Delta S_{tot} = -\frac{q}{T} = -\frac{w}{T} < 0 \quad (\text{if } w > 0). \ \times$$

↑ contradicts second law!

(if $w < 0$, process is allowed but is useless).

~~Second law forbids such~~

→ Kelvin's statement of second law: "impossible to construct a perfect heat engine".

→ perfect heat engine requires spontaneous occurence of a process in ~~the~~ which some amount of energy, distributed randomly among the enormous # of DOF of the bath, converts into motion of single DOF doing work (e.g., a piston). ; i.e., decrease in total S.

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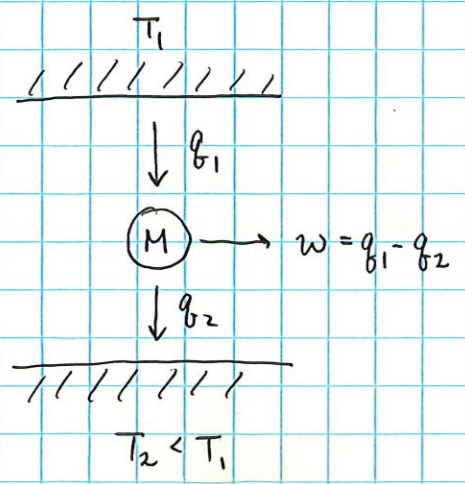
- However, by introducing <u>another</u> heat bath at lower T, where entropy increases in the process, we can fix the situation:



second law: $\Delta S_{tot} = \Delta S_1 + \Delta S_2 + \cancel{\Delta S_M} \geq 0$ (0, cyclic process.)

$$\rightarrow \quad -\frac{q_1}{T_1} + \frac{q_2}{T_2} \geq 0$$

$$-\frac{q_1}{T_1} + \frac{(q_1 - w)}{T_2} \geq 0$$

$$\Rightarrow \quad \frac{w}{T_2} \leq q_1 \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\text{or} \quad w \leq q_1 \left(1 - \frac{T_2}{T_1} \right).$$

- Define the "efficiency" of the engine $\eta \equiv \dfrac{w}{q_1} = \dfrac{\text{(what we get out)}}{\text{(what is put in)}}$

Then second law $\Rightarrow$ $\eta \leq \left(1 - \dfrac{T_2}{T_1} \right) \leq 1.$

$\rightarrow$ an efficient engine requires $T_2 \ll T_1$; i.e., high T_1, low T_2.

- The <u>max.</u> possible efficiency is achieved for a <u>reversible</u> process, when $\Delta S_{tot} = 0$. $\Rightarrow$ $\eta_{max} = 1 - \dfrac{T_2}{T_1} = \dfrac{T_1 - T_2}{T_1}$. "Carnot engine".

$\left\{ \begin{array}{l} \text{Roughly: no "friction" in the process.} \\ \text{More ~~pe~~ precisely: avoid friction \& "large" heat transfers (which} \\ \quad \text{would be irreversible) in order to make an} \\ \quad \text{efficient heat engine.} \end{array} \right.$

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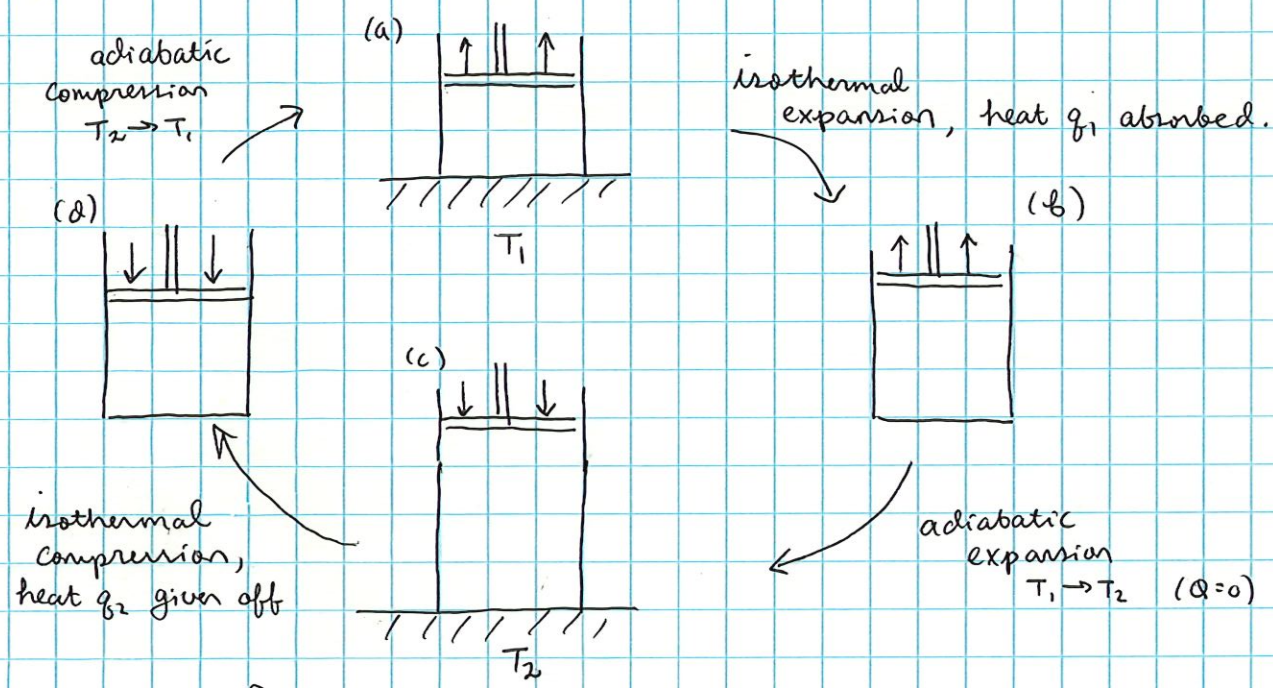
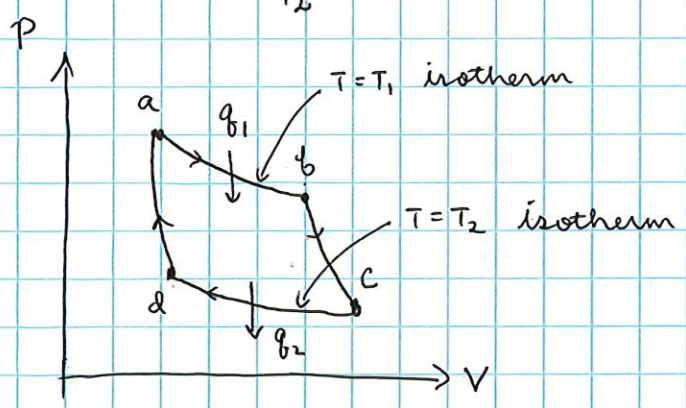
<u>Ex</u>: Consider the following 4-step process carried out on a gas – "Carnot cycle".

(need not be ideal, could even be a liquid.)





→ each stage of the cycle is reversible ⇒ $\eta = 1 - \frac{T_2}{T_1} = \eta_{max}$.

The "working substance" (ie the substance absorbing/expelling heat & doing work) can be anything. For a concrete example, we will compute explicitly η for an ideal gas.

Ex: working substance = ideal gas $\Rightarrow$ $pV = NT$ & $E = C_V T$.

$a \to b$: isothermal process $(T = T_1)$ $\quad W_{a\to b} = \int_{V_a}^{V_b} p\,dV = NT_1 \int_{V_a}^{V_b} \frac{dV}{V} = NT_1 \ln \frac{V_b}{V_a}$.

$b \to c$: adiabatic process $(T_1 \to T_2)$ $\quad W_{b\to c} = -\Delta E = -C_V (T_2 - T_1)$

$c \to d$: isothermal process $(T = T_2)$ $\quad W_{c\to d} = \int_{V_c}^{V_d} p\,dV = NT_2 \int_{V_c}^{V_d} \frac{dV}{V} = NT_2 \ln \frac{V_d}{V_c}$.

$d \to a$: adiabatic process $(T_2 \to T_1)$ $\quad W_{d\to a} = -\Delta E = -C_V (T_1 - T_2)$.

$$\Rightarrow w = W_{a\to b} + W_{b\to c} + W_{c\to d} + W_{d\to a} = NT_1 \ln \frac{V_b}{V_a} + NT_2 \ln \frac{V_d}{V_c}.$$

To simplify, use adiabatic cond.'n $TV^{\gamma-1} = \text{const}$.

$$\Rightarrow T_1 V_b^{\gamma-1} = T_2 V_c^{\gamma-1}$$

$$\& \quad T_1 V_a^{\gamma-1} = T_2 V_d^{\gamma-1}$$

$$\Rightarrow \frac{V_b}{V_a} = \frac{V_c}{d}.$$

$$\Rightarrow w = N(T_1 - T_2) \ln \frac{V_b}{V_a}.$$

To find η, need q_1: $\quad q_1 = Q_{a\to b} = \Delta E_b + W_{a\to b}$ $\quad \Delta E$ for isothermal $T = T_1$ process

$$= +NT_1 \ln \frac{V_b}{V_a}.$$

$$\Rightarrow \eta = \frac{w}{q_1} = \frac{T_1 - T_2}{T_1} \quad \checkmark.$$

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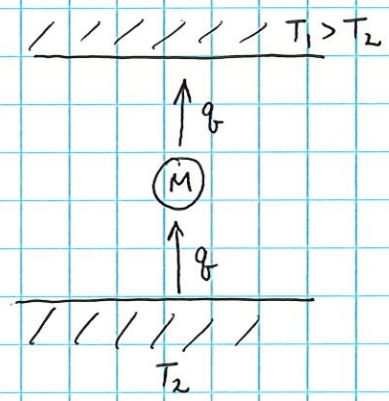
refrigerator = device, operating in a cycle, that removes heat from low-T reservoir & rejects to reservoir at higher-T (essentially: heat engine in reverse).

→ a "perfect" refrigerator:



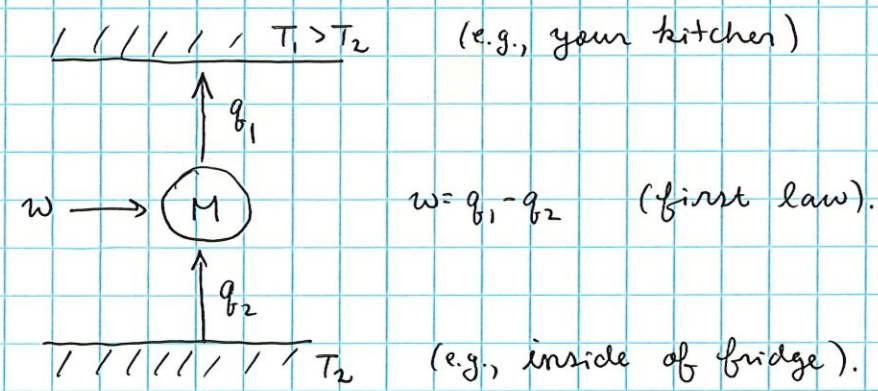
→ violates second law: $\Delta S_{tot} = \Delta S_1 + \Delta S_2$ (in a cycle)

$$= \frac{q}{T_1} - \frac{q}{T_2}$$

$$= q\left(\frac{1}{T_1} - \frac{1}{T_2}\right) < 0 \quad \times .$$

→ Clausius formulation of second law: "impossible to construct a perfect refrigerator".

a "real" refrigerator:



→ "coefficient of performance" $\kappa \equiv \frac{q_2}{w}$

second law $\Rightarrow \kappa \leq \frac{T_2}{T_1 - T_2}$.

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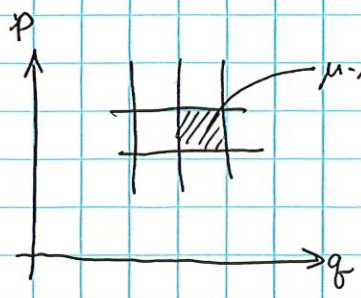
Summary.

- Stat. description of systems of particles:



μ-state = phase space cell w/ vol. $(2\pi\hbar)^s$

s = # of DOF.

(classical)

μ-state $\longleftrightarrow \psi_{n_1 n_2 \ldots n_f}$.

specified by f quantum #'s $\{n_1, n_2, \ldots n_f\}$

(quantum).

→ $\Omega(E)$ = # of accessible states w/ energy E (or energy $\in (E, E+\delta E)$).

$S = \ln \Omega$ (entropy).

→ Fundamental postulate: prob. (μ-state) $= \dfrac{1}{\Omega(E)}$, all μ-states equally probable.

- Return to μ-scopic stat. approach. Fundamental ~~exp~~ aspects have already been laid out, now learn how to calculate in various different circumstances.

Microcanonical ensemble:

- In discussing stat. approach, we have mainly dealt w/ isolated/closed systems. Such a sys. characterized by conserved tot. energy E, (or narrow range of ~~energy~~ energies $(E, E+\delta E)$). Also assumed to have fixed particle # = N & fixed vol. V (could have other externally specified param.'s; e.g., magnetization M, etc. but consider only V now).

- In equil: prob. (μ-state) $= \dfrac{1}{\Omega(E)}$ "microcanonical distb.'n".

$\Omega(E)$ = # of accessible w/ energy E

→ In stat. approach, we always imagine an <u>ensemble</u> of similarly prepared systems. In case of isolated sys., all member of ensemble have same (E, N, V). ~~Ensemble of such system~~

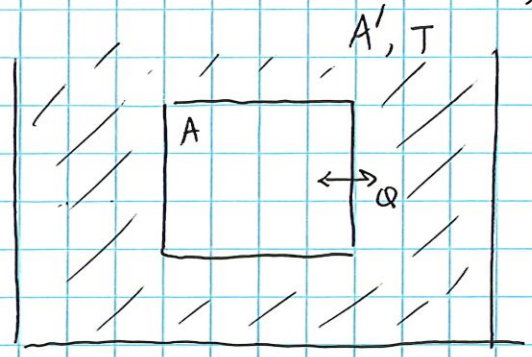
→ ensemble of such system = "microcanonical ensemble".

<u>Canonical ensemble:</u>

· In practice, it is useful to know ~~how~~ the stat. description of a system not at fixed E (like in μ-canonical ensemble) but fixed <u>temp.</u> T.

→ Sys. A of interest in thermal contact w/ heat reservoir A' that maintains const. temp. T. Requires $|A'| \gg |A|$

notation means A' has many more DOF than A.



→ sys. $A^{(0)} = A + A'$ = closed

A <u>not</u> closed

<u>Q</u>: what is prob. P_r to find sys. in any individual μ-state r w/ energy E_r? (Here we adopt QM description; similar in CM).

→ we have studied this problem before. Let $A^{(0)} = A + A'$ = closed sys. then tot. energy $E^{(0)}$ of $A^{(0)}$ = const. & $E^{(0)} = E_r + E'$ or $E' = E^{(0)} - E_r$.

energy of A'

⇒ # of accessible states s.t. A ~~has~~ is in state r = $\Omega'(E^{(0)} - E_r)$.

$\Rightarrow P_r \propto \Omega'(E^{(0)} - E_r) \rightarrow$ prob. prop. to # of accessible states w/ specified condition

& normalization $\sum_r P_r = 1$.

· now use the fact that $|A'| \gg |A|$, so that $E^{(0)} \gg E_r$:

$$\Omega'(E^{(0)} - E_r) = e^{S'(E^{(0)} - E_r)} \qquad (S' = \text{entropy of } A').$$

& expand S': $$S'(E^{(0)} - E_r) \simeq S'(E^{(0)}) - \underbrace{\left(\frac{\partial S'}{\partial E'}\right)_{E' = E^{(0)}}}_{= \frac{1}{T},\ T = \text{temp. of reservoir.}} E_r + \dots$$

$$\Rightarrow S'(E^{(0)} - E_r) \simeq S'(E^{(0)}) - \frac{E_r}{T}.$$

$$\Rightarrow \Omega'(E^{(0)} - E_r) \simeq \Omega'(E^{(0)})\, e^{-E_r/T}.$$

& $P_r \propto e^{-E_r/T}$. ($\Omega'(E^{(0)})$ is simply a const.)

or $P_r = C\, e^{-E_r/T}$.

$\rightarrow C$ is determined by normalization $\sum_r P_r = 1$. $\Rightarrow C^{-1} = \sum_r e^{-E_r/T}$.

$$\Rightarrow \boxed{P_r = \frac{e^{-E_r/T}}{\sum_r e^{-E_r/T}}}.$$

$\rightarrow$ prob. to find sys. in μ-state r w/ energy E_r when in contact w/ heat res. at temp. T.

"canonical (or Gibbs) distb.'n".

Notation: The normalization const. plays an especially important role in stat. phys.: $\boxed{Z \equiv \sum_r e^{-E_r/T}}$ "partition fn.".

$$\rightarrow P_r = \frac{e^{-E_r/T}}{Z}.$$

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Notation: $\beta \equiv \frac{1}{T}$: $P_r = \frac{e^{-\beta E_r}}{Z}$, $Z = \sum_r e^{-\beta E_r}$.

→ <u>ensemble</u> of system in contact w/ heat res. at temp. T (& w/ same N, V), distributed according to $P_r = e^{-\beta E_r}/Z$ is called the "canonical ensemble".

- averages calculated according to:

$$\overline{O} = \sum_r P_r O_r, \qquad O_r = \text{value of observable } O \text{ in } \mu\text{-state } r.$$

$$= \sum_r \frac{e^{-\beta E_r}}{Z} O_r.$$

<u>Ex</u>: $O \to E$ = energy of A: $\overline{E} = \sum_r \frac{e^{-\beta E_r}}{Z} E_r$.

⇒ In canonical ensemble, $\overline{E}$ is not specified but is derived

(→ Come back to fluctuation of E in canonical ensemble.)

- In classical case: $P_r \to P(q,p)\frac{dq\,dp}{(2\pi\hbar)^s} = e^{-\beta E(q,p)}\frac{dq\,dp}{(2\pi\hbar)^s}$

$$\begin{cases} q = (q_1 q_2 \cdots q_s) \\ p = (p_1 p_2 \cdots p_s) \end{cases}$$

↑ # of states in vol. $dq\,dp$ in phase space

$$dq\,dp = dq_1 \cdots dq_s\, dp_1 \cdots dp_s.$$

$$\sum_r \to \int \frac{dq\,dp}{(2\pi\hbar)^s}.$$

$$\& \quad \overline{O} = \int \frac{dq\,dp}{(2\pi\hbar)^s} \frac{e^{-\beta E(q,p)}}{Z} O(q,p).$$

$$Z = \int \frac{dq\,dp}{(2\pi\hbar)^s} e^{-\beta E(q,p)}$$

* provisional — we'll have to correct this later b/c of QM.

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· Note that we need to distinguish btwn. P_r = prob. to find syst. in μ-state r vs. $P(E)$ = prob. syst. has energy E (or energy in range $(E, E+\delta E)$).

$$\rightarrow P(E) = \sum_r{}' P_r$$

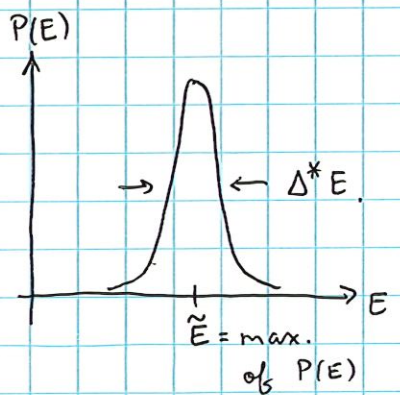
sum over states r s.t. $E < E_r < E+\delta E$.

$$= \frac{e^{-\beta E}}{Z} \underbrace{\left(\sum_r{}'\right)}_{=\Omega(E)}$$

$\Omega(E)$, # of states s.t. $E < E_r < E+\delta E$.

$$\Rightarrow P(E) = \frac{\Omega(E)\, e^{-\beta E}}{Z}.$$

$\rightarrow$



· $\Omega(E)$ increasing & $e^{-\beta E}$ decreasing

$\Rightarrow P(E)$ peaked at some $\tilde{E}$

· max is sharper w/ increasing size of A (return to this).

# of DOF.

Ex: (Maxwell velocity distb.'n). Usually, we will take syst. A' to be macro.; i.e., contain large # of DOF. However, canonical distb.'n also applies when syst. A is small; e.g., consisting of just a single particle.

$\rightarrow$ Consider a classical monatomic gas. Take A = single gas particle & A' = remaining molecules, acting as heat res. at temp. T.

$$E = \frac{1}{2} m \vec{v}^2 = \frac{\vec{p}^2}{2m} \quad \text{(energy of single particle).}$$

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· Canonical distb.'n $\Rightarrow$ $P(\vec{x},\vec{p})\, d^3\vec{x}\, d^3\vec{p} \propto e^{-\beta \vec{p}^2/2m}\, d^3\vec{x}\, d^3\vec{p}$ ($q \to \vec{x}$)

$\to$ prob. that particle's position is in range $\vec{x}$ & $\vec{x}+d\vec{x}$, & momentum btwn. $\vec{p}$ & $\vec{p}+d\vec{p}$

· prob. that particle has momentum $\in (\vec{p}, \vec{p}+d\vec{p})$, indep. of $\vec{x}$, is:

$$g(\vec{p})\, d^3\vec{p} = \int d^3\vec{x}\; P(\vec{x},\vec{p}) \propto e^{-\beta\vec{p}^2/2m}\, d^3\vec{p}$$

$\uparrow$ momentum distb.'n fn.

write $g(\vec{p}) = C e^{-\beta\vec{p}^2/2m}$ & obtain C by normalization $\int d^3\vec{p}\, g(\vec{p}) = 1$:

$$\int d^3\vec{p}\; g(\vec{p}) = C \int d^3\vec{p}\; e^{-\beta\vec{p}^2/2m}$$

$$= C\left(\int_{-\infty}^{+\infty} dp_x\, e^{-\beta p_x^2/2m}\right)\left(\int_{-\infty}^{+\infty} dp_y\, e^{-\beta p_y^2/2m}\right)\left(\int_{-\infty}^{+\infty} dp_z\, e^{-\beta p_z^2/2m}\right)$$

$$= C\left(\int_{-\infty}^{+\infty} dp\; e^{-\beta p^2/2m}\right)^3 \qquad y = \sqrt{\frac{\beta}{2m}}\, p$$

$$= C\left(\frac{2m}{\beta}\right)^{3/2} \underbrace{\left(\int_{-\infty}^{+\infty} dy\, e^{-y^2}\right)^3}_{=\sqrt{\pi}}$$

$$= 1$$

$$\Rightarrow \quad C = \left(\frac{1}{2\pi m T}\right)^{3/2} \qquad (T = 1/\beta).$$

$$\Rightarrow \quad g(\vec{p}) = \left(\frac{1}{2\pi m T}\right)^{3/2} e^{-\vec{p}^2/2mT}.$$

using $\vec{p} = m\vec{v}$, also obtain distb.'n fn. of velocity $f(\vec{v})$ from $f(\vec{v})\, d^3\vec{v} = g(\vec{p})\, d^3\vec{p}$:

$$\boxed{f(\vec{v}) = \left(\frac{m}{2\pi T}\right)^{3/2} e^{-\frac{m\vec{v}^2}{2T}}}$$

"maxwell velocity distb.'n".

$\to f(\vec{v})\, d^3\vec{v}$ = prob. that particle has velocity in range $\vec{v}$ to $\vec{v}+d\vec{v}$.

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Summary.

Microcanonical ensemble (μCE)	Canonical ensemble (CE).
• Closed sys.	• sys. in contact w/ heat res. at T
• E = fixed (or $(E, E+\delta E)$)	• T = fixed
• $P_r = \begin{cases} \frac{1}{\Omega(E)} & \text{if } E < E_r < E+\delta E \\ 0 & \text{else} \end{cases}$ $\uparrow$ μ-state label	• $P_r = \frac{e^{-E_r/T}}{Z}$, $Z = \sum_r e^{-E_r/T}$ (partition fn.) $(\beta \equiv 1/T)$

Ex: (spin in H-field) Consider single spin 1/2 in contact w/ heat res. at temp. T in ext. magnetic field H.

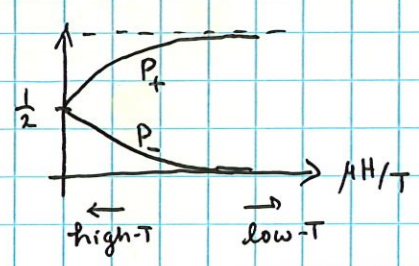
Let m = spin projection along dir. of H.

$$\rightarrow \text{energies} = \begin{cases} -\mu H & m = +\frac{1}{2} \\ +\mu H & m = -\frac{1}{2} \end{cases} \Rightarrow E_r \rightarrow E_\pm = \mp \mu H \quad (2 \text{ states}).$$

$$\Rightarrow P_r \rightarrow P_\pm = \frac{e^{-\beta E_\pm}}{Z} = \frac{e^{\pm \beta \mu H}}{Z}$$

$$\& \quad Z = \sum_{r=\pm} e^{-\beta E_r} = e^{-\beta E_+} + e^{-\beta E_-} = e^{\beta \mu H} + e^{-\beta \mu H} = 2\cosh(\beta \mu H).$$

$$\Rightarrow P_\pm = \frac{e^{\pm \beta \mu H}}{2\cosh(\beta \mu H)}, \quad \text{important parameter} = \beta \mu H = \frac{\mu H}{T} \quad \text{(ratio of field strength to temp.)}$$



avg. moment: $\bar{\mu} = \sum_{r=\pm} P_r \mu_r = P_+ \mu + P_- (-\mu) = \mu \times \frac{e^{\beta \mu H} - e^{-\beta \mu H}}{e^{\beta \mu H} + e^{-\beta \mu H}} = \mu \tanh(\beta \mu H)$

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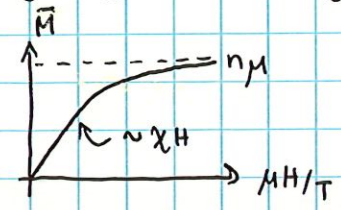
$$\Rightarrow \quad \bar{\mu} = \mu \tanh\left(\frac{\mu H}{T}\right)$$

If sys. has n spin-$1/2$'s per unit vol., the magnetization density is

$$\bar{M} = n\bar{\mu} = n\mu \tanh\left(\frac{\mu H}{T}\right).$$



At low fields $\mu H \ll T$, use $\tanh x \simeq x$ $(x \ll 1)$, to obtain:

$$\bar{M} \simeq \frac{n\mu^2}{T} \times H = \chi H, \qquad \chi \equiv \frac{n\mu^2}{T}$$

(χ: "magnetic susceptibility") $\rightarrow$ $\chi \sim 1/T$ is "Curie's law" for paramagnetic materials

---

<u>Properties of Z:</u>

$\rightarrow$ knowledge of Z allows us to obtain stat. averages.

<u>Ex:</u> (avg. energy)

$$\bar{E} = \sum_r P_r E_r = \frac{1}{Z} \sum_r e^{-\beta E_r} E_r$$

$$= -\frac{1}{Z} \frac{\partial}{\partial \beta} \sum_r e^{-\beta E_r}$$

$$= -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

$$\Rightarrow \boxed{\bar{E} = -\frac{\partial}{\partial \beta} \ln Z}$$

<u>Ex:</u> (avg. moment for spin-$\frac{1}{2}$)

$$\bar{\mu} = \sum_{r=\pm} P_r \mu_r = \frac{1}{Z} \sum_{r=\pm} e^{+\beta \mu_r H} \mu_r \qquad (\mu_\pm = \pm\mu)$$

$$= +\frac{1}{\beta} \frac{1}{Z} \frac{\partial}{\partial H} Z$$

$$\Rightarrow \bar{\mu} = +T \frac{\partial}{\partial H} \ln Z.$$

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Ex: (energy dispersion) $\overline{\Delta E^2} = \overline{E^2} - \overline{E}^2$

$$\rightarrow \overline{E^2} = \sum_r P_r E_r^2 = \frac{1}{Z}\sum_r e^{-\beta E_r} E_r^2 = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}$$

$$\Rightarrow \overline{E^2} = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} = \frac{\partial}{\partial \beta}\underbrace{\left(\frac{1}{Z}\frac{\partial Z}{\partial \beta}\right)}_{-\overline{E}} + \underbrace{\frac{1}{Z^2}\left(\frac{\partial Z}{\partial \beta}\right)^2}_{\overline{E}^2}$$

$$\Rightarrow \overline{\Delta E^2} = \overline{E^2} - \overline{E}^2 = -\frac{\partial \overline{E}}{\partial \beta} \quad \text{or} \quad \overline{\Delta E^2} = \frac{\partial^2 \ln Z}{\partial \beta^2}$$

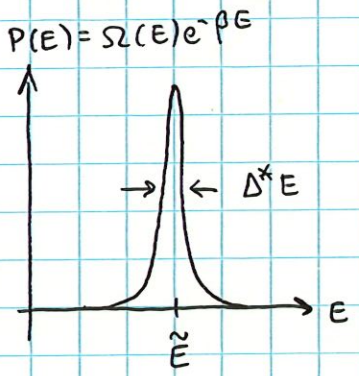
Can write this in another way: $\frac{\partial}{\partial \beta}\overline{E} = \frac{\partial}{\partial (1/T)}\overline{E} = -T^2 \frac{\partial \overline{E}}{\partial T} = -T^2 C_V$

(have implicitly kept vol. V fixed)

$$\Rightarrow \boxed{\overline{\Delta E^2} = T^2 C_V}$$

→ energy fluct. related to ability of sys. to absorb heat. (measured by heat capacity C_V).

We can now return to prob. distb'n of energy $P(E)$ in the CE:



we have found: $\Delta^* E = \sqrt{\overline{\Delta E^2}} = T\sqrt{C_V}$.

$$\Rightarrow \frac{\Delta^* E}{\tilde{E}} = \frac{T\sqrt{C_V}}{\tilde{E}}$$

$\tilde{E} \sim N$, $C_V \sim N$ are extensive (N = # of particles)

$$\Rightarrow \frac{\Delta^* E}{\tilde{E}} \sim \frac{1}{\sqrt{N}}$$

→ width of $P(E)$ vanishingly small for macro. sys. $N \gg 1$.

Ex: (monatomic ideal gas) $C_V = \frac{3}{2}N$ & $\tilde{E} = \overline{E} = \frac{3}{2}NT \Rightarrow \frac{\Delta^* E}{\tilde{E}} = \sqrt{\frac{2}{3N}}$.

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Thermodynamics in the CE:

- To analyze thermo. relations, we will adopt a generalization of the entropy $S = -\ln\Omega$ from the μCE. We define:

$$S \equiv -\sum_r P_r \ln P_r \qquad (\text{"Gibbs entropy"}).$$

→ here P_r can be any distb'n over μ-states r.

- First check that this recovers familiar entropy in μCE:

$$\mu CE \Rightarrow P_r = \begin{cases} \frac{1}{\Omega(E)} & E < E_r < E+\delta E \\ 0 & \text{else} \end{cases} \qquad (\text{recall } \Omega = \#\text{ of accessible states}).$$

$$\Rightarrow S = -\sum_r P_r \ln P_r = -\sum_r{}' \frac{1}{\Omega}\ln\frac{1}{\Omega} = +\frac{1}{\Omega}\ln\Omega\underbrace{\left(\sum_r{}'\right)}_{=\Omega} = \ln\Omega \quad \checkmark.$$

↑ sum over r s.t. $E < E_r < E+\delta E$

- In CE, we have: $P_r = \dfrac{e^{-\beta E_r}}{Z}$

$$\Rightarrow S = -\sum_r P_r \ln P_r = -\sum_r P_r(-\beta E_r - \ln Z) \qquad \sum_r P_r = 1.$$

$$= +\beta\underbrace{\sum_r P_r E_r}_{\bar{E}} + \ln Z$$

$$\Rightarrow S = \beta\bar{E} + \ln Z$$

or $-T\ln Z = \underbrace{\bar{E} - TS}_{=F,}$ Helmholtz free energy.

$$\Rightarrow \boxed{F = -T\ln Z}$$ → relates μ-scopic info. in Z to thermo. potential F (a macro. quantity)

(c.f. $\underset{\text{macro.}}{S} = \ln\underset{\text{micro.}}{\Omega}$ in μCE)

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Summary.

Canonical ensemble (CE): · fixed T (& fixed vol. V & particle # N).

· $P_r = \dfrac{e^{-E_r/T}}{Z}$, $Z = \sum_r e^{-E_r/T}$

r = μ-state label.

· $F = \bar{E} - TS = -T\ln Z = -T\ln\left(\sum_r e^{-E_r/T}\right)$ Helmholtz free energy.

· $\bar{E} = -\dfrac{\partial}{\partial\beta}\ln Z = -T^2\dfrac{\partial}{\partial T}\left(\dfrac{F}{T}\right)$

· $S = -\sum_r P_r \ln P_r = -\dfrac{\partial}{\partial T}(T\ln Z) = -\dfrac{\partial F}{\partial T}$.

· Connect S in CE w/ S in μCE.

$$\rightarrow \quad Z = \sum_r e^{-\beta E_r} = \sum_E \Omega(E)\, e^{-\beta E}$$

$\downarrow$ $\Omega(E)e^{-\beta E}$ sharply peaked near $E = \tilde{E}$. (in macro. sys.)

$$\simeq \Omega(\tilde{E})\, e^{-\beta\tilde{E}}$$

$\downarrow$ ~~in a macro sys.~~ sharp peak $\Rightarrow$ $\bar{E} = \tilde{E}$

$$= \Omega(\bar{E})\, e^{-\beta\bar{E}}$$

$$\Rightarrow \ln Z = \ln\Omega(\bar{E}) - \beta\bar{E}.$$

& we also have $-T\ln Z = F = \bar{E} - TS \Rightarrow \ln Z = S - \beta\bar{E}$

$\Rightarrow S = \ln\Omega(\bar{E})$. $\rightarrow$ entropy in CE is same as ~~entropy in a~~ μ-canonical entropy of closed sys. w/ energy $E = \bar{E}$.

[Note: to relate entropy in μCE & CE, we use fact that $P(E) \propto \Omega(E)e^{-\beta E}$ is sharply peaked. This is true in a macroscopic system. If sys is not macro., entropies will, in general, be different; i.e. $S_{CE} \neq S_{\mu CE}$

$\beta\bar{E} + \ln Z$ $\qquad$ $\ln\Omega(\bar{E})$]

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· In the μCE, we found the fundamental equil. rel.'n:

$$dE = TdS - pdV \quad \text{or} \quad dS = \frac{1}{T}dE + \frac{p}{T}dV.$$

→ we would like to determine the analogous rel.'n starting in the CE.

→ Start from $\sum_r P_r = 1 \Rightarrow \underbrace{\sum_r e^{(F-E_r)/T}}_{} = 1$ (using $Z = e^{-F/T}$).

view this as fn. of T & any other external param.'s specifying macro-state.

→ For simplicity, take vol. V as single external param.

Taking the differential of the rel.'n above:

$$\sum_r \underbrace{d\left[\frac{(F-E_r)}{T}\right]}_{\frac{1}{T}(dF - dE_r) - \frac{1}{T^2}(F-E_r)dT.} e^{(F-E_r)/T} = 0.$$

$$\Rightarrow \sum_r \frac{e^{(F-E_r)/T}}{T}\left[dF - dE_r - \frac{(F-E_r)}{T}dT\right] = 0.$$

$$\Rightarrow \underbrace{\left(\sum_r e^{(F-E_r)/T}\right)}_{=\sum_r P_r = 1} dF = \underbrace{\sum_r e^{(F-E_r)/T} dE_r}_{} + \frac{dT}{T}\underbrace{\left(F - \underbrace{\sum_r e^{(F-E_r)/T} E_r}_{\sum_r P_r E_r = \bar{E}}\right)}_{F - \bar{E} = -TS}$$

$$= \left(\sum_r e^{(F-E_r)/T} \frac{\partial E_r}{\partial V}\right) dV = \left(-\sum_r e^{(F-E_r)/T} p_r\right) dV = -\bar{p}\, dV$$

pressure $p_r = -\frac{\partial E_r}{\partial V}$.

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

$$\Rightarrow S = -\left(\frac{\partial F}{\partial T}\right)_V \quad \& \quad p = -\left(\frac{\partial F}{\partial V}\right)_T.$$

⌈ also follows from $F = \bar{E} - TdS \Rightarrow dF = d\bar{E} - TdS - SdT = \cancel{TdS} - pdV - \cancel{TdS} - SdT = -SdT - pdV$

but now also derived purely from stat. description in the CE. ⌋

03/07/25

- In CE, second law of thermo. formulated in terms of free energy:

  spontaneous processes tend to decrease free energy $\Delta F < 0$.

  & $F = \min.$ in equil.

  (we proved this by considering total entropy S_{tot} of sys. + heat bath & using $\Delta S_{tot} \geq 0$).

- It is of some interest to see how first law is formulated in CE:

  Consider avg. energy $\bar{E} = \sum_r P_r E_r$.

→ under quasi-static change: $d\bar{E} = \sum_r E_r dP_r + \sum_r P_r dE_r$

Change in distb.'n among fixed energy levels

Change in energy levels w/ prob. of occupation fixed.

identify $đQ \equiv \sum_r E_r dP_r$ = heat absorbed.

→ check this makes sense: $đQ = \sum_r E_r dP_r$ ↳ $E_r = -T\ln Z - T\ln P_r$

$= T\sum_r (-\cancel{T}\ln Z - \ln P_r)\, dP_r$ ↳ $\sum_r dP_r = 0$, since $\sum_r P_r = 1$

$= -T\sum_r \ln P_r\, dP_r$

$= T\, d\left(-\sum_r P_r \ln P_r\right)$ ↳ $S = -\sum_r P_r \ln P_r$

$= T\, dS$ ✓

& identify $đW \equiv -\sum_r P_r dE_r$.

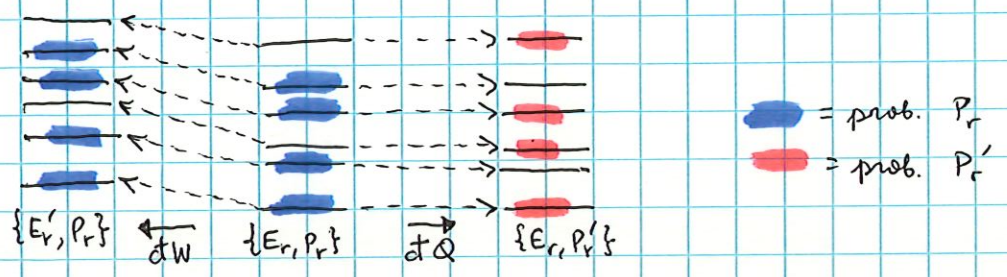
→ check: $đW = -\sum_r P_r dE_r = \left[\sum_r P_r \left(-\frac{\partial E_r}{\partial V}\right)\right] dV = \left(\sum_r P_r p_r\right) dV = \bar{p}\, dV$ ✓.

assume vol. V = only ext. param.

pressure

$\Rightarrow d\bar{E} = đQ - đW$ w/ $\begin{cases} đQ = \sum_r E_r dP_r \\ đW = -\sum_r P_r dE_r \end{cases}$

Schematically:



<u>Final note on CE:</u> CE constructed to describe sys. at fixed T in contact w/ heat res. (sys. not closed). However, when dealing w/ a macro. sys., where energy fluctuations are negligible, we can equivalently use CE to solve problems of the μCE, where energy is fixed (describing a closed sys.)

That is, given μCE w/ fixed energy E, use CE w/ T chosen s.t. $\bar{E}(T) = E$. All thermo. prop.'s will be exactly <u>equivalent</u> (except energy fluct., which vanish identically in μCE).

→ this is of significant practical importance b/c calculations are much <u>easier</u> in CE, since they involve unrestricted sum over <u>all</u> μ-states, while μCE involves restricted sum over μ-states r s.t. $E < E_r < E + \delta E$:

$$\overline{\mathcal{O}}_{\mu CE} = \frac{1}{\Omega(E)} \sum_r{}' \mathcal{O}_r \qquad \text{vs.} \qquad \overline{\mathcal{O}}_{CE} = \sum_r \frac{e^{-\frac{E_r}{T}}}{Z} \mathcal{O}_r$$

↑ sum over r s.t. $E < E_r < E + \delta E$

→ macro sys.: $\overline{\mathcal{O}}_{\mu CE} = \overline{\mathcal{O}}_{CE}$.

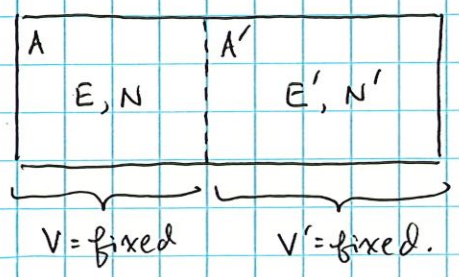
Note that in CE we also never have to introduce auxiliary quantity δE, which drops out of thermo. quantities

03/07/25

Grand canonical ensemble

- Up to now, always assumed # of particles in sys. of interest is const.

→ consider now situations where particles may be exchanged btwn. subsystems (for simplicity, assume only one species of particle).



$A + A'$ = closed sys.

$$\rightarrow \begin{cases} E + E' = E^{(0)} = \text{const.} \\ N + N' = N^{(0)} = \text{const.} \end{cases}$$

total entropy $\quad S_{tot}(E,N) = \underbrace{S(E,N)}_{\text{sys. } A} + \underbrace{S'(E',N')}_{\text{sys. } A'} = S(E,N) + S'(E^{(0)} - E, N^{(0)} - N)$.

→ in equil., $S_{tot.}$ is max w.r.t. variations of E & N:

$$dS_{tot} = \left(\frac{\partial S}{\partial E}\right)_N dE + \left(\frac{\partial S}{\partial N}\right)_E dN - \left(\frac{\partial S'}{\partial E'}\right)_{N'} dE - \left(\frac{\partial S'}{\partial N'}\right)_{E'} dN$$

$$= \left[\left(\frac{\partial S}{\partial E}\right)_N - \left(\frac{\partial S'}{\partial E'}\right)_{N'}\right] dE + \left[\left(\frac{\partial S}{\partial N}\right)_E - \left(\frac{\partial S'}{\partial N'}\right)_{E'}\right] dN$$

$= 0$ in equil.

$\Rightarrow \left(\frac{\partial S}{\partial E}\right)_N = \left(\frac{\partial S'}{\partial E'}\right)_{N'}$ (same thermal equil. cond.'n as before when N, N' = fixed)

$\rightarrow T = T', \quad \left(\frac{1}{T} = \frac{\partial S}{\partial E}\right)$

$\left(\frac{\partial S}{\partial N}\right)_E = \left(\frac{\partial S'}{\partial N'}\right)_{E'}$ (new cond.'n)

define $\boxed{\frac{\mu}{T} \equiv -\left(\frac{\partial S}{\partial N}\right)_E}$, μ = "chemical potential"

$\Rightarrow \frac{\mu}{T} = \frac{\mu'}{T'}$ in equil.

$T = T' \Rightarrow \mu = \mu'$, chemical potentials of subsystems are equal in equil.

03/10/25

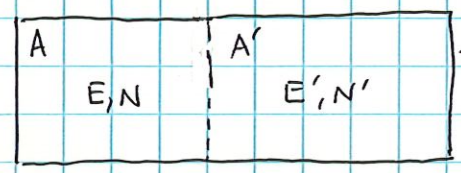
Summary.

- Canonical ensemble (CE): · sys. at fixed T

$$\cdot\, P_r = \frac{e^{-E_r/T}}{Z}, \quad Z = \sum_r e^{-E_r/T}, \quad r = \mu\text{-state}.$$

$$\cdot\, F = \bar{E} - TS = -T \ln Z.$$

- Systems in "diffusive contact" (can exchange particles).



$\rightarrow$ equil: $S_{tot} = S + S' = \max \quad (dS_{tot} = 0)$

$$\Rightarrow T = T' \qquad \left(T^{-1} = \left(\frac{\partial S}{\partial E}\right)_N\right)$$

$$\begin{cases} E + E' = E^{(0)} = \text{const.} \\ N + N' = N^{(0)} = \text{const.} \end{cases} \quad \& \quad \frac{\mu}{T} = \frac{\mu'}{T'}, \qquad \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_E, \quad \mu = \text{"chemical potential"}.$$

Another interpretation of μ:

- view $S = S(E, V, N)$: $\quad dS = \left(\frac{\partial S}{\partial E}\right)_{N,V} dE + \left(\frac{\partial S}{\partial V}\right)_{N,E} dV + \left(\frac{\partial S}{\partial N}\right)_{V,E} dN$

$$= \frac{dE}{T} + \frac{p}{T} dV - \frac{\mu}{T} dN.$$

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

$$\Rightarrow \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V} \rightarrow \mu = \text{energy cost to add one particle to sys. w/ } S \text{ \& } V \text{ fixed.}$$

equiv: $E = E(S, V, N) \xrightarrow[\text{add 1 particle}]{} \Delta E = E(S, V, N+1) - E(S, V, N) \doteq \left(\frac{\partial E}{\partial N}\right)_{S,V} = \mu.$

- Similarly, in CE deal w/ $F = E - TS$, $F = F(T, V, N)$.

$$\rightarrow dF = dE - TdS - SdT = (\cancel{TdS} - pdV + \mu dN) - \cancel{TdS} - SdT$$

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

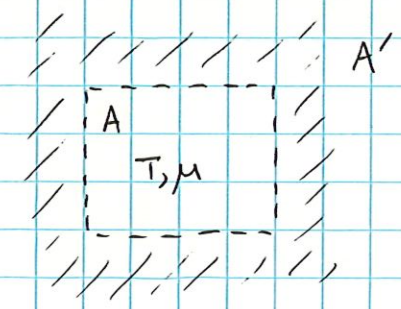
$$\Rightarrow \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}.$$

03/10/25

Grand canonical ensemble

Now consider situation where $|A| \ll |A'|$, so that A' acts as a heat bath & "particle reservoir" for A.

→ keeps T & μ of sys. A const., w/ A able to exchange energy & particles w/ A'.



$$\begin{cases} E + E' = E^{(0)} = \text{const.} \\ N + N' = N^{(0)} = \text{const.} \end{cases}$$

Q: what is prob. distb'n of μ-states of A when E & N can fluctuate? (analogous to CE, where E fluctuates).

→ more precisely: μ-state r has energy E_r & particle # N_r → what is P_r?

→ proceed as we did for CE: $P_r \propto \Omega'(E' = E^{(0)} - E_r, N' = N^{(0)} - N_r) = e^{S'(E', N')}$

→ prob. ~~of~~ prop. to # of states of res. A' w/ specified E' & N'.

Since $|A| \ll |A'|$, we have $E_r \ll E^{(0)}$ & $N_r \ll N^{(0)}$ & we expand:

$$S'(E^{(0)} - E_r, N^{(0)} - N_r) \simeq S'(E^{(0)}, N^{(0)}) - \left(\frac{\partial S'}{\partial E'}\right)_0 E_r - \left(\frac{\partial S'}{\partial N'}\right)_0 N_r$$

evaluated at $E' = E^{(0)}$ & $N' = N^{(0)}$.

using $\left(\frac{\partial S'}{\partial E'}\right)_{N'} = \frac{1}{T}$ & $\left(\frac{\partial S'}{\partial N'}\right)_{E'} = \frac{\mu}{T}$, we find:

$$S'(E', N') \simeq S'(E^{(0)}, N^{(0)}) - \frac{E_r}{T} + \frac{\mu N_r}{T}$$

$$\Rightarrow P_r \propto \Omega'(E^{(0)}, N^{(0)})\, e^{-(E_r - \mu N_r)/T}.$$

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normalizing the distb?n:

$$\boxed{P_r = \frac{e^{-(E_r - \mu N_r)/T}}{\mathcal{Z}}}$$ "grand canonical distb?n"

$$\mathcal{Z} \equiv \sum_r e^{-(E_r - \mu N_r)/T}$$ "grand partition fn.".

→ "grand canonical ensemble" (GCE) = ensemble of systems in contact w/ res. that maintain $T, \mu = \text{const}$ w/ prob. of μ-states $P_r = \frac{e^{-(E_r - \mu N_r)/T}}{\mathcal{Z}}$.

→ In GCE, particle # fluctuates. The avg. is: $\bar{N} = \sum_r \frac{e^{-(E_r - \mu N_r)/T}}{\mathcal{Z}} N_r$.

However, just as energy fluct. are negligible in CE, ~~possible~~ in the GCE of a macro. sys. the fluct. in particle # are negligible:

$$\frac{\sqrt{\overline{\Delta N^2}}}{\bar{N}} \sim \frac{1}{\sqrt{\bar{N}}} \longrightarrow 0 \text{ in macro. sys.}$$

⇒ GCE can be used to study sys. w/ given (fixed) particle # (just as CE can be used to study sys. w/ fixed energy).

· Notation: $r \to (N\,r)$ w/ r labelling μ-states for given N

⇒ $E_r \to E_{Nr}$ = energy level r for sys. w/ N particles.

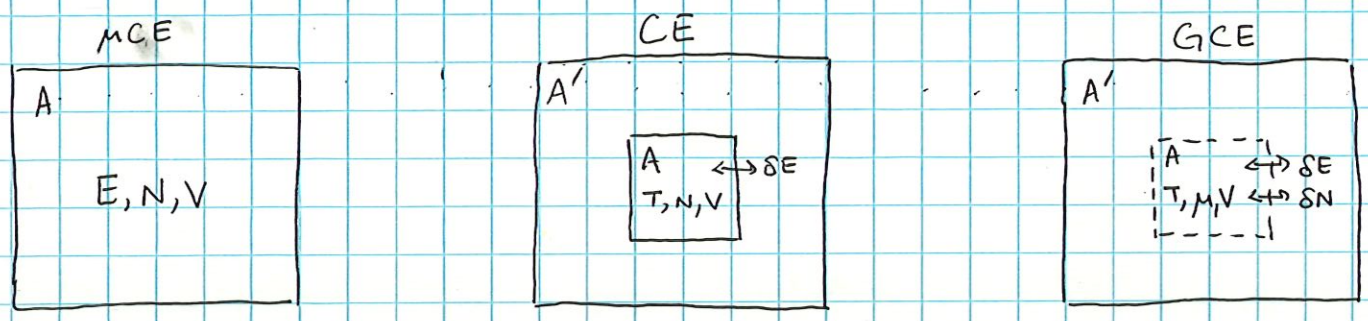
similarly, $P_r \to P_{Nr}$, $\sum_r \to \sum_N \sum_r$

This leads to a useful rewriting of $\mathcal{Z}$:

$$\mathcal{Z} = \sum_N e^{\mu N/T} \sum_r e^{-E_{Nr}/T} = \sum_N e^{\mu N/T} Z(T,N)$$

↑ canonical partition fn. for sys. w/ N particles.

Summary of ensembles:



$$P_r = \begin{cases} \frac{1}{\Omega(E)} & \text{if } E < E_r < E + \delta E \\ 0 & \text{else} \end{cases}$$

$\Omega(E)$ = # of accessible states

$$P_r = \frac{1}{Z} e^{-E_r/T}$$

$$Z = \sum_r e^{-E_r/T}$$

$$P_r = \frac{1}{\mathcal{Z}} e^{-(E_r - \mu N_r)/T}$$

$$\mathcal{Z} = \sum_r e^{-(E_r - \mu N_r)/T}.$$

→ when A = macro. sys., all ensembles essentially equiv., i.e.,

$$\overline{O}_{\mu CE} = \overline{O}_{CE} = \overline{O}_{GCE}, \quad \left(\overline{O} = \sum_r P_r O_r \right)$$

& we choose ensemble most convenient for particular problem.

(usually CE or GCE).

<u>Statistical ensembles from maximum entropy</u>. (Ref: "Information theory & stat. mech" - E.T. Jaynes, 1957).

(Bonus topic - will not be tested).

- There is a unified way to think about the different stat. ensembles, based on a <u>variational principle</u>

→ Consider system w/ μ-states r & associated (as of yet unknown) probabilities P_r. Define the entropy functional:

$$S[\{P_r\}] = -\sum_r P_r \ln P_r$$

↳ entropy viewed as functional of prob.'s $\{P_1, P_2, \ldots\}$

- "Maximum entropy principle": prob. distb.'n P_r maximizes S, subject to known info. about sys.

→ gives "least biased" distb.'n, given the known info. about the sys.

[Motivation comes from "information theory" (Shannon, 1948).

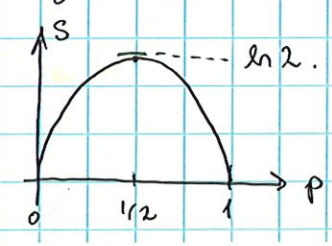
In info. theory, S = measure of "uncertainty" or "ignorance" represented by prob. distb.'n. Won't develop this further here, instead illustrate simple ex.'s:

<u>Ex:</u> $P_r = \begin{cases} 1 & r=1 \\ 0 & \text{else} \end{cases}$ $\Rightarrow$ $S = -\sum_r P_r \ln P_r = 0$.

→ entropy vanishes, since we know w/ complete certainty the outcome of a measurement.

<u>Ex:</u> Coin w/ prob. p of heads & prob $1-p$ of tails. $(0 \le p \le 1)$

$\Rightarrow S = -\sum_r P_r \ln P_r = -p\ln p - (1-p)\ln(1-p)$



$\Rightarrow S = \max$ when $p = 1/2$; i.e., when we have "least certainty" of outcome of toss]

In stat. mech.: want to maximize $S = -\sum_r P_r \ln P_r$ over prob.'s P_r

(r = accessible μ-states).

→ this is a <u>constrained</u> maximization problem, since we also need to maintain normalization cond.'n $\sum_r P_r = 1$.

Thus, absent any other info. about the system, the problem is:

maximize $S = -\sum_r P_r \ln P_r$, subject to

constraint $\sum_r P_r = 1$.

→ deal w/ this through method of "Lagrange multipliers".

$$\Rightarrow \quad S[\{P_r\}] \rightarrow \tilde{S}[\{P_r, \lambda\}] \equiv S[\{P_r\}] - \lambda\left(\sum_r P_r - 1\right)$$

"Lagrange multiplier" constraint.

now maximize $\tilde{S}$ w.r.t. P_r & λ:

$$P_r: \quad \frac{\partial \tilde{S}}{\partial P_r} = \frac{\partial S}{\partial P_r} - \lambda = 0 \qquad (1)$$

$$\lambda: \quad \frac{\partial \tilde{S}}{\partial \lambda} = \sum_r P_r - 1 = 0 \qquad (2). \leftarrow \text{reproduces constraint.}$$

$$(1): \quad \frac{\partial S}{\partial P_r} = -\ln P_r - 1 \Rightarrow \frac{\partial \tilde{S}}{\partial P_r} = -\ln P_r - 1 - \lambda = 0 \Rightarrow P_r = e^{-(1+\lambda)} = \text{const.}$$

$$(2) \quad \sum_r P_r = \sum_r e^{-(1+\lambda)} = e^{-(1+\lambda)} \times \underset{\substack{\uparrow \\ = \#\text{ of accessible} \\ \text{states}}}{\Omega} = 1 \Rightarrow e^{-(1+\lambda)} = \frac{1}{\Omega} \Rightarrow P_r = \frac{1}{\Omega}$$

→ thus, we find $P_r = \frac{1}{\Omega}$; i.e., distb'n of max. entropy is the <u>uniform</u> distb'n & coincides w/ the μ-canonical distb'n fn.

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- Now suppose we have addn.'l info. about the sys.

→ Suppose we know avg. energy $\bar{E}$.

⇒ maximize S subject to 2 constraints: $\sum_r P_r = 1$ & $\sum_r P_r E_r = \bar{E}$

$$\Rightarrow \quad S \to \tilde{S} = S - \lambda_1 \left(\sum_r P_r - 1\right) - \lambda_2 \left(\sum_r P_r E_r - \bar{E}\right), \qquad \lambda_1, \lambda_2 = 2 \text{ Lagrange multipliers.}$$

maximize:

$$P_r: \quad \frac{\partial \tilde{S}}{\partial P_r} = \frac{\partial S}{\partial P_r} - \lambda_1 - \lambda_2 E_r = 0. \qquad (1)$$

$$\lambda_1: \quad \frac{\partial \tilde{S}}{\partial \lambda_1} = \sum_r P_r - 1 = 0 \qquad (2)$$

$$\lambda_2: \quad \frac{\partial \tilde{S}}{\partial \lambda_2} = \sum_r P_r E_r - \bar{E} = 0 \qquad (3)$$

} reproduce constraint eqn.'s.

(1) $$\frac{\partial S}{\partial P_r} = -\ln P_r - 1 \quad \Rightarrow \quad \frac{\partial \tilde{S}}{\partial P_r} = -\ln P_r - 1 - \lambda_1 - \lambda_2 E_r = 0$$

$$\Rightarrow \quad P_r = e^{-(1+\lambda_1)} e^{-\lambda_2 E_r} \equiv C e^{-\lambda_2 E_r}$$

$$\left(C \equiv e^{-(1+\lambda_1)}\right)$$

(2) $$\sum_r P_r = C \sum_r e^{-\lambda_2 E_r} = 1 \quad \Rightarrow \quad C = \frac{1}{\sum_r e^{-\lambda_2 E_r}}$$

$$\Rightarrow \quad P_r = \frac{e^{-\lambda_2 E_r}}{\sum_r e^{-\lambda_2 E_r}} = \text{canonical distb.'n fn.}$$

(w/ identification $\lambda_2 = \frac{1}{T}$)

(3) $$\sum_r P_r E_r = \sum_r \frac{e^{-\lambda_2 E_r}}{C} E_r = \bar{E} \quad \leftarrow \text{implicit eqn. for } \lambda_2 = \lambda_2(\bar{E})$$

(i.e., temp. as fn. of avg. energy).

- Thus, CE follows from max. ent. cond.'n, subject to known avg. energy $\bar{E}$

→ Can similarly obtain GCE from max. ent. subject to known avg. energy $\bar{E}$ & known avg. particle # $\bar{N}$.

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Summary

- Canonical ensemble (CE): · fixed T.

  · $P_r = \dfrac{e^{-\beta E_r}}{Z}$, $\quad Z = \sum_r e^{-\beta E_r}$, $\quad \beta = \dfrac{1}{T}$.

  · $F = \bar{E} - TS = -T \ln Z$

$$F = F(T, V, N) \rightarrow dF = -S\,dT - p\,dV + \mu\,dN$$

$$\Rightarrow S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \quad p = -\left(\frac{\partial F}{\partial V}\right)_{T,N}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}.$$

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln Z = -T^2 \frac{\partial}{\partial T}\left(\frac{F}{T}\right)$$

~~Class~~ We now take up several important examples in stat. mech, using CE (i.e., considering sys. at fixed T, in contact w/ heat res.)

<u>Classical ideal gas</u>. (monatomic).

μ-states $r \rightarrow$ phase space cells: $\sum_r \rightarrow \int \dfrac{d^s q\, d^s p}{(2\pi\hbar)^s}$, $\quad s = \#$ of DOF.

from QM., phase space cell vol.

& $$Z' = \int \frac{d^s q\, d^s p}{(2\pi\hbar)^s}\, e^{-\beta E(q,p)}, \quad q = (q_1 \ldots q_s), \quad p = (p_1 \ldots p_s)$$

(provisional formula for Z, hence "Z'". We'll fix it shortly).

Use Cartesian coord.'s: $\begin{cases} q \rightarrow \vec{x}_i \\ p \rightarrow \vec{p}_i \end{cases}$ $\quad i = 1, \ldots, N = \#$ of particles $\rightarrow s = 3N$ DOF.

The energy is $$E(q,p) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + U(\vec{x}_1, \vec{x}_2, \ldots, \vec{x}_N).$$

$$= K(p) + U(q) \quad \text{(shorthand notation)}.$$

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$$\rightarrow Z' = \frac{1}{(2\pi\hbar)^{3N}} \int \prod_{i=1}^{N} d^3\vec{p}_i \, d^3\vec{x}_i \; e^{-\beta[K(p)+U(q)]}$$

q & p integrations factorize.

$$= \left[\int \prod_{i=1}^{N} \frac{d^3\vec{p}_i}{(2\pi\hbar)^3} e^{-\beta K(p)}\right] \times \left[\int \prod_{i=1}^{N} d^3\vec{x}_i \; e^{-\beta U(q)}\right]$$

For an ideal gas, we neglect interaction btwn. particles $\Rightarrow U=0$.

$$\& \int \prod_{i=1}^{N} d^3\vec{x}_i \; e^{-\beta U} \underset{U=0}{=} \int \prod_{i=1}^{N} d^3\vec{x}_i = \underbrace{\int d^3\vec{x}_1}_{V=\text{vol.}} \underbrace{\int d^3\vec{x}_2}_{V} \cdots \underbrace{\int d^3\vec{x}_N}_{V} = V^N.$$

For the momentum integrations:

$$\int \prod_{i=1}^{N} \frac{d^3\vec{p}_i}{(2\pi\hbar)^3} e^{-\beta K(p)} = \int \frac{d^3\vec{p}_1}{(2\pi\hbar)^3} \cdots \frac{d^3\vec{p}_N}{(2\pi\hbar)^3} e^{-\beta\left(\frac{\vec{p}_1^{\,2}}{2m} + \cdots + \frac{\vec{p}_N^{\,2}}{2m}\right)}$$

momentum integration factorize.

$$= \left[\int \frac{d^3\vec{p}_1}{(2\pi\hbar)^3} e^{-\beta\vec{p}_1^{\,2}/2m}\right] \times \cdots \times \left[\int \frac{d^3\vec{p}_N}{(2\pi\hbar)^3} e^{-\beta\vec{p}_N^{\,2}/2m}\right]$$

$$= \left[\underbrace{\int \frac{d^3\vec{p}}{(2\pi\hbar)^3} e^{-\beta\vec{p}^{\,2}/2m}}\right]^N$$

$$= \left[\int \frac{dp_x}{(2\pi\hbar)} e^{-\beta p_x^2/2m}\right] \times \left[\int \frac{dp_y}{(2\pi\hbar)} e^{-\beta p_y^2/2m}\right] \times \left[\int \frac{dp_z}{(2\pi\hbar)} e^{-\beta p_z^2/2m}\right]$$

$$= \left[\underbrace{\int_{-\infty}^{+\infty} \frac{dp}{2\pi\hbar} e^{-\beta p^2/2m}}_{= \sqrt{\frac{m}{2\pi\hbar^2\beta}}}\right]^3$$

$$\Rightarrow Z' = \xi^N$$

$$\xi = V\left(\frac{m}{2\pi\hbar^2\beta}\right)^{3/2} = V\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}.$$

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$$\Rightarrow \quad F' = -T \ln Z' = -NT\left(\ln V + \frac{3}{2}\ln T + \frac{3}{2}\ln\frac{m}{2\pi\hbar^2}\right).$$

- w/ free energy F' we can now compute thermo. avg.'s of interest:

  - $p = -\left(\frac{\partial F'}{\partial V}\right)_{T,N} = +\frac{NT}{V}$

    $\Rightarrow pV = NT \rightarrow$ we recover ideal gas eqn. of state.

    (derived it earlier using $\mu(E)$).

  - $\bar{E} = -T^2 \frac{\partial}{\partial T}\left(\frac{F'}{T}\right) = +NT^2 \times \frac{3}{2}\frac{1}{T} = \frac{3}{2}NT$ ✓

    & $C_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V = \frac{3}{2}N$ ✓.

  - $S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} = N\left(\ln V + \frac{3}{2}\ln T + \frac{3}{2}\ln\frac{m}{2\pi\hbar^2} + \frac{3}{2}\right)$

    $\rightarrow S = N\left(\ln V + \frac{3}{2}\ln T + \sigma\right), \quad \sigma \equiv \frac{3}{2}\ln\left(\frac{m}{2\pi\hbar^2}\right) + \frac{3}{2}$

    !! This eqn., however, is <u>incorrect</u>!!

- while the expressions for p & $\bar{E}$ ~~are~~ are correct, the result for S is manifestly wrong. ~~Take~~ The issue is that S is <u>not</u> properly <u>extensive</u>: If we rescale the sys. size, $V \to \lambda V$ & $N \to \lambda N$,

  we find $S \rightarrow \lambda(S + N\ln\lambda)$.

  For an extensive quantity, we expect $S \rightarrow \lambda S$.

  (e.g., if we double sys. size, entropy should double).

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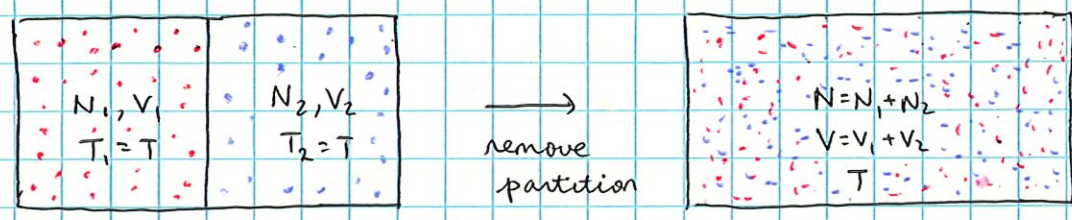
→ The issue is related to the "mixing entropy" of two gases.

· To illustrate this, consider first two <u>distinct</u> ideal gases (e.g. O_2 & N_2).



initially separated gases by partition

final state gases are mixed.

initial entropy: $S_i = S_1 + S_2$

$$= N_1(\ln V_1 + \Delta_1) + N_2(\ln V_2 + \Delta_2)$$

w/ $\Delta_i = \Delta_i(T) = \frac{3}{2}\ln T + \sigma_i$

final entropy: $S_f = (N_1 + N_2)\ln(V_1 + V_2) + N_1\Delta_1 + N_2\Delta_2$.

→ the "mixing entropy" is $\Delta S_{mix} = S_f - S_i$

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

$$= -N\left(\frac{N_1}{N}\ln\frac{V_1}{V} + \frac{N_2}{N}\ln\frac{V_2}{V}\right). \qquad (*).$$

Now suppose the gases are <u>identical</u> & initially w/ equal densities $n = \frac{N_1}{V_2} = \frac{N_2}{V_2}$

$n = \frac{N_1}{V_1}$ $\quad n = \frac{N_2}{V_2}$

system <u>unchanged</u>

$n_f = \frac{N_1 + N_2}{V_1 + V_2} = n$ (density unchanged)

~~Also~~ Although sys. unchanged, $(*)$ implies $\Delta S_{mix} = -n\left(V_1 \ln\frac{V_1}{V} + V_2 \ln\frac{V_2}{V}\right) \neq 0$!

<u>Ex</u>: $V_1 = V_2 \Rightarrow \Delta S_{mix} = 2N\ln 2$.

→ since sys. unchanged, ΔS_{mix} <u>should</u> $= 0$. This inconsistency is the "Gibbs paradox".

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· To resolve the paradox, we resort to QM: In QM, identical particles are fundamentally <u>indistinguishable</u>.

⇒ If we swap two particles:

the initial & final configurations <u>cannot</u> be distinguished.

⇒ we have <u>overcounted</u> μ-states in our partition sum, since we treated config.'s of particles related ~~by~~ by such permutations as distinct.

→ to fix the problem, divide Z' by $N! = \#$ of possible permutations of N particles. ⇒ $Z = \frac{Z'}{N!}$

⌈ Later, we will explicitly <u>derive</u> the $\frac{1}{N!}$ starting from QM ⌋

$$\Rightarrow \boxed{Z = \frac{1}{N!} \int \frac{d^s q \, d^s p}{(2\pi\hbar)^s} e^{-\beta E(q,p)}}$$ classical partition fn.

Returning to ideal gas $Z' \to Z = Z'/N!$ gives:

$$F = -T \ln Z = -T(\ln Z' - \ln N!) \quad \text{Stirling's formula.}$$

$$= -T(\ln Z' - N \ln N + N)$$

$$= F' + T(N \ln N - N).$$

using our result $F' = -NT\left(\ln V + \frac{3}{2}\ln T + \frac{3}{2}\ln\frac{m}{2\pi\hbar^2}\right)$ gives:

$$F = -NT\left(\ln\frac{V}{N} + \frac{3}{2}\ln T + \frac{3}{2}\ln\frac{m}{2\pi\hbar^2} + 1\right).$$

or $$F = -NT \ln\left[\frac{eV}{N}\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}\right]$$

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Computing the (corrected) entropy: $S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$

$$\rightarrow \quad S = N\left[\ln\frac{V}{N} + \frac{3}{2}\ln T + \sigma_0\right], \qquad \sigma_0 \equiv \sigma + 1 = \frac{3}{2}\ln\left(\frac{m}{2\pi\hbar^2}\right) + \frac{5}{2}.$$

The entropy is now indeed properly extensive:

$$N \to \lambda N,\ V \to \lambda V \Rightarrow S \to \lambda N\left[\ln\frac{\lambda V}{\lambda N} + \frac{3}{2}\ln T + \sigma_0\right] = \lambda S \quad \checkmark.$$

The Gibbs paradox is also resolved. Calculating again ΔS_{mix} using the corrected entropy (for identical particles):

$$\Delta S_{mix} = S_f - S_i = (N_1+N_2)\ln\left(\frac{V_1+V_2}{N_1+N_2}\right) - N_1\ln\frac{V_1}{N_1} - N_2\ln\frac{V_2}{N_2} \qquad \frac{N_1}{V_1} = \frac{N_2}{V_2} = n$$

$$= -n(V_1+V_2)\ln n + nV_1\ln n + nV_2\ln n$$

$$= 0 \quad \checkmark$$

Note: Factorization of classical Z leads to a useful formula even w/ interactions btwn. particles:

$$Z = \frac{1}{N!}\int \prod_{i=1}^{N}\frac{d^3\vec{p}_i}{(2\pi\hbar)^3}\, e^{-\beta K(p)} \int \prod_{i=1}^{N} d^3\vec{x}_i\, e^{-\beta U(q)}.$$

$$\rightarrow \quad Z = \frac{\xi^N}{N!} \times \frac{1}{V^N}\underbrace{\int \prod_{i=1}^{N} d^3\vec{x}_i\, e^{-\beta U(q)}}_{\text{"configuration integral".}}$$

$$\xi = V\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}$$

→ challenge of dealing w/ interacting system of particle is evaluation of the config. integral. Return to interacting system later in the course.

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Summary.

Canonical ensemble: $\cdot P_r = \frac{e^{-\beta E_r}}{Z}$, $Z = \sum_r e^{-\beta E_r}$ $\left(\beta = \frac{1}{T}\right)$

$$\cdot Z = \frac{1}{N!} \int \prod_{i=1}^{N} \frac{d^3\vec{q}_i \, d^3\vec{p}_i}{(2\pi\hbar)^3} e^{-\beta E(q,p)}$$

classical partition fn. for N identical particles

$$= \frac{1}{N!} \xi^N \int \prod_{i=1}^{N} \frac{d^3\vec{q}_i}{V} e^{-\beta U(q)}$$

U = potential energy (for ideal gas U = 0).

$$\xi = V \left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}$$

· We have seen that a sensible partition fn. in classical stat. mech. requires ingredients from QM ($2\pi\hbar$ = phase space cell vol. & $N!$ for indistinguishable particles).

Q: When is the classical approach valid & when must we resort to a full quantum treatment?

→ start from Heisenberg uncertainty rel.'n $\Delta x \Delta p \geq \frac{\hbar}{2}$.

we can ~~use~~ use this to make some estimates of the "classical regime" (Note: This will not be rigorous, as we'll use mixed classical & quantum reasoning, but estimate still correct. Later, we'll do a more careful calculation using a full QM treatment).

→ first estimate Δp: $\frac{\overline{p^2}}{2m} \sim T$ (avg. kinetic energy $\sim T$).

$\Rightarrow$ $\Delta p \sim \sqrt{2mT}$. (high T - large spread in p
low T - small " ").

→ Δp determines QM "size" of particles (i.e., uncertainty in position) : $\Delta x \sim \frac{\hbar}{\Delta p} \sim \frac{\hbar}{\sqrt{2mT}}$.

→ leads to a length scale: $\lambda_{th} \equiv \sqrt{\frac{2\pi\hbar^2}{mT}}$ "thermal de Broglie wavelength".

→ "size" of QM. particle at temp. T.

Note that λ_{th} has already appeared in classical Z:

$$\xi = V\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2} = \frac{V}{\lambda_{th}^3}$$

$$\Rightarrow Z = \frac{1}{N!}\left(\frac{V}{\lambda_{th}^3}\right)^N \int \prod_{i=1}^{N} \frac{d^3\vec{q}_i}{V}\, e^{-\beta U(q)} .$$

· Now, it is reasonable to expect classical treatment appropriate when avg. distance "a" btwn. particles $\gg \lambda_{th}$:

$$a \gg \lambda_{th} \leftarrow \text{classical regime}$$

when $a \lesssim \lambda_{th}$, QM. becomes important.

We can rephrase cond.'n in terms of density of particles $n = \frac{N}{V}$:

$$na^3 \equiv 1 \quad \text{(defines avg. distance btwn. particles).}$$

$$(\text{or } Na^3 = V).$$

cond.'n $a \gg \lambda_{th} \Rightarrow n^{-1/3} \gg \lambda_{th}$ or $n \ll \lambda_{th}^{-3} = \left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}$

→ classical limit is reached if density n is sufficiently low or T sufficiently high.

Ex: He gas at T=300 K & p=1 atm → $n = \frac{N}{V} = \frac{p}{T} \sim 10^{19}\ cm^{-3} \Rightarrow a \sim 3\times10^{-7}$ cm.

$\lambda_{th} \sim 5\times10^{-9}$ cm $\ll a$. → classical treatment is valid.

Ex: e^- in a ~~solid~~ metal: $(m_e \ll m_{He})$

$\lambda_{th} \sim 5\times10^{-7}$ cm (T ~ 300 K)

$a \sim \text{Å} = 10^{-8}$ cm (lattice spacing)

$\lambda_{th} > a \Rightarrow e^-$ in a metal highly quantum

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Equipartition theorem

→ important result in classical stat. mech.

· In ~~certain~~ many situations ~~coordinates~~ momenta and/or coord.'s enter the energy E quadratically:

Ex: (ideal gas) $E = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}$ = quad. fn. of each mom. $\vec{p}_i$.

Ex: (Harmonic oscillator) $E = \frac{p^2}{2m} + \frac{1}{2}\kappa q^2$ = quad. fn. of p & q.

→ suppose there is a quadratic term in the energy E (either q or p).

& call this variable u, so that

$$E = \frac{1}{2}\kappa u^2 + \tilde{E}(q,p) \qquad (u \text{ can be coord. or momentum})$$

$\tilde{E}$ indep. of u.

$$\rightarrow Z = \frac{1}{N!}\int'_{qp}\int du\, e^{-\beta E} = \underbrace{\left(\frac{1}{N!}\int'_{qp} e^{-\beta\tilde{E}}\right)}_{\tilde{Z}}\underbrace{\left(\int_{-\infty}^{+\infty} du\, e^{-\beta\kappa u^2/2}\right)}_{=\sqrt{\frac{2\pi}{\kappa\beta}} \equiv \xi_u(\beta).}$$

int. over all q,p except u

$$\Rightarrow Z = \tilde{Z} \times \xi_u$$

$$\& \quad F = -T\ln Z = -T\ln\tilde{Z} + \Delta F_u, \qquad \Delta F_u \equiv -T\ln\xi_u.$$

← contribution to free energy from u.

$$\rightarrow \Delta F_u = -T\ln\xi_u = -\frac{1}{2}T\ln\left(\frac{2\pi}{\kappa\beta}\right) = +\frac{1}{2}T\ln\left(\frac{\kappa}{2\pi T}\right).$$

$$\& \quad \bar{E}_u = \overline{\tfrac{1}{2}\kappa u^2} = -\frac{\partial}{\partial\beta}\ln\xi_u = \frac{1}{2}T, \quad \text{or} \quad \bar{E}_u = \frac{1}{2}k_B T \quad (T \text{ in degrees}).$$

heat capacity: $C = \frac{\partial\bar{E}}{\partial T} = \frac{1}{2}$ or $C = \frac{1}{2}k_B$ (T in degrees).

→ "equipartition thm.": each quad. term (q or p) in the energy (or Hamiltonian) contributes $\frac{1}{2}T$ ($\frac{1}{2}k_BT$) to the avg. energy (& $\frac{1}{2}$ to heat capacity).

Note: This is only true in classical stat. mech

· Some simple application of equipartition thm:

Ex: single molecule in gas at T.

→ $K = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2)$ translational kinetic energy (COM motion for polyatomic molecule).

⇒ $\bar{K} = 3 \times \frac{1}{2}T = \frac{3}{2}T$ contribution to avg. energy.

For monatomic ideal gas: $E = \sum_{i=1}^{N} K_i$ → 3N quad. terms

⇒ $\bar{E} = 3N \times \frac{1}{2}T = \frac{3}{2}NT$ ✓.

Ex: harmonic oscillator: $E = \frac{p^2}{2m} + \frac{1}{2}kq^2$, $\omega = \sqrt{\frac{k}{m}}$ (osc. freq.)

→ 2 quad terms ⇒ $\bar{E} = 2 \times \frac{1}{2}T = T$.

Note that mean kinetic & potential energies are equal for the harmonic osc:

$$\begin{cases} \bar{K} = \overline{\frac{p^2}{2m}} = \frac{1}{2}T = \frac{\bar{E}}{2} \\ \bar{U} = \overline{\frac{1}{2}kq^2} = \frac{1}{2}T = \frac{\bar{E}}{2}. \end{cases}$$

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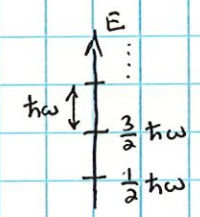
It is interesting to see how the harmonic osc. result is modified ~~[illegible]~~ in quantum stat. mech. (we'll take up a more detailed investigation of quantum stat. mech. later).

QM: $E_n = (n + 1/2)\hbar\omega \quad n = 0, 1, 2, \ldots$



energy levels of quantum harmonic osc.

μ-states r labelled by quant. # n

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

$$= e^{-\beta\hbar\omega/2} \underbrace{\sum_n e^{-\beta n\hbar\omega}}$$

$$= \sum_n \left(e^{-\beta\hbar\omega}\right)^n \quad \text{geometric series.}$$

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

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

the avg. energy is now: $\bar{E} = -\frac{\partial \ln Z}{\partial \beta}$

$$= -\frac{\partial}{\partial\beta}\left(-\frac{\beta\hbar\omega}{2} - \ln\left(1 - e^{-\beta\hbar\omega}\right)\right)$$

$$\Rightarrow \bar{E} = \hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\right).$$

When $T \gg \hbar\omega$, temp. much larger than discrete level spacing & we expect QM unimportant: $e^{\beta\hbar\omega} - 1 = e^{\frac{\hbar\omega}{T}} - 1 \simeq \frac{\hbar\omega}{T} \quad (e^x \simeq 1 + x,\ x \ll 1)$.

$$\Rightarrow \bar{E} \simeq \hbar\omega\left(\frac{1}{2} + \frac{T}{\hbar\omega}\right) \quad T \gg \hbar\omega$$

$\simeq T$, recover classical result (equipartition)

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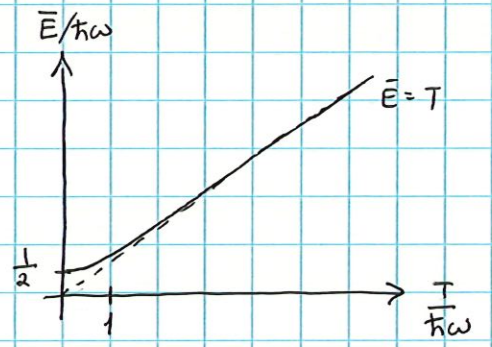
Opposite limit: $T \ll \hbar\omega$. Then $e^{\hbar\omega/T} \gg 1$ &

$$\bar{E} \simeq \hbar\omega\left(\frac{1}{2} + e^{-\hbar\omega/T}\right) \xrightarrow[T\to 0]{} \frac{\hbar\omega}{2} \quad \text{(gnd. state energy).}$$

Sketch of $\bar{E}$ across the different regimes:

$$\frac{\bar{E}}{\hbar\omega} = \frac{1}{2} + \frac{1}{e^{\hbar\omega/T}-1} \; :$$



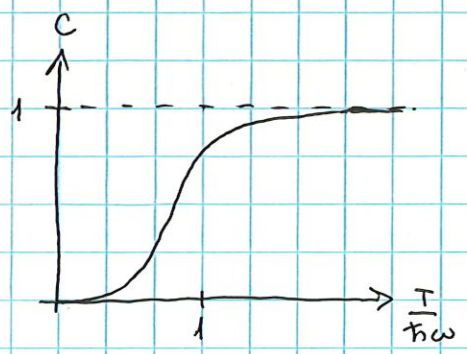
Also examine correction to heat capacity in QM:

$$C = \frac{\partial \bar{E}}{\partial T} = \left(\frac{\hbar\omega}{T}\right)^2 \frac{e^{\hbar\omega/T}}{(e^{\hbar\omega/T}-1)^2}$$

$T \gg \hbar\omega$ (classical): $\quad C \simeq \left(\frac{\hbar\omega}{T}\right)^2 \times \frac{1}{(\hbar\omega/T)^2} = 1. \qquad (e^x \simeq 1 + x)$

agrees w/ classical result $C = \frac{1}{2} + \frac{1}{2} = 1.$

$T \ll \hbar\omega$: $\quad C \simeq \left(\frac{\hbar\omega}{T}\right)^2 e^{-\hbar\omega/T} \qquad (e^{\hbar\omega/T} \gg 1$ when $T \ll \hbar\omega)$.



→ quantized energy levels lead to dramatic reduction of heat capacity at low

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Summary.

- classical partition fn: $Z = \frac{1}{N!} \int \prod_{i=1}^{N} \frac{d^3\vec{q}_i \, d^3\vec{p}_i}{(2\pi\hbar)^3} e^{-\beta E(q,p)}$ (N identical particles)

  $E = K(p) + U(q)$ = kinetic + potential

- equipartition thm.: each quad. term in E (q or p) contributes $\frac{1}{2}T$ to the avg. energy.

- quantum harmonic osc: $Z = \sum_n e^{-\beta E_n} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}$ $(E_n = (n+\frac{1}{2})\hbar\omega)$.

  $\bar{E} = \hbar\omega\left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega}-1}\right)$ $\left(\bar{E} = -\frac{\partial \ln Z}{\partial \beta}\right)$.

Specific heat of solids

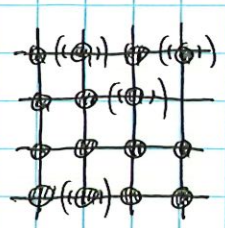
- An important application of our result for quant. stat. mech. of the harmonic osc. & the classical equipartition thm. is to the specific heat of solids.

- Consider a simple solid w/ one atom in the unit cell (e.g., elemental metal like Cu, or diamond, etc...).

→ the atoms in the solid vibrate about their equil. positions.

= "lattice vibrations".

there collective vibrations are the "normal modes" of the crystal. (sys. of coupled harmonic oscillators).



N atoms.

$$E = \sum_{i=1}^{3N} \left(\frac{p_i^2}{2m} + \frac{1}{2} m\omega_i^2 q_i^2 \right)$$

each atom has 3 DOF.

$\begin{cases} q_i = \text{normal mode coord.'s} \\ \omega_i = \text{normal mode freq.} \end{cases}$

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→ when expressed in the normal coord.'s (as above), the energy is that of 3N decoupled 1D oscillators.

· At high-T, when $T \gg \hbar\omega_{max}$, we can use a <u>classical</u> treatment.

↑ max. normal mode freq.

→ when treated classically, the equipartition thm. can be applied to give:

$$\bar{E} = 3N \times \Big(\underbrace{\tfrac{1}{2}T}_{\frac{p^2}{2m}} + \underbrace{\tfrac{1}{2}T}_{\frac{1}{2}m\omega_i^2 q_i^2} \Big) = 3NT.$$

or $\bar{E} = 3Nk_BT$ (T in deg.).

$\Rightarrow \bar{E} = 3\nu RT$ ν = # of moles.

$\Rightarrow C_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V = 3\nu R.$ (heat capacity).

& $c_V = 3R$ (molar specific heat).

→ at high enough T, the specific heat of all simple solids is = 3R.

"Dulong & Petit law."

· We can also use our knowledge of the QM harmonic osc. result to see how the Dulong-Petit law is corrected at lower T.

$$E = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + m\omega_i^2 q_i^2 \Rightarrow \bar{E} = \sum_{i=1}^{3N} \hbar\omega_i \left(\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega_i} - 1} \right).$$

→ to evaluate the sum, need to know the normal mode freq.'s ω_i.

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Make crude approx. $\omega_i = \omega = \text{const.}$; i.e., all normal mode freq.'s are equal. This is the "Einstein model". (Einstein 1907).

→ define $\theta_E \equiv \hbar\omega$ "Einstein temp." (or $k_B \theta_E = \hbar\omega$ if θ_E in deg.)

$$\Rightarrow \quad \bar{E} = 3N\theta_E \left(\frac{1}{2} + \frac{1}{e^{\beta\theta_E} - 1} \right).$$

$$\& \quad C_V = \left(\frac{\partial \bar{E}}{\partial T}\right)_V = \frac{\partial \beta}{\partial T}\left(\frac{\partial \bar{E}}{\partial \beta}\right)_V = 3N\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\beta\theta_E}}{\left(e^{\beta\theta_E} - 1\right)^2}$$

or $c_V = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{\left(e^{\theta_E/T} - 1\right)^2}$ specific heat (T & θ_E in deg.)

<u>Limits</u>: $T \gg \theta_E$: $\frac{e^{\theta_E/T}}{\left(e^{\theta_E/T} - 1\right)^2} \simeq \frac{1}{(\theta_E/T)^2}$ $\quad (e^x \simeq 1 + x,\ x \ll 1)$.

$$\Rightarrow \quad c_V = 3R \quad \text{at high temp } T \gg \theta_E \quad \checkmark.$$

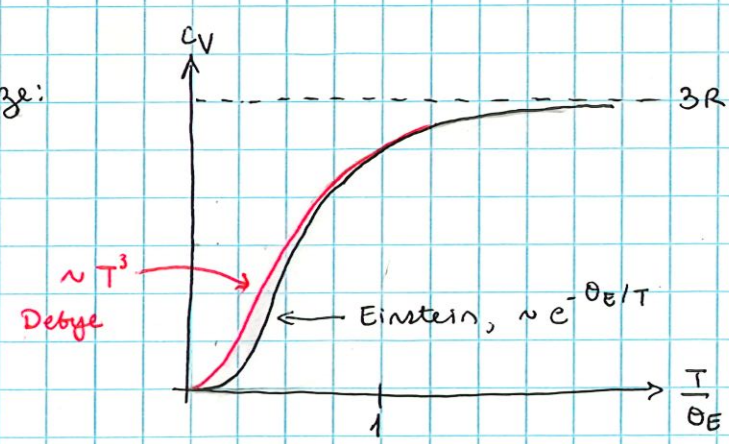
$T \ll \theta_E$: $\frac{e^{\theta_E/T}}{\left(e^{\theta_E/T} - 1\right)^2} \simeq e^{-\theta_E/T}$ $\quad (e^{\theta_E/T} \gg 1)$.

$$\Rightarrow \quad c_V = 3R\left(\frac{\theta_E}{T}\right)^2 e^{-\theta_E/T}.$$ ← strong suppression of specific heat at low-T.

→ Einstein model of single freq. turns out be too crude.

In reality, $c_V \sim T^3$ at low-T ("Debye model" - take this up later)
↳ different model for the freq.'s ω_i

Summarize:



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Paramagnetism.

As another application of stat. mech. using the canonical ensemble, we will consider the prop.'s of paramagnets.

→ paramagnet = material in which non-zero net magnetic moment is generated along direction of an applied magnetic field.

paramagnetism is a quantum phenomenon, arising from spin of unpaired e^- in a material. Nevertheless, we can analyze some important prop.'s of paramagnets w/o resorting to full machinery of quantum stat. mech.

· Consider sys. of N non-interacting atoms in a material at temp. T, placed in a magnetic field $\vec{H}$. Magnetic energy of an atom is:

$$\varepsilon = -\vec{\mu}\cdot\vec{H}, \qquad \vec{\mu} = \text{magnetic dipole moment.}$$

From QM, the dipole moment $\vec{\mu}$ is related to the quantum angular momentum $\hbar\vec{J}$ according to

$$\vec{\mu} = g\mu_B\vec{J}, \qquad J = \text{spin} = \tfrac{1}{2}, 1, \tfrac{3}{2}, 2, \ldots$$

$$\mu_B = \frac{e\hbar}{2m_e c} \quad \text{"Bohr magneton"}$$

g = "g-factor" of the atom.

⇒ energy of the atom is $\varepsilon = -\vec{\mu}\cdot\vec{H} = -g\mu_B H J_z$, where $\hat{z}$ aligned along $\vec{H}$.

Write $m = J_z$ & from QM: $m = -J, -J+1, \ldots, J-1, J$ ($2J+1$ possible values).

$$\rightarrow \varepsilon_m = -g\mu_B H m.$$

Ex: (spin-$\frac{1}{2}$ atom, single unpaired e^-) $J = \frac{1}{2}$, $2J+1 = 2$ states, $\varepsilon_\pm = \mp\frac{g\mu_B H}{2}$

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For an atom of spin-J, the partition fn. is:

$$Z = \sum_{m=-J}^{+J} e^{-\beta \varepsilon_m} = \sum_m e^{+\beta g \mu_B H m}$$

$$= \sum_{m=-J}^{+J} \left(e^{\beta g \mu_B H}\right)^m$$

geometric series

$\eta \equiv \beta g \mu_B H = \frac{g \mu_B H}{T}$

$$= \frac{e^{-J\eta} - e^{(J+1)\eta}}{1 - e^{\eta}}$$

multiply top & bottom by $e^{-\eta/2}$.

$$= \frac{e^{-(J+\frac{1}{2})\eta} - e^{+(J+\frac{1}{2})\eta}}{e^{-\eta/2} - e^{+\eta/2}}$$

$$= \frac{\sinh\left[(J+\frac{1}{2})\eta\right]}{\sinh(\eta/2)}.$$

$$\Rightarrow Z = \frac{\sinh\left[(J+1/2)\eta\right]}{\sinh(\eta/2)}, \quad \eta = \frac{g\mu_B H}{T}$$

, partition fn. for single atom in H-field.

→ from Z, obtain avg. moment $\overline{\mu_z} = \overline{g\mu_B m} = \sum_m g\mu_B m \frac{e^{+\beta g \mu_B m}}{Z}$

$$\Rightarrow \overline{\mu_z} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial H}$$

$$\Rightarrow \overline{\mu_z} = \frac{1}{\beta}\frac{\partial \ln Z}{\partial H} = \frac{1}{\beta}\frac{\partial \eta}{\partial H}\frac{\partial \ln Z}{\partial \eta} = g\mu_B \frac{\partial \ln Z}{\partial \eta}.$$

writing $\ln Z = \ln \sinh[(J+1/2)\eta] - \ln \sinh(\eta/2)$ gives:

$$\frac{\partial \ln Z}{\partial \eta} = (J+1/2)\frac{\cosh[(J+1/2)\eta]}{\sinh[(J+1/2)\eta]} - 1/2 \times \frac{\cosh(\eta/2)}{\sinh(\eta/2)}$$

$$= (J+1/2)\coth[(J+1/2)\eta] - 1/2 \times \coth(\eta/2).$$

$$\equiv J\, B_J(\eta), \qquad B_J = \text{"Brillouin fn."}$$

$$\Rightarrow \overline{\mu_z} = g\mu_B J B_J(\eta) = g\mu_B J B_J\left(\frac{g\mu_B H}{T}\right).$$

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The "magnetization" (= magnetic momentum / unit vol.) is

$$\overline{M}_z = n\,\overline{\mu}_z = n g \mu_B J B_J(\eta), \qquad n = \frac{N}{V} = \text{density of atoms.}$$

→ magnetization determined by single param. $\eta = \frac{g\mu_B H}{T}$.

Consider limits:

- $\eta \ll 1$ ($g\mu_B H \ll T$, high-T or low-field).

$$\rightarrow \coth x = \frac{e^x + e^{-x}}{e^x - e^{-x}} \simeq \frac{1}{x} + \frac{x}{3} \quad \text{for } x \ll 1 \quad \left(\text{use } e^y \simeq 1 + y + \tfrac{1}{2}y^2 + \tfrac{1}{6}y^3 \;\&\; \tfrac{1}{1+y} \simeq 1 - y \text{ for } y \ll 1\right)$$

$$\Rightarrow J B_J(\eta) \simeq \left[\frac{1}{\eta} + \frac{1}{3}(J+1/2)^2 \eta\right] - \frac{1}{2}\left[\frac{1}{\eta} + \frac{1}{12}\eta\right] \qquad (\eta \ll 1).$$

$$= \frac{\eta}{3} \times \left[(J+1/2)^2 - 1/4\right]$$

$$= \frac{J(J+1)}{3}\eta$$

$$\Rightarrow \overline{M}_z \simeq n g \mu_B \frac{J(J+1)}{3} \frac{g\mu_B H}{T} = n \frac{(g\mu_B)^2 J(J+1)}{3T} H.$$

→ write $\overline{M}_z = \chi H$, $\quad \chi = n \frac{(g\mu_B)^2 J(J+1)}{3T}$ = "magnetic susceptibility".

$\sim \frac{1}{T}$, Curie law.

- $\eta \gg 1$ ($g\mu_B H \gg T$, low-T or high-field).

→ $\coth x \simeq 1$ for $x \gg 1$ (use $e^x \gg e^{-x}$ when $x \gg 1$).

$$\Rightarrow J B_J(\eta) \simeq J \qquad (\eta \gg 1).$$

$$\Rightarrow \overline{M}_z \simeq \underbrace{n g \mu_B J}_{\text{max. possible moment of each atom.}} \quad \leftarrow \text{saturation, indep. of } H.$$

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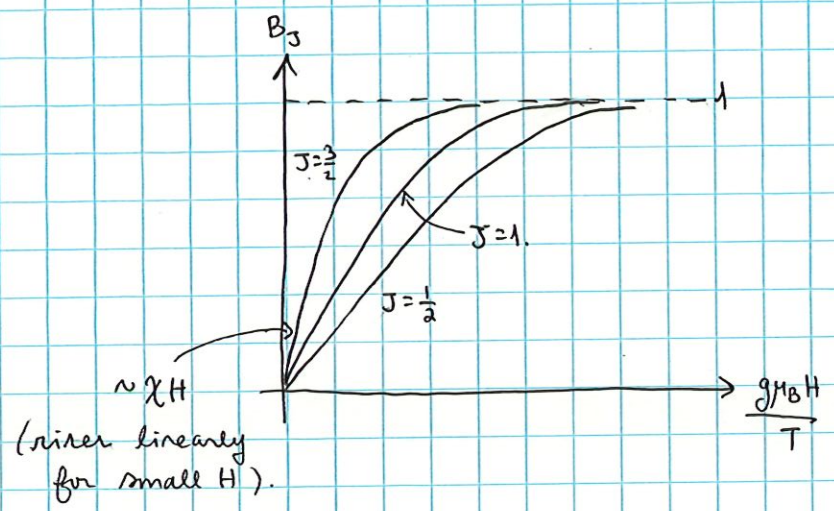

→ see Reif Fig. 7.8.3 for comparison btwn. expt. & theoretical prediction – the agreement is impressive.

· The indep. spin approx. will generally break down at sufficiently low T, where interaction btwn. spins can not be neglected. These interaction lead, at low T, to ferromagnetic or antiferromagnetic states. We may return to this subject later.

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Summary.

· Maxwell velocity distb'n: $f(\vec{v}) = \left(\frac{m}{2\pi T}\right)^{3/2} e^{-m\vec{v}^2/2T}$

$\rightarrow f(\vec{v})\, d^3\vec{v}$ = prob. that gas particle has velocity in the range $\vec{v}$ to $\vec{v}+d\vec{v}$.

(derived in Lecture 18 by considering canonical distb'n applied to single gas molecule in equil. at temp. T).

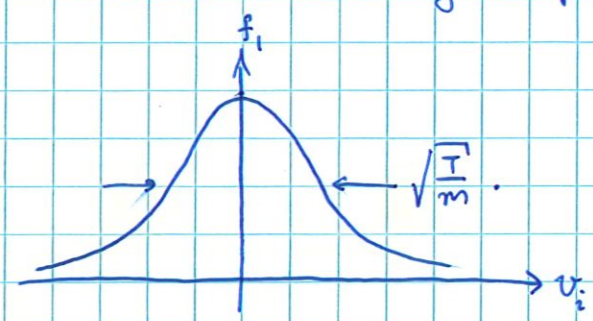
· Summarize prop.'s of $f(\vec{v})$ & use $f(\vec{v})$ to deduce some simple prop.'s of weakly interacting gases $\rightarrow$ "kinetic theory".

<u>Prop.'s of $f(\vec{v})$:</u>

· $f(\vec{v})$ can be factorized: $f(\vec{v})\, d^3\vec{v} = [f_1(v_x)\, dv_x][f_1(v_y)\, dv_y][f_1(v_z)\, dv_z]$

w/ $f_1(v_i) = \sqrt{\frac{m}{2\pi T}}\, e^{-mv_i^2/2T}$, $i = x, y, z$.

$\Rightarrow$ individual velocity comp's are statistically independent.



$$\rightarrow \overline{v_i} = \int_{-\infty}^{+\infty} dv_i\, f_1(v_i)\, v_i = 0, \quad i = x, y, z$$

$$\rightarrow \overline{v_i^2} = \int_{-\infty}^{+\infty} dv_i\, f_1(v_i)\, v_i^2 = \sqrt{\frac{m}{2\pi T}} \int_{-\infty}^{+\infty} dv_i\, e^{-\frac{mv_i^2}{2T}}\, v_i^2 = \frac{T}{m} \frac{1}{\sqrt{2\pi}} \underbrace{\int_{-\infty}^{+\infty} du\, e^{-u^2/2}\, u^2}_{\sqrt{2\pi}} = \frac{T}{m}$$

$$\Rightarrow \overline{v_i^2} = \frac{T}{m}, \quad i = x, y, z.$$

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[already knew this from equipartition: $\overline{\frac{1}{2}mv_i^2} = \frac{1}{2}T \Rightarrow \overline{v_i^2} = \frac{T}{m}$ ✓]

- Distb.'n for speed $v = |\vec{v}|$:

$F(v)dv$ = prob. that gas particle has speed in the range v to $v+dv$.

→ sum over angles: $F(v)dv = \int_{\text{angles}} f(\vec{v})\, d^3\vec{v}$. ↳ polar coord.'s.

$$= \underbrace{\int \sin\theta\, d\theta\, d\varphi}_{=4\pi} \left[\left(\frac{m}{2\pi T}\right)^{3/2} v^2 e^{-\frac{mv^2}{2T}} dv. \right]$$

$$\Rightarrow \boxed{F(v)dv = 4\pi \left(\frac{m}{2\pi T}\right)^{3/2} v^2 e^{-\frac{mv^2}{2T}} dv.}$$

Compute mean values:

- avg. speed: $\bar{v} = \int d^3\vec{v}\, f(\vec{v})\, v = \int_0^\infty dv\, F(v)\, v$

$$= 4\pi \left(\frac{m}{2\pi T}\right)^{3/2} \int_0^\infty dv\, v^3 e^{-mv^2/2T}$$

$$= 4\pi \left(\frac{m}{2\pi T}\right)^{3/2} \left(\frac{T}{m}\right)^2 \underbrace{\int_0^\infty du\, u^3 e^{-u^2/2}}_{=2.}$$

$$\Rightarrow \bar{v} = \sqrt{\frac{8}{\pi}} \times \sqrt{\frac{T}{m}}. \simeq \sqrt{2.55} \times \sqrt{\frac{T}{m}}.$$

- RMS speed: $v_{RMS}^2 = \overline{v^2} = \int d^3\vec{v}\, f(\vec{v})\, v^2$

→ equipartition: $\frac{1}{2}m\overline{v^2} = \frac{3}{2}T \Rightarrow \overline{v^2} = \frac{3T}{m}$ & $v_{RMS} = \sqrt{3} \times \sqrt{\frac{T}{m}}$.

- most probable speed: $\frac{\partial F}{\partial v} = 0 \Rightarrow \frac{\partial}{\partial v}\left(v^2 e^{-\frac{mv^2}{2T}}\right) = \left(2v - \frac{mv^3}{T}\right) e^{-\frac{mv^2}{2T}} = 0$

$$\Rightarrow \tilde{v} = \sqrt{2}\sqrt{\frac{T}{m}} \quad \text{(most probable)}.$$

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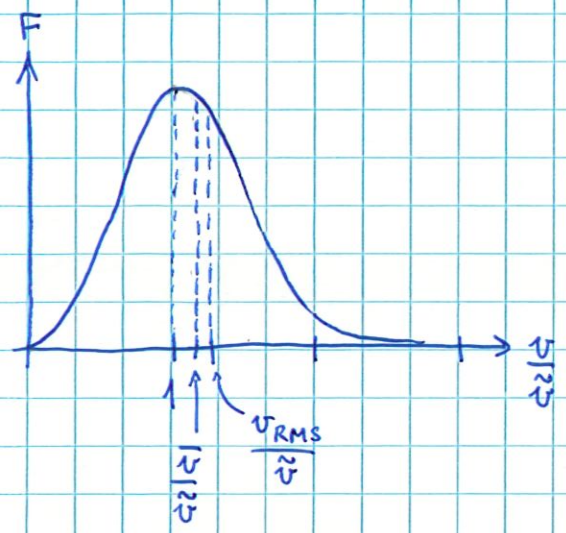
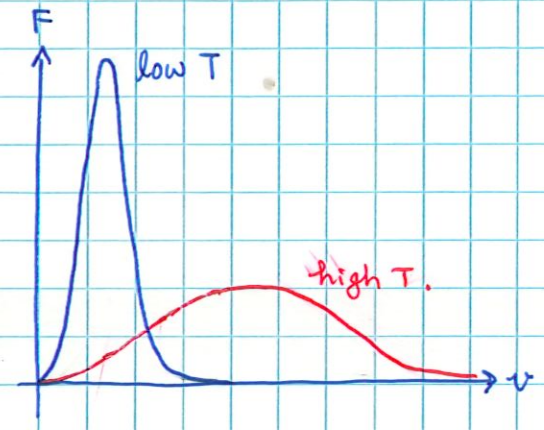
→ $\tilde{v} < \bar{v} < v_{RMS}$





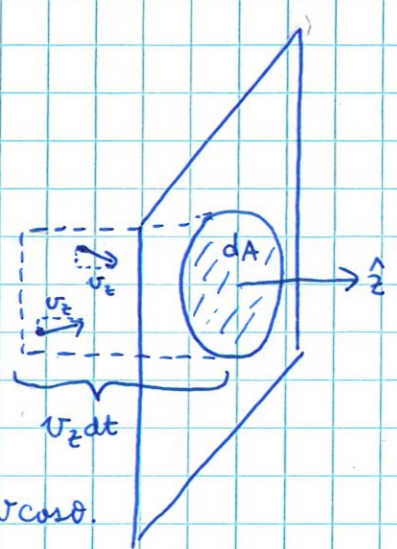
→ evolution of $F(v)$ w/ T.

· Now take up some simple examples in kinetic theory.

"kinetic theory" = study of macro. prop.'s of large #'s of particles, starting from μ-scopic EOM.

→ kinetic theory can be used to study thermo. sys. ~~is~~ out of equilibrium & how such sys. reach equil. Here we'll only consider simplest equil. situations

Number of particles striking a surface:



$v_z = \vec{v} \cdot \hat{z} = v\cos\theta$.

· Consider particles w/ velocity btwn. $\vec{v}$ & $\vec{v} + d\vec{v}$.

· In time dt, such molecules have displacement $\vec{v}\,dt$ & z-disp. $v_z\,dt$.

→ molecules that strike dA are contained in the cylinder w/ vol. = $v_z dt \times dA$.

→ # of molecules = $n \times (v_z dt\, dA)$, $n = \frac{N}{V}$ = density.

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$\Rightarrow$ # of particles w/ vel. $\in (\vec{v}, \vec{v}+d\vec{v})$ striking area dA in time dt

$$= \left[\text{prob. particle has vel.} \in (\vec{v}, \vec{v}+d\vec{v}) \right]$$

$$\times \left[\text{\# of particles striking } dA \text{ in } dt \right]$$

$$= \left[f(\vec{v})\, d^3\vec{v} \right] \times \left[n v \cos\theta \, dt \, dA \right]$$

$\Rightarrow$ # of particles w/ vel. $\in (\vec{v}, \vec{v}+d\vec{v})$ striking wall per unit area per unit time (divide by dA & dt) is:

$$\Phi(\vec{v})\, d^3\vec{v} = n f(\vec{v})\, v \cos\theta \; d^3\vec{v}. \qquad \text{(particle flux).}$$

& total ~~#~~ ~~of~~ particle flux is:

$$\Phi_0 = \int_{v_z > 0} d^3\vec{v}\; \Phi(\vec{v})$$

particles w/ $v_z < 0$ moving away from wall.

$$\Rightarrow \Phi_0 = \int_{v_z>0} d^3\vec{v}\; \Phi(\vec{v}) = \int_{v_z>0} d^3\vec{v}\; n f(\vec{v})\, v\cos\theta.$$

polar coord.'s.

$$= n \int_0^\infty v^2 dv \underbrace{\int_0^{\pi/2} \sin\theta\, d\theta}_{0 \le \theta \le \frac{\pi}{2} \text{ accounts for } v_z > 0.} \int_0^{2\pi} d\varphi\; f(\vec{v})\, v\cos\theta$$

$$= n \int_0^\infty \cancel{dv}\; v^2 dv\; v f(v) \underbrace{\int_0^{\pi/2} d\theta \sin\theta \cos\theta}_{1/2} \underbrace{\int_0^{2\pi} d\varphi}_{2\pi}$$

$$= \pi n \underbrace{\int_0^\infty v^2 dv\; v f(v)}_{\frac{1}{4\pi} \underbrace{\int d^3\vec{v}\; v f(v)}_{= \bar{v} \text{ (avg. speed).}}}$$

$$\Rightarrow \boxed{\Phi_0 = \frac{1}{4} n \bar{v}.}$$

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using $\bar{v} = \sqrt{\frac{8T}{\pi m}} \Rightarrow \Phi_0 = \frac{1}{4} n \sqrt{\frac{8T}{\pi m}}$

& eqn. of state $p = nT \Rightarrow \Phi_0 = \frac{p}{\sqrt{2\pi m T}}$. (ideal gas).

pressure

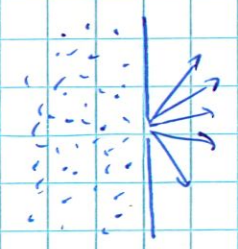
→ this result has a number of useful application.

Ex: "effusion" = process in which molecules emerge from a small hole / slit in a container.

("small" means that the hole will not disturb equil. of gas).

→ if hole has area A, then # of particles emerging per unit time is:

$$I = \Phi_0 \times A = \frac{pA}{\sqrt{2\pi m T}}.$$



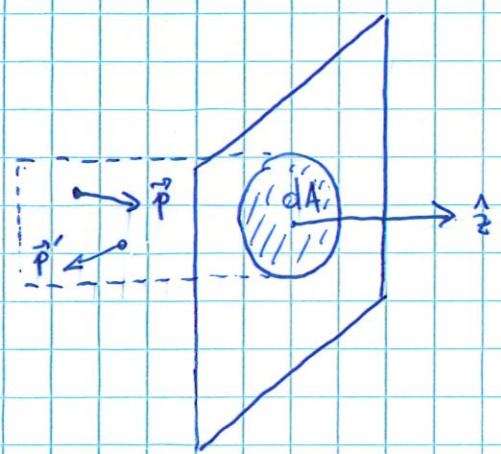
important application is isotopic separation: since $I \sim \frac{1}{\sqrt{m}}$, lighter molecules escape at a faster rate, thus rel. concentration of heavier isotopes inside container will increase as time goes on.

→ used to separate ^{235}U from ^{238}U for atomic bomb.

03/19/25

Another useful application of $\Phi(\vec{v})$: pressure of ideal gas due to collision of particles w/ walls of container; collisions exert force F on the walls. Force per unit area is mean pressure $\bar{p}$.

→ assume elastic collisions w/ wall ⇒ each collision imparts momentum $2p_z$ on the wall, where $\vec{p} = m\vec{v}$ = momentum of impinging particle & $\hat{z}$ = normal to area element:



· Consider again impinging particles w/ velocity btwn. $\vec{v}$ & $\vec{v}+d\vec{v}$.

→ # of particles hitting dA in time dt

$$= \left[\Phi(\vec{v})\, d^3\vec{v}\right] dt\, dA.$$

& momentum transferred to wall is

$$dp_{\vec{v}} = 2p_z \times \left[\Phi(\vec{v})\, d^3\vec{v}\right] dt\, dA$$

$$= 2mv_z \times \left[\Phi(\vec{v})\, d^3\vec{v}\right] dt\, dA.$$

→ force imparted on wall from particles w/ vel. ∈ $(\vec{v}, \vec{v}+d\vec{v})$ is:

$$F_{\vec{v}} = \frac{dp_{\vec{v}}}{dt} = 2mv_z \times \left[\Phi(\vec{v})\, d^3\vec{v}\right] dA.$$

Compute net force by integrating over velocities:

$$F = \int_{v_z>0} d^3\vec{v}\; 2mv_z\, \Phi(\vec{v})\, dA = 2mn \underbrace{\int_{v_z>0} d^3\vec{v}\, f(\vec{v})\, v_z^2}_{\frac{1}{2}\overline{v_z^2}\,\cdot}\, dA$$

↳ int. over particles moving toward wall

$$\Rightarrow F = mn\overline{v_z^2}\, dA \quad \& \text{ mean } \underline{\text{pressure}}\ \bar{p} = \frac{F}{dA} = mn\overline{v_z^2}$$

Finally, using $\overline{v_z^2} = \frac{T}{m}$ ⇒ $\bar{p} = nT$ or $\bar{p}V = NT$ ← ideal gas law!

03/31/25

Summary

- Canonical ensemble (CE): $P_r = \frac{e^{-\beta E_r}}{Z}$, $\beta = \frac{1}{T}$, $r = \mu$-state.

→ fixed T, N, V

energy E fluctuates.

$Z = \sum_r e^{-\beta E_r}$ partition fn.

$F = -T \ln Z$ free energy.

- Grand canonical ensemble (GCE): $P_r = \frac{e^{-\beta(E_r - \mu N_r)}}{\mathcal{Z}}$.

$\mathcal{Z} = \sum_r e^{-\beta(E_r - \mu N_r)}$ grand partition fn.

$= \sum_N e^{\beta \mu N} Z_N$ N-particle canonical partition fn.

$\Phi = -T \ln \mathcal{Z}$ grand potential.

→ $\bar{N} = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V}$ mean particle #.

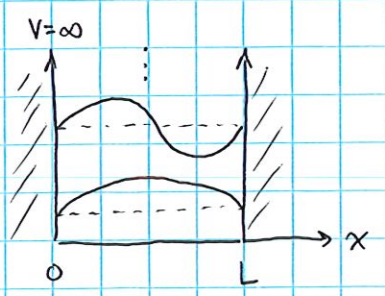
Quantum stat. mech. of ideal gases.

- Investigate stat. mech. of sys. at low T, where QM effects play an especially important role.
- New effects we will have to consider are associated w/ "exchange statistics" of identical particles.
- Discussion will be restricted to non-interacting particles → "ideal gas".

→ as we will see, even in absence of direct interaction force, effect of exch. stat. leads to a mutual coupling of particles.

· Before going into detailed formalism, we start w/ simple examples.

<u>Ex</u>: Two particles in a 1D box.



→ start w/ <u>distinguishable</u> particles, labelled "A" & "B".

→ $H = H_A + H_B$, $\quad H_{A/B} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2_{A/B}}$

Sch. eqn: $\quad H\Psi(x_A, x_B) = E\,\Psi(x_A, x_B)$.

· particles non-int. ⇒ tot. energy is a sum of individual energies:

$$E \to E_{rs} = \varepsilon_r^{(A)} + \varepsilon_s^{(B)}, \qquad \varepsilon_r = \frac{\hbar^2}{2m}\left(\frac{\pi r}{L}\right)^2 \qquad r = 1, 2, 3, \ldots$$

& same for ε_s

· In pictures:

(Ex: $r=2$, $s=3$)

→ $E_{2,3} = \varepsilon_2^{(A)} + \varepsilon_3^{(B)}$

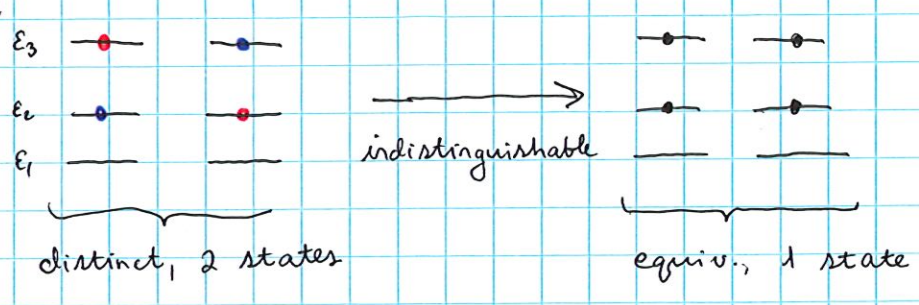
· The wave fn. is $\quad \Psi_{rs}(x_A, x_B) = \varphi_r(x_A)\,\varphi_s(x_B) \quad$ w/ $\varphi_r(x) \sim \sin\left(\frac{\pi r}{L}\right)$

& same for φ_s.

· Now suppose particles A & B are <u>indistinguishable</u>

⇒ states that were distinct become equivalent.

Ex:



In terms of wave fn.'s, we continue to use labels A & B, but now we impose a symmetry requirement on wave fn. under "exchange" of particles. There are two cases to consider:

<u>Bose-Einstein stat.</u> (BE): · wave fn. symmetric under exchange

$$\Psi_{rs}(x_A, x_B) = \Psi_{rs}(x_B, x_A).$$

$$\rightarrow \Psi_{rs}(x_A, x_B) \sim \varphi_r(x_A)\varphi_s(x_B) + \varphi_r(x_B)\varphi_s(x_A).$$

· particles w/ wave fn.'s symmetric under exchange have integer spin $S = 0, \hbar, 2\hbar, \ldots$ & are called "bosons"

<u>Ex</u>: photons, Higgs particle, He^4 atoms, ...

<u>Fermi-Dirac stat.</u> (FD): wave fn. antisymm. under exchange

$$\Psi_{rs}(x_A, x_B) = -\Psi_{rs}(x_B, x_A)$$

$$\rightarrow \Psi_{rs}(x_A, x_B) \sim \varphi_r(x_A)\varphi_s(x_B) - \varphi_r(x_B)\varphi_s(x_A)$$

· particles w/ wave fn.'s antisymm. under exch. have $\frac{1}{2}$-integer spin $S = \frac{\hbar}{2}, \frac{3\hbar}{2}, \ldots$ & are called "fermions".

<u>Ex</u>: e^-, protons/neutrons, He^3 atoms, ...

$\rightarrow$ suppose $s = r$: $\Psi_{rr}(x_A, x_B) \sim \varphi_r(x_A)\varphi_r(x_B) - \varphi_r(x_B)\varphi_r(x_A) = 0.$

$\Rightarrow$ ~~no~~ a given state may not be occupied by more than one identical particle. This is the "Pauli exclusion principle".

Note that no similar restriction applies for bosons.

For N particles:

$$\Psi(\ldots Q_i \ldots Q_j \ldots) = \begin{cases} +\Psi(\ldots Q_j \ldots Q_i \ldots) & \text{BE stat.} \\ -\Psi(\ldots Q_j \ldots Q_i \ldots) & \text{FD stat.} \end{cases}$$

$Q = (\vec{x}\, s)$ = spatial + spin coord.'s

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Make the situation more explicit by considering the case of 2 particles & 3 accessible single-particle states $\varepsilon_1, \varepsilon_2, \varepsilon_3$.

(i) distinguishable particles A & B

	ε_1	ε_2	ε_3
1.	AB	x	x
2.	x	AB	x
3.	x	x	AB
4.	A	x	B
5.	A	B	x
6.	x	A	B
7.	B	x	A
8.	B	A	x
9.	x	B	A

→ 9 states.

(ii) boson A=B (BE stat.)

# of particles in each single-particle state. = "occupation #'s".

	ε_1	ε_2	ε_3	$\{n_1, n_2, n_3\}$
1.	AA	x	x	{2, 0, 0}
2.	x	AA	x	{0, 2, 0}
3.	x	x	AA	{0, 0, 2}
4.	A	A	x	{1, 1, 0}
5.	A	x	A	{1, 0, 1}
6.	x	A	A	{0, 1, 1}

→ 6 states.

(iii) fermion A=B (FD stat.)

	ε_1	ε_2	ε_3	$\{n_1, n_2, n_3\}$
1.	A	A	x	{1, 1, 0}
2.	A	x	A	{1, 0, 1}
3.	x	A	A	{0, 1, 1}

→ 3 states.

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· Now consider general situation:

- N particles w/ single-particle states labelled by r & corresponding energy ε_r. (e.g., $\varepsilon_r = \frac{\hbar^2}{2m}\left(\frac{\pi r}{L}\right)^2$ $r = 1, 2, \ldots$).

→ when particles are indistinguishable, what is relevant is the # of particles in each state (since it is not meaningful to ask which particle is in which state).

→ "occupation #'s" n_r = # of particles in single-particle state r.

- Since particles are non-int., tot. energy of state w/ occ. #'s $\{n_1, n_2, \ldots\}$ is:

$$E_{\{n_1, n_2, \ldots\}} = n_1 \varepsilon_1 + n_2 \varepsilon_2 + \ldots = \sum_r n_r \varepsilon_r .$$

& we have constraint of fixed particle #:

$$\sum_r n_r = N.$$

⇒ in CE, the partition fn. is:

$$Z = \sum_{\{n_1 n_2 \ldots\}}{}' e^{-\beta E_{\{n_1 n_2 \ldots\}}} = \sum_{\{n_1 n_2 \ldots\}}{}' e^{-\beta(n_1 \varepsilon_1 + n_2 \varepsilon_2 + \ldots)}$$

↑ sum over strings of occ. #'s. s.t. $\sum_r n_r = N$. (see previous ex.)

→ in BE stat., allowed occ. #'s are $n_r = 0, 1, 2, \ldots$ $\forall r$ s.t. $\sum_r n_r = N$.

→ in FD stat., allowed occ. #'s are $n_r = 0, 1$ $\forall r$ s.t. $\sum_r n_r = N$

↑ ☆ Pauli exclusion principle.

04/02/2015

Summary.

· Canonical ensemble (CE): $P_r = \dfrac{e^{-\beta E_r}}{Z}$, $r = \mu$-state.

→ fixed T, N, V

$$Z = \sum_r e^{-\beta E_r}, \quad F = -T \ln Z.$$

· Grand canonical ensemble (GCE): $P_r = \dfrac{e^{-\beta(E_r - \mu N_r)}}{\mathcal{Z}}$

→ fixed T, μ, V

$$\mathcal{Z} = \sum_r e^{-\beta(E_r - \mu N_r)}, \quad \Phi = -T \ln \mathcal{Z}.$$

$$\rightarrow \mathcal{Z} = \sum_N e^{+\beta\mu N} Z_N$$

$$\bar{N} = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V} \quad \text{mean particle \#.}$$

· Quantum ideal gases (identical particles):

$$E = n_1 \varepsilon_1 + n_2 \varepsilon_2 + \ldots = \sum_r n_r \varepsilon_r \quad \text{w/} \begin{cases} \varepsilon_r = \text{single particle energies} \\ n_r = \text{occupation \#'s.} \end{cases}$$

$$\rightarrow n_r = \begin{cases} 0, 1, 2, \ldots & \text{BE stat.} \\ 0, 1 & \text{FD stat} \end{cases}$$

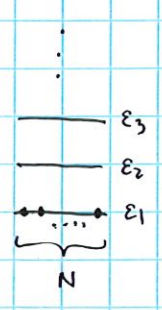
s.t. $\sum_r n_r = N.$ = total particle #.

· To see clearly drastic difference btwn. BE & FD stat., consider situation at $T=0$, when sys. is in QM. gnd. state.

→ order single particle energies $\varepsilon_1 < \varepsilon_2 < \varepsilon_3 < \ldots$

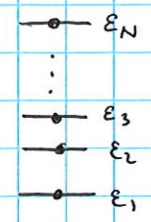
<u>BE gnd. state</u>: $E_{BE} = N \times \varepsilon_1$

$$\rightarrow n_r = \begin{cases} N & r = 1 \\ 0 & r > 1 \end{cases}$$



<u>FD gnd. state:</u> $E_{FD} = \varepsilon_1 + \varepsilon_2 + \ldots + \varepsilon_N$

$$\rightarrow n_r = \begin{cases} 1 & r \leq N \\ 0 & r > N \end{cases}$$



$\Rightarrow$ even in gnd. state, high energy single-particle states occupied.

(Note $E_{FD} > E_{BE}$).

$\rightarrow$ when $T > 0$, particles will be "thermally excited" to higher energy states $\Rightarrow$ change in mean occ. #:

$$\text{BE:} \quad \bar{n}_r \rightarrow \begin{cases} < N & r = 1 \\ > 0 & r > 1 \end{cases}$$

$$\text{FD:} \quad \bar{n}_r \rightarrow \begin{cases} < 1 & r \leq N \\ > 0 & r > N \end{cases}.$$

More precisely, in the CE we calc. $\bar{n}_r$ for state r as:

$$\bar{n}_r = \sum_{\{n_1 n_2 \ldots\}}{}' \frac{e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \ldots)}}{Z} n_r$$

mean sum over occ. #'s $\{n_1 n_2 \ldots\}$ s.t. $\sum_r n_r = N$.

$$= \frac{1}{Z} \sum_{\{n_1 n_2 \ldots\}}{}' \left(-\frac{1}{\beta}\frac{\partial}{\partial \varepsilon_r}\right) e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \ldots)}$$

$$\Rightarrow \bar{n}_r = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \varepsilon_r} \quad \text{or} \quad \bar{n}_r = \frac{\partial F}{\partial \varepsilon_r} \quad (F = -T \ln Z).$$

$\Rightarrow$ mean occ. # $\bar{n}_r$, as well as other thermo. quantities, can be obtained from Z (or, equiv., F).

However, calc. sum $Z = \sum_{\{n_1 n_2 \ldots\}}{}' e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \ldots)}$ becomes challenging when N is large due to constraint $\sum_r n_r = N$.

$\rightarrow$ <u>lift constraint</u> by working in <u>GCE</u>, where μ fixed by ext. reservoir & particle # fluct. (μ, T, V determine mean particle # $\bar{N}$).

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$$\mathcal{Z} = \sum_N e^{\beta\mu N} Z_N$$

$$= \sum_{\{n_1 n_2 \ldots\}} e^{\beta\mu(n_1+n_2+\ldots)} \, e^{-\beta(n_1\varepsilon_1+n_2\varepsilon_2+\ldots)}$$

unrestricted sum.

$$= \sum_{\{n_1 n_2 \ldots\}} e^{-\beta(\varepsilon_1-\mu)n_1} \, e^{-\beta(\varepsilon_2-\mu)n_2} \times \ldots$$

$$= \left(\sum_{n_1} e^{-\beta(\varepsilon_1-\mu)n_1}\right) \times \left(\sum_{n_2} e^{-\beta(\varepsilon_2-\mu)n_2}\right) \times \ldots$$

sum over $n_r = \begin{cases} 0,1,2,\ldots & \text{BE} \\ 0,1 & \text{FD.} \end{cases}$

<u>BE stat:</u> $\displaystyle\sum_{n_r=0}^{\infty} e^{-\beta(\varepsilon_r-\mu)n_r} = \frac{1}{1-e^{-\beta(\varepsilon_r-\mu)}}$ (geometric series).

$$\Rightarrow \mathcal{Z}_{BE} = \left(\frac{1}{1-e^{-\beta(\varepsilon_1-\mu)}}\right) \times \left(\frac{1}{1-e^{-\beta(\varepsilon_2-\mu)}}\right) \times \ldots$$

$$\Phi = -T\ln\mathcal{Z} \Rightarrow \boxed{\Phi_{BE} = T\sum_r \ln\left(1-e^{-\beta(\varepsilon_r-\mu)}\right)}$$

[<u>Note</u>: For sum above to be convergent, need $e^{-\beta(\varepsilon_r-\mu)} < 1$

$\Rightarrow \varepsilon_r - \mu > 0$ or $\varepsilon_r > \mu \;\; \forall r$ (or $\mu < \varepsilon_{min}$.)]

<u>FD stat:</u> $\displaystyle\sum_{n_r=0,1} e^{-\beta(\varepsilon_r-\mu)n_r} = 1 + e^{-\beta(\varepsilon_r-\mu)}$

$$\Rightarrow \mathcal{Z}_{FD} = \left(1+e^{-\beta(\varepsilon_1-\mu)}\right) \times \left(1+e^{-\beta(\varepsilon_2-\mu)}\right) \times \ldots$$

$$\Rightarrow \boxed{\Phi_{FD} = -T\sum_r \ln\left(1+e^{-\beta(\varepsilon_r-\mu)}\right)}$$

in a single expression: $\displaystyle\Phi = \pm T\sum_r \ln\left(1 \mp e^{-\beta(\varepsilon_r-\mu)}\right)$ upper sign = BE, lower sign = FD

We may now compute mean occ. # $\bar{n}_r$ in GCE:

$$\bar{n}_r = \sum_{\{n_1 n_2 \ldots\}} \frac{e^{-\beta(n_1\varepsilon_1 + n_2\varepsilon_2 + \ldots)}}{\mathcal{Z}} n_r$$

$$= \frac{1}{\mathcal{Z}} \left(\sum_{n_1} e^{-\beta(\varepsilon_1-\mu)n_1} \right) \left(\sum_{n_2} e^{-\beta(\varepsilon_2-\mu)n_2} \right) \times \ldots \times \left(\sum_{n_r} e^{-\beta(\varepsilon_r-\mu)n_r} n_r \right) \times \ldots$$

$$\Rightarrow \quad \bar{n}_r = \frac{\sum_{n_r} e^{-\beta(\varepsilon_r-\mu)n_r} n_r}{\sum_{n_r} e^{-\beta(\varepsilon_r-\mu)n_r}}$$

, all other term cancel btwn. numerator & denominator.

<u>BE stat:</u>

$$\bar{n}_r = \frac{\sum_{n_r=0}^{\infty} e^{-\beta(\varepsilon_r-\mu)n_r} n_r}{\sum_{n_r=0}^{\infty} e^{-\beta(\varepsilon_r-\mu)n_r}}$$

$$= -\frac{1}{\beta} \frac{\partial}{\partial \varepsilon_r} \ln \left(\sum_{n_r=0}^{\infty} e^{-\beta(\varepsilon_r-\mu)n_r} \right)$$

geometric series

$$= +\frac{1}{\beta} \frac{\partial}{\partial \varepsilon_r} \ln \left(1 - e^{-\beta(\varepsilon_r-\mu)} \right).$$

$$= \frac{e^{-\beta(\varepsilon_r-\mu)}}{1 - e^{-\beta(\varepsilon_r-\mu)}}$$

$$\Rightarrow \quad \boxed{\bar{n}_r = \frac{1}{e^{\beta(\varepsilon_r-\mu)} - 1}}$$

"Bose-Einstein distb.'n".
= mean # of bosons in state r

<u>FD stat:</u>

$$\bar{n}_r = \frac{\sum_{n_r=0,1} e^{-\beta(\varepsilon_r-\mu)n_r} n_r}{\sum_{n_r=0,1} e^{-\beta(\varepsilon_r-\mu)n_r}} = \frac{0 + e^{-\beta(\varepsilon_r-\mu)}}{1 + e^{-\beta(\varepsilon_r-\mu)}}$$

$$\Rightarrow \quad \boxed{\bar{n}_r = \frac{1}{e^{\beta(\varepsilon_r-\mu)} + 1}}$$

"Fermi-Dirac distb.'n"
= mean # of fermions in state r

Note: in both cases (BE & FD) could have obtained $\bar{n}_r$ from

$$\bar{n}_r = \frac{\partial \Phi}{\partial \varepsilon_r}$$

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In either stat., (BE or FD), mean particle # is:

$$\bar{N} = -\left(\frac{\partial \Phi}{\partial \mu}\right)_{T,V}$$

$$\Rightarrow \bar{N} = -\frac{\partial}{\partial \mu}\left(\pm T \sum_r \ln\left(1 \mp e^{-\beta(\varepsilon_r - \mu)}\right)\right)$$

$$= \sum_r \frac{1}{e^{\beta(\varepsilon_r - \mu)} \mp 1}$$

$$= \sum_r \bar{n}_r$$

$$\Rightarrow \bar{N} = \sum_r \bar{n}_r \qquad \text{(an obvious result).}$$

Note: If we view particle # N as fixed, then this also yields a relation that determines μ as a fn. of T, N, V; i.e. $\mu = \mu(T, N, V)$.

Now consider some special/limiting cases.

<u>photon statistics</u>: there are certain bosonic particles whose total particle # is <u>not fixed</u> (or not conserved).

Ex: photons (quantized oscillations of E & M field)

– can be emitted & absorbed by atoms.

also certain "elementary excitations" in solids, phonons, magnons, etc. – come back to this.

→ In CE: $$Z = \sum_{\{n_1 n_2 \ldots\}} e^{-\beta(n_1 \varepsilon_1 + n_2 \varepsilon_2 + \ldots)}$$

↑ now unrestricted sum, since N not ~~to~~ fixed.

$$\Rightarrow Z = \left(\sum_{n_1=0}^{\infty} e^{-\beta \varepsilon_1 n_1}\right) \times \left(\sum_{n_2=0}^{\infty} e^{-\beta \varepsilon_2 n_2}\right) \times \ldots$$

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each $\sum_{n_r=0}^{\infty} \left(e^{-\beta\varepsilon_r}\right)^n = \frac{1}{1-e^{-\beta\varepsilon_r}}$ (geometric series)

& $\bar{n}_r = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial \varepsilon_r} \Rightarrow \boxed{\bar{n}_r = \frac{1}{e^{\beta\varepsilon_r}-1}}$ "Planck distb'n"

→ equiv. to BE distb'n in GCE w/ $\mu=0$.

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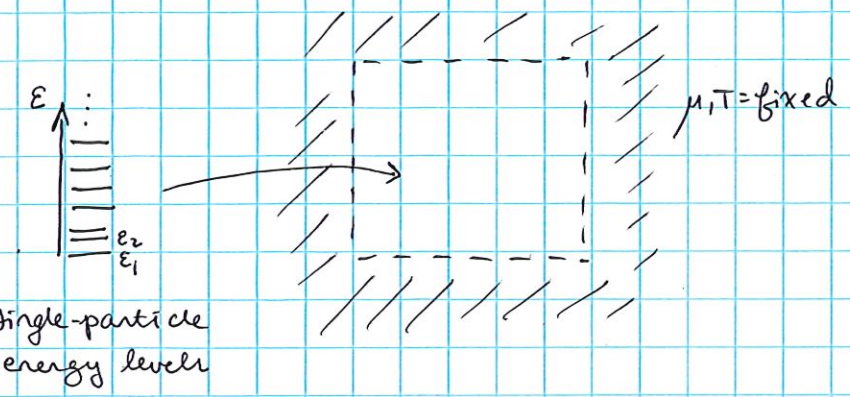
Summary



· grand partition fn:

$$\Phi = \pm T \sum_r \ln\left(1 \mp e^{-\beta(\varepsilon_r - \mu)}\right)$$

upper sign = BE
lower sign = FD.

· mean occ. #:

$$\bar{n}_r = \frac{1}{e^{\beta(\varepsilon_r - \mu)} \mp 1}, \quad \sum_r \bar{n}_r = N$$

(avg.) total particle #

Classical limit of BE/FD stat.:

→ classical limit of BE/FD stat. corresponds to $\bar{n}_r \ll 1$; i.e., mean occ. of each single-particle state is very low. In this case, prob. of two particles being in same state is very low, & statistics irrelevant.

$\bar{n}_r \ll 1$ can be achieved if:

(a) at fixed density $n = N/V$ temp. T is made sufficiently high, so that particles thermally excited across many levels.

(b) at fixed T, density n made sufficiently low so that cond.'n $\sum_r \bar{n}_r = N \Rightarrow \bar{n}_r \ll 1$.

Note: these conditions equiv. to our earlier observation that classical approx. is good when $\lambda_{th} \ll a$, where $\lambda_{th} = \sqrt{\frac{2\pi\hbar^2}{mT}}$ & a = avg. interparticle distance $\sim n^{-1/3}$

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Now, cond.'n $\bar{n}_r \ll 1$ requires $e^{\beta(\varepsilon_r - \mu)} \gg 1 \quad \forall r$.

$$\Rightarrow \boxed{\bar{n}_r \simeq e^{-\beta(\varepsilon_r - \mu)}}$$ "Maxwell-Boltzmann distb.'n" (MB)

$\rightarrow$ classical lim. of BE & FD distbn.'s

also refer to this limit as "MB statistics"

For given particle # N, μ determined by $\sum_r \bar{n}_r = N$.

$$\Rightarrow \sum_r \bar{n}_r = \sum_r e^{-\beta(\varepsilon_r - \mu)} = e^{\beta\mu} \sum_r e^{-\beta\varepsilon_r} = N$$

$$\Rightarrow e^{\beta\mu} = \frac{N}{\sum_r e^{-\beta\varepsilon_r}} \qquad (*)$$

& $\bar{n}_r = e^{\beta\mu} e^{-\beta\varepsilon_r} \Rightarrow \bar{n}_r = N \dfrac{e^{-\beta\varepsilon_r}}{\sum_r e^{-\beta\varepsilon_r}}$

We can connect MB distb.'n to our earlier results for partition fn. of classical particles. We have:

$$\Phi = \pm T \sum_r \ln\left(1 \mp e^{-\beta(\varepsilon_r - \mu)}\right)$$

$e^{-\beta(\varepsilon_r - \mu)} \ll 1$ & $\ln(1+x) \simeq x, \; x \ll 1$.

$$\simeq -T \sum_r e^{-\beta(\varepsilon_r - \mu)}$$

using $(*)$.

$$= -TN$$

We have also previously shown (see Section 9) that grand potential Φ & free energy F are related, in general, by:

$$\Phi = F - \mu N.$$

using $\Phi = -TN \Rightarrow F = \mu N - TN$

using $(*) \Rightarrow \mu = T \ln N - T \ln \sum_r e^{-\beta\varepsilon_r}$

$$\Rightarrow F = -T\left(N \ln \sum_r e^{-\beta\varepsilon_r} - N \ln N + N\right).$$

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Using Stirling's approx; $\ln N! \simeq N \ln N - N$:

$$F = -T\left(N \ln \sum_r e^{-\beta \varepsilon_r} - \ln N! \right)$$

$$\Rightarrow \quad F = -T \ln \left[\frac{1}{N!} \left(\sum_r e^{-\beta \varepsilon_r} \right)^N \right]$$

Since $F = -T \ln Z$, we find:

$$Z = \frac{1}{N!} \left(\sum_r e^{-\beta \varepsilon_r} \right)^N$$

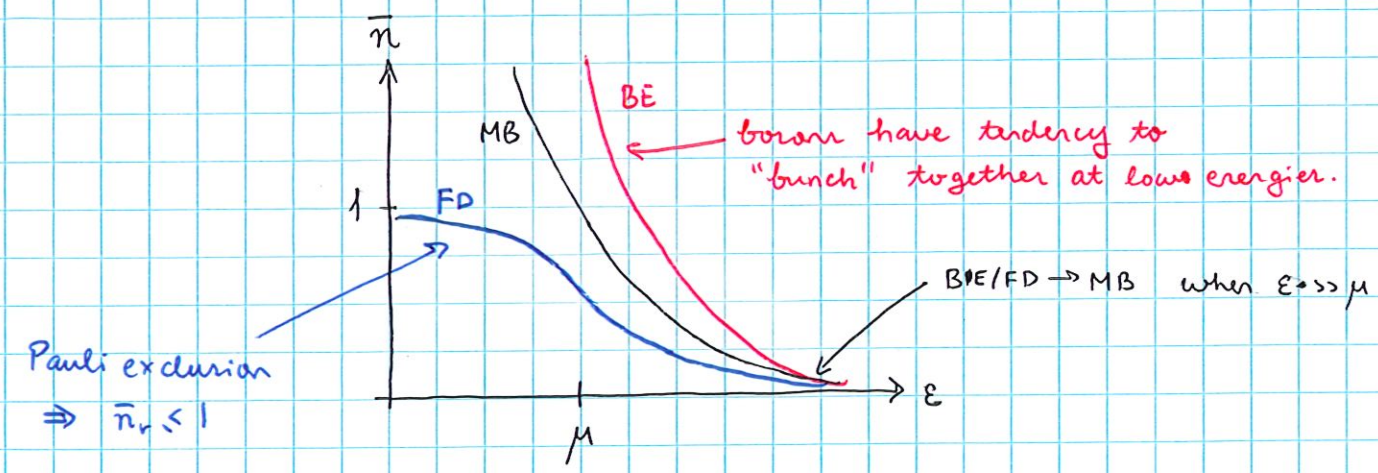
factor correcting for overcounting identical particles

partition fn. for single particle

→ previously, factor $1/N!$ was put in by hand. We have now <u>derived</u> this result by taking classical lim. of BE/FD stat.

To summarize the different distbn.'s:

$$\bar{n}_r = \begin{cases} \left(e^{\beta(\varepsilon_r - \mu)} - 1\right)^{-1} & \text{(BE)} \\ \left(e^{\beta(\varepsilon_r - \mu)} + 1\right)^{-1} & \text{(FD)} \\ e^{-\beta(\varepsilon_r - \mu)} & \text{(MB).} \end{cases}$$



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Single-particle density of states (DOS).

- Thermo. avg.'s are obtained from grand potential:

$$\Phi = \pm T \sum_r \ln\left(1 \mp e^{-\beta(\varepsilon_r - \mu)}\right)$$

Q: How do we evaluate the sum $\sum_r$ over single-particle states?

→ recall the single-particle states are obtained from Schrödinger eqn:

$$H\psi_r(\vec{x}) = \varepsilon_r \psi_r(\vec{x})$$

+ appropriate bndry. conditions (BC's).

Ex: particle in a box, of length L: BC is $\psi(x=0) = \psi(x=L) = 0$

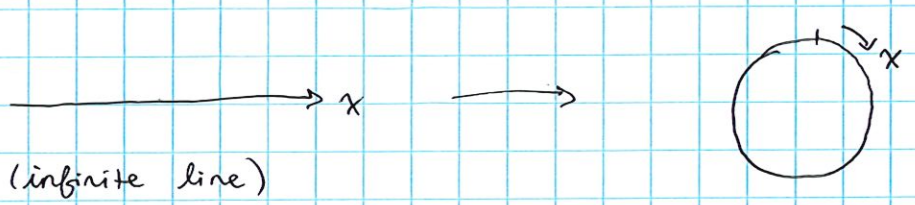
in absence of any external potential $H = \frac{-\hbar^2}{2m}\nabla^2$

Now, when we deal w/ a large sys., w/ relevant dimensions $\sim L$, the precise details of the BC's are not important for understanding sys. prop.'s (except very near the bndry.)

⇒ choose convenient BC's. For large sys., results will be independent of this choice.

- To see how the counting of single-particle states works out, we'll start w/ simple ex. of particle moving in 1D (then generalize).

→ a simple choice of BC's are "periodic bndry conditions" (PBC).



(infinite line)

circumference = L

(particle moving on a (large) circle).

PBC: $\psi(x+L) = \psi(x)$.

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Sch. eqn.: $\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\psi = \varepsilon\psi \Rightarrow \psi \sim e^{ikx}$ & $\varepsilon = \frac{\hbar^2 k^2}{2m}$.

$$\text{PBC} \Rightarrow e^{ik(x+L)} = e^{ikx}$$

$$\Rightarrow e^{ikL} = 1$$

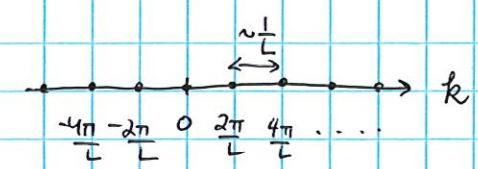
$$\Rightarrow kL = 2\pi n, \quad n = 0, \pm 1, \pm 2, \ldots$$

$$\text{or } k = \frac{2\pi}{L} n$$

→ the discrete energies are then $\varepsilon_n = \frac{2\pi^2\hbar^2}{mL^2} n^2$

& the sum over single-particle states becomes $\sum_r \to \sum_{n=0,\pm1,\pm2,\ldots}$

Now, when L is large, the spacing btwn. allowed wave-numbers k becomes small:



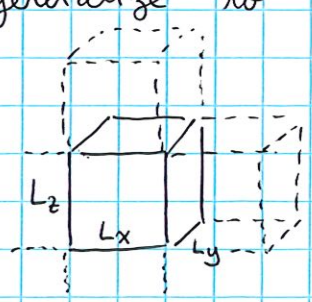
→ in a small range of wave-~~no~~ number dk, the # of states is:

$$(\#\text{ states in range } k \text{ to } k+dk) = \frac{L}{2\pi}\,dk.$$

When L is large, summation over states goes over into an integration:

$$\sum_n \xrightarrow[L\to\infty]{} \int_{k=-\infty}^{+\infty} \frac{L\,dk}{2\pi}.$$

· Now generalize to 3-dim:



PBC:
$$\begin{cases} \psi(x+L_x, y, z) = \psi(x,y,z) \\ \psi(x, y+L_y, z) = \psi(x,y,z) \\ \psi(x, y, z+L_z) = \psi(x,y,z) \end{cases}$$

→ sys. periodic in all 3 dim.

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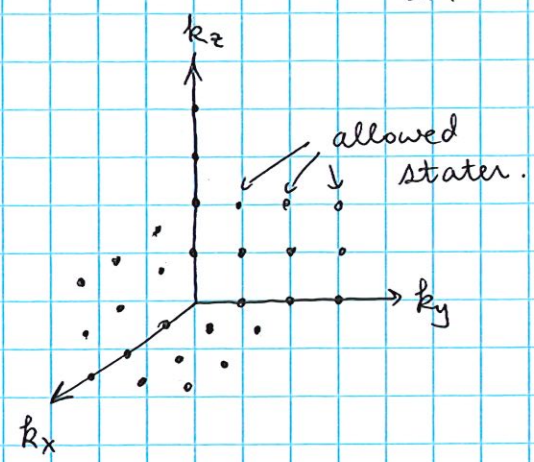
• Sch. eqn: $\frac{-\hbar^2}{2m}\nabla^2\psi(\vec{x}) = \varepsilon\psi(\vec{x}) \Rightarrow \psi(\vec{x}) \sim e^{i\vec{k}\cdot\vec{x}}$ w/ $\varepsilon = \frac{\hbar^2 k^2}{2m}$.

& PBC $\Rightarrow$
$$\begin{cases} k_x = \frac{2\pi}{L_x} n_x \\ k_y = \frac{2\pi}{L_y} n_y \\ k_z = \frac{2\pi}{L_z} n_z \end{cases}$$



$n_x, n_y, n_z = 0, \pm 1, \pm 2, \ldots$

• We again count the # of states in a region of $\vec{k}$-space:

$$(\#\text{ of states in range } \vec{k} \text{ to } \vec{k}+d\vec{k}) = \left(\frac{L_x}{2\pi}dk_x\right)\left(\frac{L_y}{2\pi}dk_y\right)\left(\frac{L_z}{2\pi}dk_z\right)$$

$$= \frac{V}{(2\pi)^3} d^3\vec{k} \qquad V = L_x L_y L_z = \text{vol.}$$

Sum over states $\rightarrow$ integration over wave-vectors:

$$\sum_{n_x n_y n_z} \xrightarrow[V\to\infty]{} V \int \frac{d^3\vec{k}}{(2\pi)^3}.$$

We also define the "density of states" (DOS) $\rho_{\vec{k}} = \frac{V}{(2\pi)^3}$, so that

$$\rho_{\vec{k}}\, d^3\vec{k} = (\#\text{ of states in range } \vec{k} \text{ to } \vec{k}+d\vec{k})$$

• We can now evaluate the grand potential:

$$\Phi = \pm T \sum_r \ln\left(1 \mp e^{-\beta(\varepsilon_r - \mu)}\right) \rightarrow \boxed{\Phi = \pm T V \int \frac{d^3\vec{k}}{(2\pi)^3} \ln\left(1 \mp e^{-\beta(\varepsilon_{\vec{k}} - \mu)}\right)}.$$

Since $\varepsilon_{\vec{k}} = \frac{\hbar^2 k^2}{2m}$, integration is simplified in spherical polar coord.'s:

$$\Phi = \pm \frac{TV}{(2\pi)^3} \int_0^\infty k^2 dk \ln\left(1 \mp e^{-\beta(\varepsilon_k - \mu)}\right) \underbrace{\int \sin\theta_k\, d\theta_k\, d\varphi_k}_{=4\pi}.$$

$$= \pm \frac{TV}{2\pi^2} \int_0^\infty k^2 dk \ln\left(1 \mp e^{-\beta(\varepsilon_k - \mu)}\right).$$

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In the final step, change variables:

$$\varepsilon = \frac{\hbar^2 k^2}{2m} \Rightarrow d\varepsilon = \frac{\hbar^2}{m} k\,dk \Rightarrow k^2 dk = \frac{\sqrt{2m^3}}{\hbar^3}\sqrt{\varepsilon}\, d\varepsilon .$$

$$\Rightarrow \boxed{\Phi = \pm T \frac{V m^{3/2}}{\sqrt{2}\,\pi^2 \hbar^3} \int_0^\infty d\varepsilon \sqrt{\varepsilon}\, \ln\left(1 \mp e^{-\beta(\varepsilon-\mu)}\right)}$$

→ leads to an energy-dependent DOS:

$$\rho_\varepsilon = \frac{V}{4\pi^2} (2m)^{3/2} \sqrt{\varepsilon} .$$

s.t. $\rho_\varepsilon d\varepsilon$ = # of states in energy range $(\varepsilon, \varepsilon + d\varepsilon)$

& we may directly replace sum over states:

$$\sum_r \longrightarrow \int d\varepsilon\, \rho_\varepsilon .$$

· The total particle # N can now be expressed:

$$N = \sum_r \bar{n}_r \longrightarrow \boxed{\begin{aligned} N &= V \int \frac{d^3\vec{k}}{(2\pi)^3} \frac{1}{e^{\beta(\varepsilon_{\vec{k}}-\mu)} \mp 1} \\ \text{or} \quad N &= \int d\varepsilon\, \rho_\varepsilon \frac{1}{e^{\beta(\varepsilon-\mu)} \mp 1} \end{aligned}}$$

→ given N, this integral relation determines μ.

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Summary.

- Quantum ideal gases:

$$\Phi = \underset{\text{FD}}{\overset{\text{BE}}{\pm}} T \sum_r \ln\left(1 \mp e^{-\beta(\varepsilon_r - \mu)}\right)$$

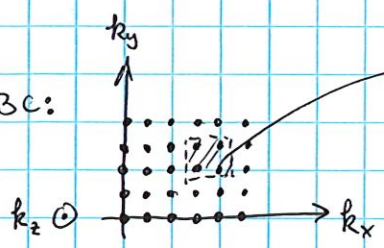
sum over single-particle states.

$$\bar{n}_r = \frac{1}{e^{\beta(\varepsilon_r-\mu)} \mp 1} \xrightarrow[\text{lim.}]{\text{classical}} \simeq e^{-\beta(\varepsilon_r-\mu)} \quad (\text{MB}).$$

$$\sum_r \bar{n}_r = N.$$

- Single-particle DOS

PBC:



states in range $\vec{k}$ to $\vec{k}+d\vec{k}$ = $\dfrac{V}{(2\pi)^3}\, d^3\vec{k}$

$$k_i = \frac{2\pi}{L_i} n_i, \quad i = x, y, z$$

$$V = L_x L_y L_z$$

$$\sum_r \xrightarrow[V\to\infty]{} g V \int \frac{d^3\vec{k}}{(2\pi)^3}, \quad g = 2J+1 = \text{spin-degeneracy of each level } (J = \text{spin})$$

$$\Rightarrow \Phi = \pm g T V \int \frac{d^3\vec{k}}{(2\pi)^3} \ln\left(1 \mp e^{-\beta(\varepsilon_{\vec{k}} - \mu)}\right), \quad \varepsilon_{\vec{k}} = \frac{\hbar^2 k^2}{2m}.$$

Single-particle DOS, cont.:

- Simplify expression for Φ by going to spherical polar coord.'s $(k\ \theta_k\ \varphi_k)$

$$d^3\vec{k} = k^2 dk \sin\theta_k d\theta_k d\varphi_k$$

$$\rightarrow \Phi = \pm g T V \int_0^\infty \frac{k^2 dk}{(2\pi)^3} \ln\left(1 \mp e^{-\beta(\varepsilon_k - \mu)}\right) \underbrace{\int \sin\theta_k d\theta_k d\varphi_k}_{=4\pi}.$$

Change var.'s: $\varepsilon = \dfrac{\hbar^2 k^2}{2m} \Rightarrow d\varepsilon = \dfrac{\hbar^2}{m} k dk$ & $k^2 dk = \dfrac{\sqrt{2}\, m^{3/2}}{\hbar^3} \sqrt{\varepsilon}\, d\varepsilon$.

$$\Rightarrow \Phi = \pm g T \int_0^\infty d\varepsilon \underbrace{\left[\frac{V}{4\pi^2} \frac{(2m)^{3/2}}{\hbar^3} \sqrt{\varepsilon}\right]}_{\equiv \rho(\varepsilon)} \ln\left(1 \mp e^{-\beta(\varepsilon-\mu)}\right).$$

$\rightarrow \rho(\varepsilon)\, d\varepsilon$ = # states in energy range $(\varepsilon, \varepsilon + d\varepsilon)$.

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- We may also thus replace sums over states: $\sum_r \longrightarrow \int d\varepsilon\, g(\varepsilon)$.

Also write: $N = \sum_r \bar{n}_r \longrightarrow N = gV \int \frac{d^3\vec{k}}{(2\pi)^3} \frac{1}{e^{\beta(\varepsilon_{\vec{k}}-\mu)} \mp 1}$

or $N = g \int d\varepsilon\, g(\varepsilon) \frac{1}{e^{\beta(\varepsilon-\mu)} \mp 1}$ given N, these integrals determine μ.

- Now that we know how to count states we can obtain some important results.

- First, recall free energy in the classical lim. derived earlier:

$$F = -T \ln\left[\frac{1}{N!} \left(\sum_r e^{-\beta\varepsilon_r} \right)^N \right] \quad \text{(MB stat.)}$$

$$\Rightarrow Z = \frac{1}{N!} \left(\sum_r e^{-\beta\varepsilon_r} \right)^N .$$

Now evaluate sum: $\sum_r e^{-\beta\varepsilon_r} \longrightarrow V \int \frac{d^3\vec{k}}{(2\pi)^3} e^{-\beta\varepsilon_{\vec{k}}}$, $\varepsilon_{\vec{k}} = \frac{\hbar^2 k^2}{2m}$.

(spinless particles, for simplicity)

Use de Broglie rel.'n btwn. wave-vector & momentum $\vec{p} = \hbar\vec{k}$

$$\Rightarrow \varepsilon_{\vec{p}} = \frac{\vec{p}^{\,2}}{2m} \quad \& \quad d^3\vec{k} = \frac{d^3\vec{p}}{\hbar^3}$$

$$\Rightarrow Z = \frac{1}{N!} V^N \left(\int \frac{d^3\vec{p}}{(2\pi\hbar)^3} e^{-\frac{\vec{p}^{\,2}}{2mT}} \right)^N$$

$\rightarrow$ precisely the classical N-particle partition fn., but now we have <u>derived</u> factor $1/N!$ & have found that factor $2\pi\hbar$ comes from counting discrete QM states.

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· now consider eqn. of state of ideal quantum gas.

→ the pressure of the gas is $p = -\left(\frac{\partial \Phi}{\partial V}\right)_{T,\mu}$ (see Section 9).

$$\Phi = \mp g T \int d\varepsilon\, \rho(\varepsilon) \ln\left(1 \mp e^{-\beta(\varepsilon-\mu)}\right) \quad \& \quad \rho(\varepsilon) \sim V \quad \text{(i.e., linear in } V\text{)}$$

$$\Rightarrow \quad \frac{p}{T} = \mp g \int d\varepsilon\, \frac{\rho(\varepsilon)}{V} \ln\left(1 \mp e^{-\beta(\varepsilon-\mu)}\right). \qquad (*)$$

$$\& \quad \underbrace{N}_{\text{density}} = g \int d\varepsilon\, \rho(\varepsilon) \frac{1}{e^{\beta(\varepsilon-\mu)} \mp 1}$$

← keep this eqn. to eliminate μ in favor of N.

Q: what are QM corrections to ideal gas law $\frac{p}{T} = \frac{N}{V}$?

First, verify the classical result, which corresponds to $e^{-\beta(\varepsilon-\mu)} \ll 1$:

$$\frac{p}{T} \simeq \mp \frac{g}{V} \int d\varepsilon\, \rho(\varepsilon) \left(\mp e^{-\beta(\varepsilon-\mu)}\right) \quad \text{(using } \ln(1+x) \simeq x \text{ for } x \ll 1\text{)}.$$

$$= \frac{g}{V} \int d\varepsilon\, \rho(\varepsilon)\, e^{-\beta(\varepsilon-\mu)}$$

$$\& \quad N \simeq g \int d\varepsilon\, \rho(\varepsilon)\, e^{-\beta(\varepsilon-\mu)}$$

$$\Rightarrow \quad \frac{p}{T} = \frac{N}{V} \quad \checkmark.$$

To compute corrections, simplify integrals:

$$\frac{p}{T} = \mp g \int d\varepsilon\, \frac{1}{4\pi^2} \frac{(2m)^{3/2}}{\hbar^3} \sqrt{\varepsilon} \ln\left(1 \mp e^{-\beta(\varepsilon-\mu)}\right). \qquad x = \beta\varepsilon = \frac{\varepsilon}{T}$$

$$= \mp \frac{2}{\sqrt{\pi}} \frac{g}{\lambda_{th}^3} \int_0^\infty dx\, \sqrt{x} \ln\left(1 \mp e^{-(x-\mu/T)}\right), \quad \lambda_{th} = \sqrt{\frac{2\pi\hbar^2}{mT}}.$$

$$\& \quad \underbrace{\frac{N}{V}}_{\equiv n,\ \text{density}} = \frac{2}{\sqrt{\pi}} \frac{g}{\lambda_{th}^3} \int_0^\infty dx\, \sqrt{x} \frac{1}{e^{(x-\mu/T)} \mp 1}$$

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Since classical ~~dec~~ lim. is $e^{-\beta(\varepsilon-\mu)} = e^{-(x-\mu/T)} \ll 1$, we treat this quantity as a small parameter & expand: ("semi-classical" expansion)

$\ln(1+y) \simeq y - \frac{y^2}{2} \Rightarrow$

$$\frac{p}{T} \simeq \mp \frac{2}{\sqrt{\pi}} \frac{g}{\lambda_{th}^3} \int dx \sqrt{x} \left(\mp e^{\mu/T} e^{-x} - \frac{1}{2} e^{2\mu/T} e^{-2x} \right)$$

$$= \frac{g}{\lambda_{th}^3} \left[e^{\mu/T} \underbrace{\left(\frac{2}{\sqrt{\pi}} \int_0^\infty dx \sqrt{x}\, e^{-x} \right)}_{=1} \pm \frac{1}{2} e^{2\mu/T} \underbrace{\left(\frac{2}{\sqrt{\pi}} \int_0^\infty dx \sqrt{x}\, e^{-2x} \right)}_{= 2^{-3/2}} \right].$$

$$= \frac{g}{\lambda_{th}^3} \left(e^{\mu/T} \pm \frac{1}{2^{5/2}} e^{2\mu/T} \right).$$

& $$n = \frac{2}{\sqrt{\pi}} \frac{g}{\lambda_{th}^3} \int dx \sqrt{x} \frac{e^{-(x-\mu/T)}}{1 \mp e^{-(x-\mu/T)}} \qquad \frac{1}{1+y} \simeq 1-y, \quad y \ll 1$$

$$\simeq \frac{2}{\sqrt{\pi}} \frac{g}{\lambda_{th}^3} \int dx \sqrt{x}\, e^{-(x-\mu/T)} \left(1 \pm e^{-(x-\mu/T)} \right).$$

$$= \frac{g}{\lambda_{th}^3} \left[e^{\mu/T} \underbrace{\left(\frac{2}{\sqrt{\pi}} \int_0^\infty dx \sqrt{x}\, e^{-x} \right)}_{=1} \pm e^{2\mu/T} \underbrace{\left(\frac{2}{\sqrt{\pi}} \int_0^\infty dx \sqrt{x}\, e^{-2x} \right)}_{2^{-3/2}} \right].$$

$$= \frac{g}{\lambda_{th}^3} \left(e^{\mu/T} \pm \frac{1}{2^{3/2}} e^{2\mu/T} \right).$$

Setting $z = e^{\mu/T}$, we can write:

$$\begin{cases} \dfrac{p}{T} = \dfrac{g}{\lambda_{th}^3} \left(z \pm \dfrac{1}{2^{5/2}} z^2 \right) \\[2ex] n \lambda_{th}^3 = g \left(z \pm \dfrac{1}{2^{3/2}} z^2 \right) \end{cases}$$

→ we see that the semi-classical expansion is also an expansion in the small param. $z = e^{\mu/T} \ll 1$. (Note $z \ll 1 \Rightarrow e^{-\beta(\varepsilon-\mu)} = z e^{-\beta\varepsilon} \ll 1$ ✓)

the second eqn. can be (approx.) inverted to find z as fn. of n:

$$z = \frac{n \lambda_{th}^3}{g} \mp 2^{-3/2} z^2 \Rightarrow z = \frac{n \lambda_{th}^3}{g} \mp 2^{-3/2} \left(\frac{n \lambda_{th}^3}{g} \mp 2^{-3/2} z^2 \right)^2 \simeq \frac{n \lambda_{th}^3}{g} \mp 2^{-3/2} \left(\frac{n \lambda_{th}^3}{g} \right)^2$$

& we have used again the semi-classical approx. $n\lambda_{th}^3 \ll 1$

to approx: $$z \simeq \frac{n\lambda_{th}^3}{g} \mp \frac{1}{2^{3/2}}\left(\frac{n\lambda_{th}^3}{g}\right)^2$$

$$\Rightarrow \quad \frac{p}{T} \simeq \frac{g}{\lambda_{th}^3}\left[\frac{n\lambda_{th}^3}{g} \mp \frac{1}{2^{3/2}}\left(\frac{n\lambda_{th}^3}{g}\right)^2 \pm \frac{1}{2^{5/2}}\left(\frac{n\lambda_{th}^3}{g}\right)^2\right]$$

$$= \frac{g}{\lambda_{th}^3}\left[\frac{n\lambda_{th}^3}{g} \mp \frac{1}{2^{5/2}}\left(\frac{n\lambda_{th}^3}{g}\right)^2\right]$$

$$\Rightarrow \quad \frac{p}{T} = n\left[1 \mp \frac{1}{2^{5/2}}\left(\frac{n\lambda_{th}^3}{g}\right) + \underbrace{\cdots}_{\text{higher order in powers of } n\lambda_{th}^3}\right]$$

$$\Rightarrow \quad pV = NT \times \begin{cases} 1 - \frac{1}{2^{5/2}}\left(\frac{n\lambda_{th}^3}{g}\right) + \cdots & \text{(BE)} \\ 1 + \frac{1}{2^{5/2}}\left(\frac{n\lambda_{th}^3}{g}\right) + \cdots & \text{(FD).} \end{cases}$$

→ for BE stat., QM effects tend to <u>reduce</u> pressure

⇒ even in absence of interaction, quant. statistics lead to an effective "attraction" btwn. particles.

→ for FD stat., QM effects tend to <u>increase</u> pressure.

⇒ effective "repulsion" btwn. particles due to Fermi stat.

· We can also obtain an exact result (i.e., true at any T in both Q.M. & classical regimes) relating avg. energy $\overline{E}$ & the pressure.

→ energy of a state of the gas is $E = n_1\varepsilon_1 + n_2\varepsilon_2 + \cdots = \sum_r n_r \varepsilon_r$

$$\Rightarrow \quad \overline{E} = \sum_r \overline{n}_r \varepsilon_r \longrightarrow \overline{E} = g\int d\varepsilon\, \rho(\varepsilon)\, \overline{n}(\varepsilon)\, \varepsilon .$$

& eqn. (*) earlier $\Rightarrow$ $$pV = \mp gT \int d\varepsilon\, \rho(\varepsilon) \ln\left(1 \mp e^{-\beta(\varepsilon-\mu)}\right).$$

04/09/05

Since $\rho(\varepsilon) = A\sqrt{\varepsilon}$, we can write:

$$pV = \mp g T \int_0^\infty d\varepsilon \left\{ \frac{d}{d\varepsilon}\left[\frac{2}{3} A \varepsilon^{3/2} \ln\left(1 \mp e^{-\beta(\varepsilon-\mu)}\right)\right] \mp \frac{2}{3} A \varepsilon^{3/2} \beta \bar{n}(\varepsilon) \right\}$$

$$= \mp g T \; \cancel{\frac{2}{3} A \varepsilon^{3/2} \ln\left(1 \mp e^{-\beta(\varepsilon-\mu)}\right) \Big|_0^\infty} \; 0$$

write $A\varepsilon^{3/2} = (A\sqrt{\varepsilon}) \times \varepsilon = \rho(\varepsilon)\varepsilon$.

$$+ \frac{2g}{3} \int d\varepsilon \; \rho(\varepsilon)\, \bar{n}(\varepsilon)\, \varepsilon$$

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

$$\Rightarrow \boxed{pV = \frac{2}{3} \bar{E}}$$

Check that this works in the classical lim., where $\bar{E} = \frac{3}{2} N T$ (monatomic ideal gas)

$$pV = \frac{2}{3} \bar{E} = \frac{2}{3}\left(\frac{3}{2} N T\right) = N T \quad \checkmark.$$

04/11/25

Summary

- FD stat:

$$\begin{cases} \bar{n}_r = \dfrac{1}{e^{\beta(\varepsilon_r-\mu)}+1} \\ \Phi = -T\sum_r \ln\left(1+e^{-\beta(\varepsilon_r-\mu)}\right). \end{cases}$$

- DOS:

$$\sum_r \longrightarrow \begin{cases} gV\int \dfrac{d^3\vec{k}}{(2\pi)^3} \\ g\int d\varepsilon\, \rho(\varepsilon) \end{cases}$$

$g = 2J+1$ = spin degeneracy (J = spin).

$$\rho(\varepsilon) = \frac{V}{4\pi^2}\frac{(2m)^{3/2}}{\hbar^3}\sqrt{\varepsilon},$$

$\rho(\varepsilon)d\varepsilon$ = # of states w/ energy $\in (\varepsilon, \varepsilon+d\varepsilon)$.

- So far, we have developed aspects of general theory of ideal QM gases.

→ now focus on specific case of FD stat. = "Fermi gas".

Fermi gas (FG).

Ex: conduction e^- in a metal, white dwarf & neutron stars, liquid He^3, ...

- The mean occ. # will play a central role in this analysis.

viewed as a fn. of energy ε, usually called the "Fermi fn.":

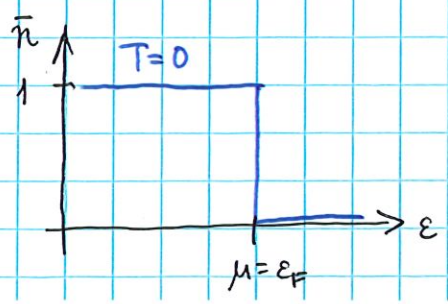
$$\bar{n}(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)}+1} \qquad \text{(Fermi fn.)}.$$

→ Start at $T=0$: FG will be in QM gnd. state, obtained by successively filling up single-particle states (due to exclusion principle).

$$\bar{n}(\varepsilon) \xrightarrow[(\beta\to\infty)]{T\to 0} \begin{cases} 1 & \varepsilon < \mu \\ 0 & \varepsilon > \mu. \end{cases}$$

$\mu(T=0) \equiv \varepsilon_F$ "Fermi energy".

= energy of highest occupied state.



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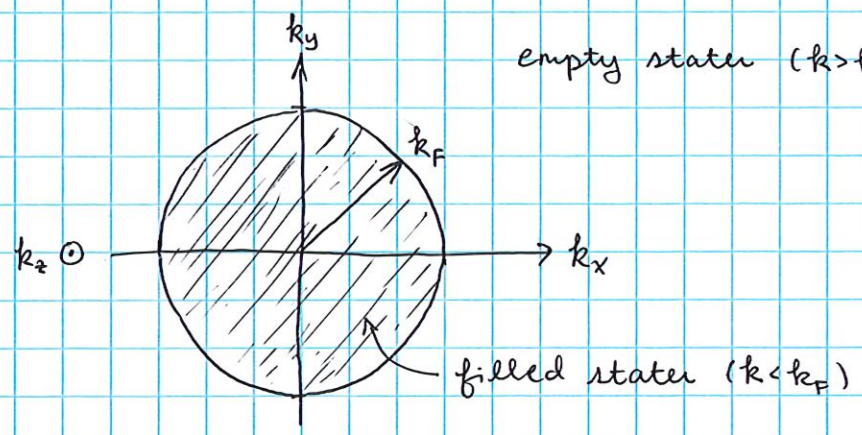
→ filled states w/ $\varepsilon < \varepsilon_F$ form the "Fermi sea".

In $\vec{k}$-space, the Fermi sea corresponds to filling up $\vec{k}$ states up to a limiting wave-vector k_F ($k = |\vec{k}|$), k_F: "Fermi wave-vector".



→ sphere defined by $|\vec{k}| = k_F$ known as the "Fermi surface".

$p_F = \hbar k_F$ "Fermi momentum".

$\varepsilon_F = \dfrac{\hbar^2 k_F^2}{2m}$ ← expression for Fermi energy in terms of k_F.

· The limiting wave-vector k_F is determined by the particle # N:

$$N = g\,V \int \frac{d^3\vec{k}}{(2\pi)^3}\, \bar{n}_{\vec{k}} \qquad \bar{n}_{\vec{k}} = \begin{cases} 1 & k < k_F \\ 0 & k > k_F \end{cases}.$$

$$= \frac{gV}{(2\pi)^3} \underbrace{\int_0^{k_F} k^2 dk}_{\frac{1}{3}k_F^3} \underbrace{\int \sin\theta_k\, d\theta_k\, d\varphi_k}_{=4\pi}$$

$$\Rightarrow \underset{\text{density}}{n} = \frac{N}{V} = \frac{g}{6\pi^2} k_F^3$$

$$\Rightarrow \boxed{k_F = \left(\frac{6\pi^2 n}{g}\right)^{1/3}} \xrightarrow[g=2 \text{ for } e^- \text{ in a metal}]{} k_F = (3\pi^2 n)^{1/3}.$$

→ can also express $\varepsilon_F = \frac{\hbar^2 k_F^2}{2m}$ in terms of density n:

$$\boxed{\varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2 n}{g}\right)^{2/3}}$$

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Alt: $n = g\int_0^\infty d\varepsilon\, \frac{\rho(\varepsilon)}{V}\, \bar{n}(\varepsilon) \overset{(T=0)}{=} g\int_0^{\varepsilon_F} d\varepsilon\, \frac{\rho(\varepsilon)}{V}$

$$= g\,\frac{(2m)^{3/2}}{4\pi^2\hbar^3}\underbrace{\int_0^{\varepsilon_F} d\varepsilon\, \sqrt{\varepsilon}}_{=\frac{2}{3}\varepsilon_F^{3/2}}$$

$$\Rightarrow \varepsilon_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2 n}{g}\right)^{2/3} \quad \checkmark$$

- Useful to record DOS $\rho(\varepsilon)$ at $\varepsilon = \varepsilon_F$:

$T=0$: $\quad N = g\int_0^{\varepsilon_F} d\varepsilon\, \rho(\varepsilon) = gA\int_0^{\varepsilon_F} d\varepsilon\, \sqrt{\varepsilon} = \frac{2g}{3} A\varepsilon_F^{3/2} = \frac{2g}{3}\rho(\varepsilon_F)\varepsilon_F$.

$$\Rightarrow \rho(\varepsilon_F) = \frac{3}{2g}\frac{N}{\varepsilon_F}.$$

- We can also obtain the total (mean) energy E & pressure p of the FG at $T=0$:

$$E = \sum_r \bar{n}_r \varepsilon_r \longrightarrow E = g\int_0^\infty d\varepsilon\, \rho(\varepsilon)\bar{n}(\varepsilon)\varepsilon$$

$T=0$.

$$= g\int_0^{\varepsilon_F} d\varepsilon\, \rho(\varepsilon)\varepsilon$$

$$= g\,\frac{V}{4\pi^2}\frac{(2m)^{3/2}}{\hbar^3}\underbrace{\int_0^{\varepsilon_F} d\varepsilon\, \varepsilon^{3/2}}_{=\frac{2}{5}\varepsilon_F^{5/2}}$$

$\Rightarrow E(T=0) = \frac{3}{5}N\varepsilon_F$ & we find that energy of FG is non-zero at $T=0$.

c.f. classical ideal gas: $E = \frac{3}{2}NT \xrightarrow[T\to 0]{} 0$.

Using $p = -\frac{\partial E}{\partial V} \Rightarrow p = \frac{2}{3}\frac{E}{V}$ & $p(T=0) = \frac{2}{5}n\varepsilon_F$ "degeneracy pressure"

$n = N/V$.

$\rightarrow$ pressure of FG is non-zero at $T=0$.

c.f. classical ideal gas: $p = nT \xrightarrow[T\to 0]{} 0$.

• Now consider $T>0$. The important temp. (or energy) scale distinguishing the "low" & "high" T regimes is ε_F.

(or $T_F = \varepsilon_F / k_B$ = "Fermi temp" in Kelvin).

$\rightarrow$ $T \ll \varepsilon_F$ is low-T "degenerate" regime.

$T \gg \varepsilon_F$ is high-T "non-degenerate" regime.

Note: $$\frac{T}{\varepsilon_F} = \frac{2mT}{\hbar^2}\left(\frac{6\pi^2 n}{g}\right)^{-2/3} \sim \frac{mT}{\hbar^2} n^{-2/3} \sim (n\lambda_{th})^{-2/3} \qquad \left(\lambda_{th} \sim \sqrt{\frac{\hbar^2}{mT}}\right).$$

$\Rightarrow$ $T \ll \varepsilon_F$ equiv. to $n\lambda_{th}^3 \gg 1$, where we expect QM effects are important

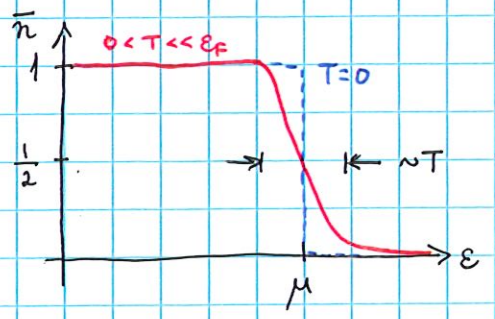
$T \gg \varepsilon_F$ " " $n\lambda_{th}^3 \ll 1$, classical (or MB) regime.

<u>Ex</u>: In metals ε_F (or T_F) is <u>very</u> high $\sim 10^4$ K (!)

$\Rightarrow$ for metals at room temp, e^- are highly degenerate & QM effects dominate.

• Consider Fermi fn. $\bar{n}(\varepsilon)$ when $0 < T \ll \varepsilon_F$:

$$\bar{n}(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)}+1}$$



• transition region where $\bar{n}(\varepsilon)$ is appreciably different from one or zero is of order T.

Qualitatively: when $T \ll \varepsilon_F$, only particles within energy range of order T can be thermally excited. States deep in the Fermi sea are blocked off by occupied states above.

$\rightarrow$ the "effective" # of particles that participate in thermal activity is:

$$N_{eff} \sim \int_{\varepsilon_F - T}^{\varepsilon_F + T} d\varepsilon\, \rho(\varepsilon) \sim \rho(\varepsilon_F)\, T \sim N \times \left(\frac{T}{\varepsilon_F}\right) \ll N \text{ when } T \ll \varepsilon_F.$$

· This prop. that $N_{eff} \sim N \times (T/\varepsilon_F)$ has important consequences for thermo. prop's of FG's (& metals in particular).

For example, we may estimate the energy E at low-T as:

$$E \simeq E_0 + N_{eff} \times T$$

gnd. state energy

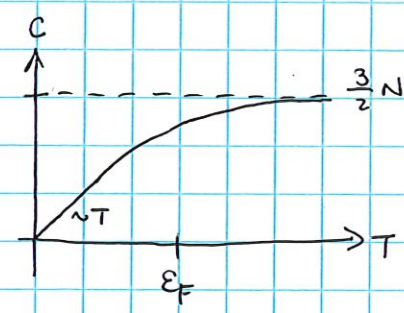
each ~~particle~~ excited particle contributes ~~an~~ energy $\sim T$ to mean energy.

$$N_{eff} \sim N \times \frac{T}{\varepsilon_F} \quad \Rightarrow \quad E \sim E_0 + N\frac{T^2}{\varepsilon_F}$$

$$\Rightarrow \quad C_V = \left(\frac{\partial E}{\partial T}\right)_V \sim N\frac{T}{\varepsilon_F}$$

c.f. classical result: $C_V \sim N = \text{const.}$

$\rightarrow$



· We now make these estimates more precise:

$$\begin{cases} N = g \int_0^\infty d\varepsilon \, \rho(\varepsilon)\, \bar{n}(\varepsilon) \\ E = g \int_0^\infty d\varepsilon \, \rho(\varepsilon)\, \bar{n}(\varepsilon)\, \varepsilon \end{cases}$$

$\leftarrow$ need this eqn. to find μ for given N. ($\mu = \mu(T)$).

$\rightarrow$ integrals have the form: $I = \int_0^\infty d\varepsilon \; f(\varepsilon)\, \bar{n}(\varepsilon)$, $\quad f(\varepsilon) = \begin{cases} \varepsilon^{1/2} & \text{for } N \\ \varepsilon^{3/2} & \text{for } E. \end{cases}$

$$= \int_0^\infty d\varepsilon \; \frac{f(\varepsilon)}{e^{\beta(\varepsilon-\mu)}+1}$$

& we need to evaluate the integral in the regime $T \ll \varepsilon_F$, where fn. $\bar{n}(\varepsilon)$ changes rapidly in a narrow range of T about ε_F. (next lecture).

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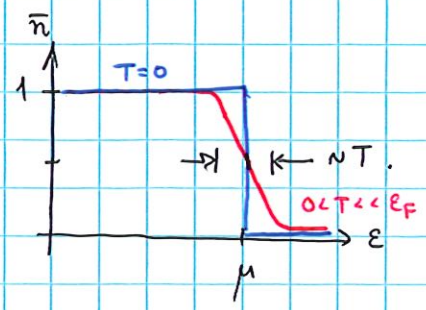
Summary

· Fermi gas (FG): $\bar{n}(\varepsilon) = \dfrac{1}{e^{\beta(\varepsilon-\mu)}+1}$ (Fermi fn.)



$$N = g \int_0^\infty d\varepsilon\, \rho(\varepsilon)\, \bar{n}(\varepsilon), \qquad \rho(\varepsilon) = \frac{V}{4\pi^2}\frac{(2m)^{3/2}}{\hbar^3}\sqrt{\varepsilon} \quad \text{(DOS)}$$

$$\Phi = -gT \int_0^\infty d\varepsilon\, \rho(\varepsilon)\, \ln\left(1+e^{-\beta(\varepsilon-\mu)}\right).$$

$T=0$: $\bar{n}(\varepsilon) \longrightarrow \begin{cases} 1 & \varepsilon<\mu \\ 0 & \varepsilon>\mu \end{cases}$ $\qquad \mu(T=0) = \varepsilon_F$ (Fermi energy).

$k_F = \left(\dfrac{6\pi^2 n}{g}\right)^{1/3}$ (Fermi wave-vector).
$n = N/V$ = density.

$p_F = \hbar k_F$ (Fermi momentum) $\longrightarrow$ $\varepsilon_F = \dfrac{p_F^2}{2m}$.

$0 \le T << \varepsilon_F$: $N_{eff} \sim N \times \left(\dfrac{T}{\varepsilon_F}\right)$ "effective" # of particles participating in thermal activity at temp. $T << \varepsilon_F$.

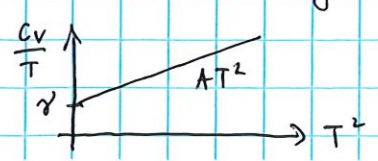
$$\Rightarrow C_V \sim N_{eff} \sim N \times \left(\frac{T}{\varepsilon_F}\right)$$

Comment on heat capacity of metals:

· specific heat of metals is due to conduction e^-, contributing $c_V^{(el)} \sim \dfrac{T}{\varepsilon_F} \equiv \gamma T$,

& lattice vibrations, contributing $c_V^{(latt)} = AT^3$ (we'll prove this later).

$\Rightarrow c_V = c_V^{(el)} + c_V^{(latt)} = \gamma T + AT^3$. Usually, c_V/T is plotted as fn. of T^2:



← holds well across many metals (see Reif Fig. 9.16.4).

We now make our calculation of thermo. prop.'s of the FG in the temp. regime $0 \leq T \ll \varepsilon_F$ more precise.

$$\rightarrow \quad N = g \int_0^\infty d\varepsilon \; \rho(\varepsilon)\, \bar{n}(\varepsilon) \quad \leftarrow \text{this eqn. determines } \mu(n,T).$$

$$E = g \int_0^\infty d\varepsilon \; \rho(\varepsilon)\, \bar{n}(\varepsilon)\, \varepsilon$$

$\rightarrow$ integrals to be evaluated are of the form:

$$I = \int_0^\infty d\varepsilon \; f(\varepsilon)\, \bar{n}(\varepsilon), \qquad f(\varepsilon) \sim \begin{cases} \varepsilon^{1/2} & \text{for } N \\ \varepsilon^{3/2} & \text{for } E. \end{cases}$$

$$= \int_0^\infty d\varepsilon \; \frac{f(\varepsilon)}{e^{\beta(\varepsilon-\mu)}+1}$$

& we need to evaluate I in the regime $T \ll \varepsilon_F$, where $\bar{n}(\varepsilon)$ changes rapidly in a narrow range of T. Proceed as follows:

$$I = \int_0^\infty d\varepsilon \; \frac{f(\varepsilon)}{e^{\beta(\varepsilon-\mu)}+1} = \int_0^\mu d\varepsilon \; f(\varepsilon) + \Bigg[\underbrace{\int_0^\infty d\varepsilon \; \frac{f(\varepsilon)}{e^{\beta(\varepsilon-\mu)}+1}}_{= \int_0^\mu + \int_\mu^\infty} - \int_0^\mu d\varepsilon \; \frac{f(\varepsilon)}{e^{\beta(\varepsilon-\mu)}+1} \Bigg]$$

$$= \int_0^\mu d\varepsilon \; f(\varepsilon) + \int_0^\mu d\varepsilon \underbrace{\left[\frac{1}{e^{\beta(\varepsilon-\mu)}+1} - 1 \right]}_{= \frac{-1}{e^{-\beta(\varepsilon-\mu)}+1}} f(\varepsilon) + \int_\mu^\infty d\varepsilon \; \frac{f(\varepsilon)}{e^{\beta(\varepsilon-\mu)}+1}$$

$\downarrow \; x = \beta(\varepsilon-\mu)$

$$= \int_0^\mu d\varepsilon \; f(\varepsilon) - T \underbrace{\int_{-\mu/T}^{0} dx \; \frac{f(\mu+Tx)}{e^{-x}+1}}_{= \int_0^{\mu/T} dx \; \frac{f(\mu-Tx)}{e^{x}+1}} + T \int_0^\infty dx \; \frac{f(\mu+Tx)}{e^{x}+1}$$

$$\simeq \int_0^\infty dx \; \frac{f(\mu-Tx)}{e^{x}+1}$$

since we assume $T \ll \mu$, we can safely extend upper limit $\rightarrow \infty$.

$$\Rightarrow \quad I = \int_0^\mu d\varepsilon\, f(\varepsilon) + T\int_0^\infty dx \; \frac{f(\mu+Tx) - f(\mu-Tx)}{e^x+1}$$

when $T \ll \mu$, we may expand:

$$f(\mu+Tx) - f(\mu-Tx) \simeq \left[f(\mu) + f'(\mu)Tx + \ldots\right] - \left[f(\mu) + f'(\mu)(-Tx) + \ldots\right]$$

$$\simeq 2f'(\mu)Tx.$$

$$\Rightarrow \quad I \simeq \int_0^\mu d\varepsilon\, f(\varepsilon) + 2f'(\mu)T^2 \underbrace{\int_0^\infty dx \frac{x}{e^x+1}}_{=\frac{\pi^2}{12}.} + \underbrace{\ldots}_{\text{higher powers of } T.}$$

(see end of notes for proof).

$$\Rightarrow \quad I \simeq \int_0^\mu d\varepsilon\, f(\varepsilon) + \frac{\pi^2}{6} f'(\mu) T^2 + \ldots$$

Finally, note that $\mu = \mu(T)$ & write $\mu(T) = \mu(T=0) + \delta\mu(T) = \varepsilon_F + \delta\mu(T)$.

$$\Rightarrow \quad I \simeq \int_0^{\varepsilon_F} d\varepsilon\, f(\varepsilon) + \int_{\varepsilon_F}^{\varepsilon_F+\delta\mu} d\varepsilon\, f(\varepsilon) + \frac{\pi^2}{6} f'(\varepsilon_F + \delta\mu) T^2 + \ldots$$

$\delta\mu \ll \varepsilon_F$

$$\simeq \int_0^{\varepsilon_F} d\varepsilon\, f(\varepsilon) + f(\varepsilon_F)\delta\mu + \frac{\pi^2}{6} f'(\varepsilon_F) T^2$$

Now apply this to particle # N to find $\delta\mu(T)$:

$$f(\varepsilon) \to g\rho(\varepsilon) \quad \Rightarrow \quad N \simeq \underbrace{g\int_0^{\varepsilon_F} d\varepsilon\, \rho(\varepsilon)}_{N} + g\rho(\varepsilon_F)\delta\mu + \frac{\pi^2}{6} g\rho'(\varepsilon_F) T^2$$

$$\Rightarrow \quad \rho(\varepsilon_F)\delta\mu \simeq -\frac{\pi^2}{6}\rho'(\varepsilon_F) T^2$$

$\rho'(\varepsilon_F) = \frac{1}{2}\frac{\rho(\varepsilon_F)}{\varepsilon_F}$

or $\quad \delta\mu = -\frac{\pi^2}{12}\frac{T^2}{\varepsilon_F}, \quad \mu(T) \simeq \varepsilon_F\left[1 - \frac{\pi^2}{12}\left(\frac{T}{\varepsilon_F}\right)^2\right]$

For the energy E we have $f(\varepsilon) \to g\rho(\varepsilon)\varepsilon$:

$$E = g\int_0^{\varepsilon_F} d\varepsilon\, \rho(\varepsilon)\varepsilon + \underbrace{g\rho(\varepsilon_F)\varepsilon_F\delta\mu + \frac{\pi^2}{6} g\rho'(\varepsilon_F)\varepsilon_F T^2}_{= g\varepsilon_F\left(-\frac{\pi^2}{6}\rho'(\varepsilon_F)T^2 + \frac{\pi^2}{6}\rho'(\varepsilon_F)T^2\right) = 0.} + \frac{\pi^2}{6} g\rho(\varepsilon_F)T^2$$

$$\Rightarrow E \simeq E(T=0) + \frac{\pi^2}{6} g\rho(\varepsilon_F)T^2$$

or, using $E_0 = \frac{3}{5}N\varepsilon_F$ & $\rho(\varepsilon_F) = \frac{3}{2g}\frac{N}{\varepsilon_F}$: $\quad E(T) \simeq \frac{3}{5}N\varepsilon_F\left(1 + \frac{5\pi^2}{12}\left(\frac{T}{\varepsilon_F}\right)^2\right)$

$\to$ for specific heat we obtain: $\quad C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{\pi^2}{3} g\rho(\varepsilon_F)T$

$$\text{or} \quad C_V = \frac{\pi^2}{2} N \times \left(\frac{T}{\varepsilon_F}\right)$$

$\to$ specific heat is indeed linear for $T \ll \varepsilon_F$, as argued qualitatively before.

Proof that $\int_0^\infty dx \, \frac{x}{e^x+1} = \frac{\pi^2}{12}$: 04/14/25

$$\int_0^\infty dx \, \frac{x}{e^x+1} = \int_0^\infty dx \; x e^{-x} \frac{1}{1+e^{-x}}$$

since $e^{-x} \leq 1$ for $0 \leq x < \infty$, we can series expand

$$= \int_0^\infty dx \; x e^{-x} \sum_{n=0}^\infty (-1)^n e^{-nx}$$

$$= \sum_{n=0}^\infty (-1)^n \int_0^\infty dx \; x \, e^{-(n+1)x}$$

shift sum $n \to n-1$ & set $y = nx$.

$$= \sum_{n=1}^\infty \frac{(-1)^{n+1}}{n^2} \underbrace{\int_0^\infty dy \; y e^{-y}}_{=1}$$

$$= \sum_{n=1}^\infty \frac{(-1)^{n+1}}{n^2}$$

can be obtained by separating out n=even & n=odd.

$$= \frac{1}{2} \sum_{n=1}^\infty \frac{1}{n^2}$$

There is a beautiful proof due to Euler that $\sum_{n=1}^\infty \frac{1}{n^2} = \frac{\pi^2}{6}$.

→ Consider series expansion of $\sin x = x - \frac{x^3}{3!} + \frac{x^5}{5!} + \dots$

$$\Rightarrow \frac{\sin x}{x} = 1 - \frac{x^2}{3!} + \frac{x^4}{5!} + \dots \qquad (*)$$

On the other hand, viewing $\sin x$ as a (infinite degree) polynomial w/ roots $x = n\pi$, $n = 0, \pm 1, \pm 2, \dots$ we ~~write~~ write:

$$\sin x = x\left(1 - \frac{x}{\pi}\right)\left(1 + \frac{x}{\pi}\right)\left(1 - \frac{x}{2\pi}\right)\left(1 + \frac{x}{2\pi}\right)\dots$$

$$\Rightarrow \frac{\sin x}{x} = \left(1 - \frac{x^2}{\pi^2}\right)\left(1 - \frac{x^2}{4\pi^2}\right)\left(1 - \frac{x^2}{9\pi^2}\right)\dots$$

$\Rightarrow$ coeff. of x^2 is: $-\left(\frac{1}{\pi^2} + \frac{1}{4\pi^2} + \frac{1}{9\pi^2} + \dots\right) = -\frac{1}{\pi^2}\sum_{n=1}^\infty \frac{1}{n^2}$

Comparing to ~~series expansion~~ coeff. of x^2 in $(*)$: $-\frac{1}{\pi^2}\sum_{n=1}^\infty \frac{1}{n^2} = -\frac{1}{3!} \Rightarrow \sum_{n=1}^\infty \frac{1}{n^2} = \frac{\pi^2}{6}$ ∎

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Summary.

Bose gas (BG): gas of weakly interacting particles obeying BE stat.

- $$\mathcal{Z} = \prod_r \left[\sum_{n_r=0}^{\infty} e^{-\beta(\varepsilon_r-\mu)n_r} \right] = \prod_r \frac{1}{1-e^{-\beta(\varepsilon_r-\mu)}}.$$

  convergence of infinite sum requires $\mu < \varepsilon_r \ \forall r$

- $$\Phi = -T\ln\mathcal{Z} = T\sum_r \ln\left(1-e^{-\beta(\varepsilon_r-\mu)}\right).$$

- $$N = \sum_r \bar{n}_r = \sum_r \underbrace{\frac{1}{e^{\beta(\varepsilon_r-\mu)}-1}}_{=\bar{n}_r}. \qquad \left[N = -\left(\frac{\partial\Phi}{\partial\mu}\right)_{T,V} \right].$$

$$\sum_r \longrightarrow \int d\varepsilon\, \rho(\varepsilon) \quad : \quad \Phi = gT\int d\varepsilon\, \rho(\varepsilon)\ln\left(1-e^{-\beta(\varepsilon-\mu)}\right).$$

$g = 2J+1$ = spin deg.

$$\rho(\varepsilon) = \frac{V}{4\pi^2}\frac{(2m)^{3/2}}{\hbar^3}\sqrt{\varepsilon} \qquad N = g\int d\varepsilon \frac{\rho(\varepsilon)}{e^{\beta(\varepsilon-\mu)}-1}$$

Bose gas: prop.'s of BG at low-T dramatically different from those of FG. We will see phenomenon of ~~"Bose-Einstein~~ "Bose-Einstein condensation" = large occupation of gnd. state, even for $T>0$.

→ for this discussion set zero of energy $\varepsilon_0 = 0$ (lowest energy single-particle state) $\Rightarrow \mu < 0$.

- At $T=0$, BG in QM. gnd. state $\Rightarrow$ all N particles occupy lowest energy single-particle state $\varepsilon_0 = 0$.

Q: what happens when we cool the BG from higher T?

→ consider evolution of μ, determined by N & T:

$$N = g\int d\varepsilon \frac{\rho(\varepsilon)}{e^{\beta(\varepsilon-\mu)}-1} = gV\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2} \times \left[\frac{2}{\sqrt{\pi}}\int_0^\infty \frac{\sqrt{x}}{z^{-1}e^{x}-1}\right], \quad z = e^{\mu/T}.$$

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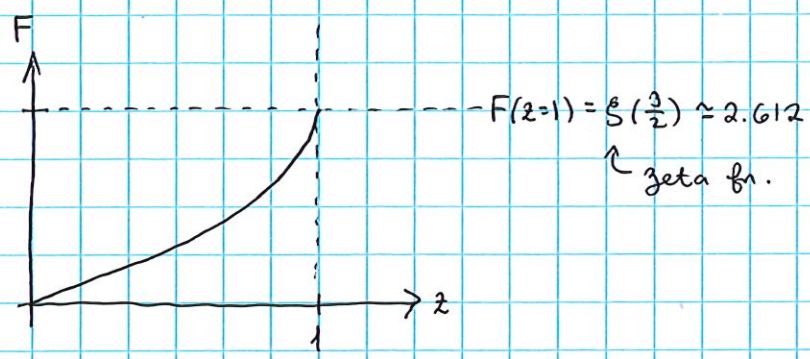
write this as: $N = gV \underbrace{\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}}_{=\lambda_{th}^{-3}} F(z)$, $\quad F(z) \equiv \frac{2}{\sqrt{\pi}} \int_0^\infty dx \frac{\sqrt{x}}{z^{-1}e^x - 1}$

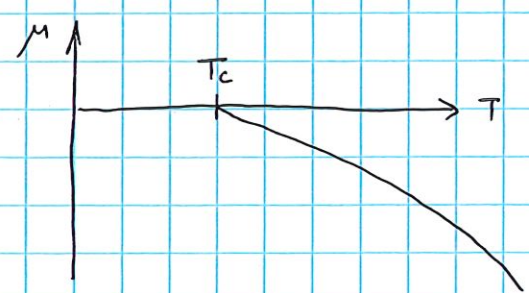
since $\mu < 0$, $z = e^{\mu/T}$ lies in the range $0 < z < 1$. & fn F behaves as:



→ as T decreases, $z = e^{\mu/T}$ has to increase to keep N fixed.

⇒ μ increases (or $|\mu|$ decreases), since $\mu < 0$.

Eventually, T is low enough that μ approaches its limiting value $\mu \to 0$ ($z \to 1$ & $F(z) \to F(z=1) = \zeta(\frac{3}{2}) \simeq 2.612$).



$\mu \to 0$ as $T \to T_c$

T_c determined by $\quad n = \frac{N}{V} = g\left(\frac{mT_c}{2\pi\hbar^2}\right)^{3/2} F(z=1) = g\left(\frac{mT_c}{2\pi\hbar^2}\right)^{3/2} \zeta(\frac{3}{2})$.

$$\Rightarrow \boxed{T_c(n) = \frac{2\pi\hbar^2}{m}\left(\frac{n}{g\zeta(\frac{3}{2})}\right)^{2/3} \simeq \frac{3.313}{g^{2/3}} \frac{\hbar^2}{m} n^{2/3}} \quad (*)$$

degen

Q: what happens for $T < T_c$?

- $\mu > 0$ not allowed. Otherwise $N = g\int d\varepsilon \frac{\rho(\varepsilon)}{e^{\beta(\varepsilon-\mu)}-1}$ would diverge as $\varepsilon \to \mu$.

Note that this divergence doesn't occur when $\mu=0$, since $\rho(\varepsilon)\sim\sqrt{\varepsilon}\to 0$ as $\varepsilon\to 0$.

- simply demanding $\mu(T<T_c)=0$ also not ~~allo~~ allowed, since that would imply particle # $N = gV\zeta(\frac{3}{2})\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}$ would decrease w/ decreasing T.

→ to resolve this paradox, return to <u>discrete</u> representation, & ask what happens as $\mu\to 0$:

$$N = \sum_r \bar{n}_r = \sum_r \frac{1}{e^{\beta(\varepsilon_r-\mu)}-1} \quad \text{\&} \quad \varepsilon_0=0.$$

$$= \underbrace{\frac{1}{e^{-\beta\mu}-1}}_{\equiv N_{\varepsilon=0}} + \underbrace{\sum_{\substack{r \text{ s.t.}\\ \varepsilon_r>0}} \frac{1}{e^{\beta(\varepsilon_r-\mu)}-1}}_{\equiv N_{\varepsilon>0}}$$

# of particles in lowest energy state $\varepsilon_0=0$ — # of particles in excited states.

- As $\mu\to 0$, $N_{\varepsilon=0}$ becomes so large that replacement of sum by integral is no longer legitimate.

(at $T=0$, $N_{\varepsilon=0}=N$ → all particles in gnd. state).

- On the other hand, as $\mu\to 0$ all terms in $N_{\varepsilon>0}$ remain finite & we can replace $\sum_r \to g\int d\varepsilon\, \rho(\varepsilon)$. w/ $\mu=0$.

- Thus, for $T<T_c$, we have that $\frac{N_{\varepsilon=0}}{N}$ is non-zero as $N\to\infty$, implying that a <u>macroscopic</u> # of particles occupy the $\varepsilon_0=0$ state.

→ "Bose-Einstein Condensation".

→ particles in $\varepsilon_0=0$ state referred to as the "condensate".

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& the remaining particles determined by:

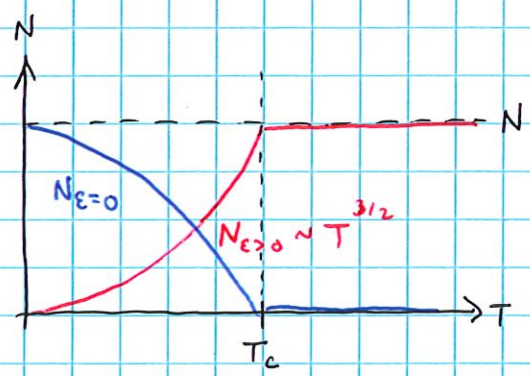
$$N_{\varepsilon>0} = gV\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}\left[\frac{2}{\sqrt{\pi}}\int_0^\infty dx\,\frac{\sqrt{x}}{e^x-1}\right]$$

→ the chemical potential μ stays at $\mu=0$ for $T<T_c$.

· Looking back at (*), we can write:

$$\boxed{N_{\varepsilon>0} = N\left(\frac{T}{T_c}\right)^{3/2} \quad \text{for } T\le T_c}$$

& $N = N_{\varepsilon=0} + N_{\varepsilon>0}$ $\Rightarrow$ $\boxed{N_{\varepsilon=0} = N\left[1-\left(\frac{T}{T_c}\right)^{3/2}\right] \quad \text{for } T\le T_c.}$



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now investigate other thermo. prop.'s for $T<T_c$:

$$E = g\int_0^\infty d\varepsilon\,\frac{\rho(\varepsilon)\,\varepsilon}{e^{\beta\varepsilon}-1}$$

($\mu=0$ for $T<T_c$ & gnd. state $\varepsilon_0=0$ does not contribute).

$$= gV\left(\frac{m}{2\pi\hbar^2}\right)^{3/2} T^{5/2} \times \frac{2}{\sqrt{\pi}}\int_0^\infty dx\,\frac{x^{3/2}}{e^x-1}$$

$T=T_c$: $\quad E(T_c) = gV\left(\frac{m}{2\pi\hbar^2}\right)^{3/2} T_c^{5/2} \times \frac{3}{2}\zeta\left(\frac{5}{2}\right) \simeq 0.7701\, N T_c.$

for $T\le T_c$: $\quad E(T) = E(T_c)\left(\frac{T}{T_c}\right)^{5/2}.$

· Using $pV = \frac{2}{3}E$: $\quad p(T_c) \simeq \frac{2}{3}\times 0.7701\, nT_c \simeq 0.5134\, nT_c.$

pressure

& $\quad p(T) = p(T_c)\left(\frac{T}{T_c}\right)^{5/2}.$

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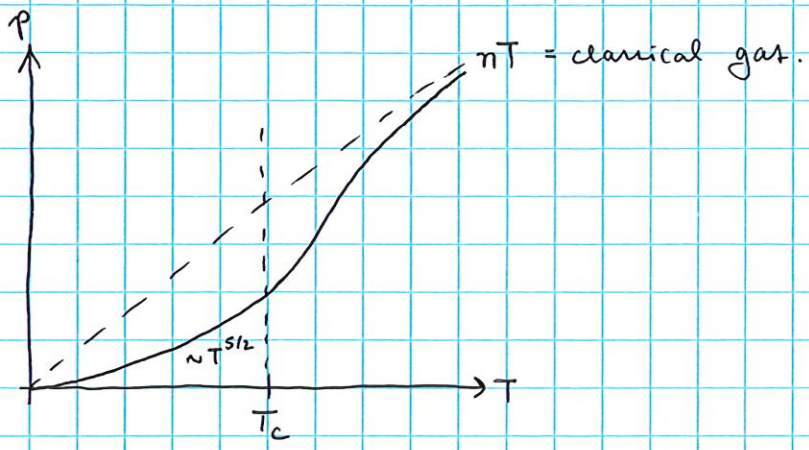


Note that ~~p~~ p is indep. of vol. V for $T < T_c$:

$$p(T) \simeq 0.0851 \, \frac{g m^{3/2}}{\hbar^3} \, T^{5/2} .$$

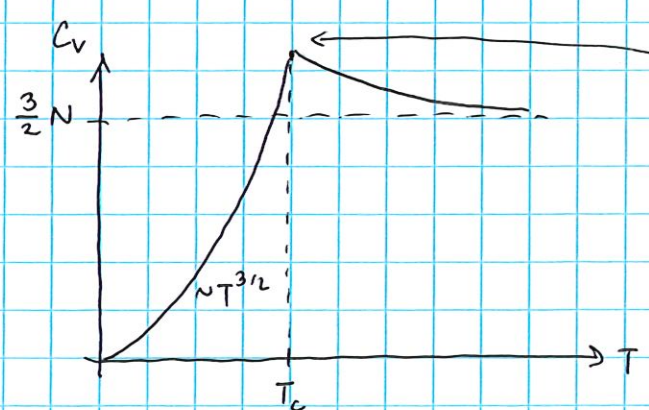
→ the reason is that, when V decreases (w/ N = fixed), more particles go into the condensate & condensate particles do not contribute to pressure ($\varepsilon_0 = 0 \Rightarrow$ momentum $\vec{p} = 0$).

· Finally, consider $C_V = \left(\frac{\partial E}{\partial T}\right)_V$ (heat capacity).

→ for $T \leq T_c$ $\quad C_V = E(T_c) \times \frac{5}{2} \frac{T^{3/2}}{T_c^{5/2}} \sim T^{3/2}$.

$$\& \quad C_V(T_c) = \frac{5}{2} \frac{E(T_c)}{T_c} \simeq 1.925 \, N .$$

c.f. classical value: $C_V = \frac{3}{2} N = 1.5 \, N < C_V(T_c)$.



cusp in C_V at $T = T_c$:

$$\left.\frac{\partial C_V}{\partial T}\right|_{T \to T_c^-} \neq \left.\frac{\partial C_V}{\partial T}\right|_{T \to T_c^+}$$

Note: cusp is special to non-interacting particles. Interaction effects tend to make singularity even stronger.

The behavior $C_V \sim T^{3/2}$ for $T < T_c$ can also be obtained from qualitative consideration: At $T=0$, all particles is $\varepsilon_0 = 0$ ($\vec{k}=0$) state.

→ For small $T>0$, states w/ $|\vec{k}| < k_{max}$ are excited w/ $\frac{\hbar^2 k_{max}^2}{2m} \sim T$.

$$\Rightarrow N_{excited} \sim V \int_{k<k_{max}} d^3\vec{k} \sim V k_{max}^3 \sim T^{3/2}$$

$$\& \quad C_V \sim N_{excited} \Rightarrow C_V \sim T^{3/2}. \quad \checkmark.$$

BEC's in the real world:

- BEC of dilute gases first observed by C. Wiemann, et. al (^{87}Rb) & W. Ketterele, et. al. (^{23}Na) in 1995
  - → most similar to theory we have developed.
- BEC also appears in other important contexts:
  - superfluidity of ^4He for $T \lesssim 2K$ → BEC of ^4He atoms
  - " " ^3He for $T \lesssim 2\,mK$.
    - → ^3He atoms are fermions. Fermions first "pair" to form bosons & then condense.
  - superconductivity: similar to ^3He, e^- in a metal form "Cooper pairs" = bosons. BEC of Cooper pairs → superconductivity.

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Summary.

photon stat: (see Lecture 28)

- $\bar{n}_r = \dfrac{1}{e^{\beta\varepsilon_r} - 1}$ "Planck distb.'n".

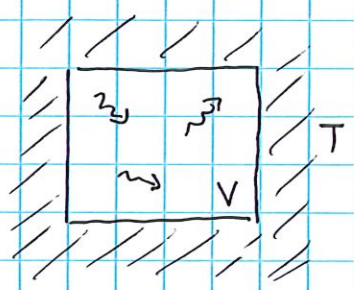
  → applies to bosonic particles where total particle # not conserved (e.g. photons).

- $Z = \prod_r \dfrac{1}{1 - e^{-\beta\varepsilon_r}}$ canonical partition fn. for particles obeying photon stat.

→ $F = -T\ln Z = +T\sum_r \ln(1 - e^{-\beta\varepsilon_r})$, $F = F(T, V)$.

Black-body radiation

- "black-body radiation" = electromagnetic (EM) radiation in thermal equil.



- Consider EM rad. in box of vol. V, whose walls maintained at temp. T.

  → particles in the walls continually absorb & emit radiation (which is why prop.'s of EM rad. depend on T).

- wave-particle duality of QM ⇒ in QM description, EM waves can be described as particles = "photons".

Note: interactions btwn. photons are ~~actually~~ negligible (this is b/c Maxwell's eqn.'s are linear) & we may treat the "photon gas" as an ideal gas.

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Q: How do we specify single-particle state r of a photon?

→ Maxwell's eqn.'s: (in vacuum)

$$\begin{cases} \nabla\cdot\vec{E} = 0 \\ \nabla\times\vec{E} = -\frac{1}{c}\frac{\partial\vec{B}}{\partial t} \\ \nabla\cdot\vec{B} = 0 \\ \nabla\times\vec{B} = \frac{1}{c}\frac{\partial\vec{E}}{\partial t} \end{cases}$$

(Gaussian units).

$$\rightarrow \quad \underbrace{\nabla\times(\nabla\times\vec{E})}_{\nabla\underbrace{(\nabla\cdot\vec{E})}_{=0} - \nabla^2\vec{E}} = -\frac{1}{c}\frac{\partial}{\partial t}(\nabla\times\vec{B}) = -\frac{1}{c^2}\frac{\partial^2\vec{E}}{\partial t^2}$$

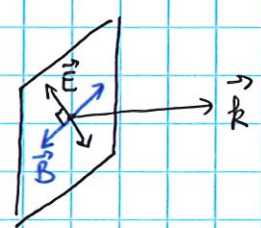
$$\Rightarrow \quad \nabla^2\vec{E} = \frac{1}{c^2}\frac{\partial^2\vec{E}}{\partial t^2} \qquad \text{wave eqn.}$$

$$\vec{E} = \mathrm{Re}\{\vec{E}_0 e^{i(\vec{k}\cdot\vec{x}-\omega t)}\} \quad \Rightarrow \quad k^2 = \omega^2/c^2 \quad \text{or} \quad \omega = ck$$

→ EM wave w/ wave-vector $\vec{k}$ has freq. $\omega = ck$.

$$\nabla\cdot\vec{E} = 0 \quad \Rightarrow \quad \vec{k}\cdot\vec{E}_0 = 0 \quad \Rightarrow \quad \vec{k}\perp\vec{E}_0$$

⇒ two linearly indep. modes of oscillation (or polarizations) of $\vec{E}$-field $\perp \vec{k}$.



$(\vec{B} = \hat{k}\times\vec{E})$.

QM: wave-particle duality ⇒ $\vec{p} = \hbar\vec{k}$ momentum of photon.
$\varepsilon = \hbar\omega$ energy " "

$\omega = ck \Rightarrow \varepsilon = cp$, energy-momentum relation for photons.

⇒ state r of photon specified by wave-vector $\vec{k}$ (or momentum $\vec{p}$).

& direction of polarization $\perp \vec{k}$. $\varepsilon_r \rightarrow \varepsilon = \hbar ck = \hbar\omega$ (indep. of polarization).

· In particle description, photons = indistinguishable bosons, whose particle # not conserved (can be absorbed / emitted by matter).

→ distrib'n fn. (Planck) $\bar{n}_r = \dfrac{1}{e^{\beta\varepsilon_r} - 1}$ → $\bar{n}_{\vec{k}} = \dfrac{1}{e^{\beta\hbar c k} - 1}$

= mean # of photons w/ wave-vector $\vec{k}$ & a particular polarization $\perp \vec{k}$.

· To count photon $\vec{k}$-states, we again impose periodic bndry cond.'s (PBC) on box of vol. $V = L_x L_y L_z$ (keeping in mind that details of BC's should be unimportant for a large system).

$$\Rightarrow \quad k_i = \frac{2\pi}{L_i} n_i \qquad i = x, y, z, \qquad n_i = 0, \pm 1, \pm 2, \ldots$$

(allowed wave-vectors w/ PBC's)

& # of states w/ wave-vector $\in (\vec{k}, \vec{k} + d\vec{k}) = \dfrac{V}{(2\pi)^3} d^3\vec{k}$.

For each $\vec{k}$, photon can have 2 indep. polarization states, so we also multiply result by 2:

$$\sum_r \longrightarrow 2 \times V \int \frac{d^3\vec{k}}{(2\pi)^3}$$

↓ angular int. $\int \sin\theta_k \, d\theta_k \, d\varphi_k = 4\pi$

$$= \frac{8\pi V}{(2\pi)^3} \int_0^\infty k^2 dk$$

↓ $\omega = ck$

$$= \frac{V}{\pi^2 c^3} \int_0^\infty \omega^2 d\omega .$$

→ rule for replacement of $\sum_r$ by $\int_0^\infty d\omega \, g(\omega)$, where $g(\omega) d\omega = \dfrac{V}{\pi^2 c^3} \omega^2 d\omega$ = # of photon states w/ freq. $\in (\omega, \omega + d\omega)$.

Use this result to investigate mean energy of the photon gas:

$$E = \sum_r \bar{n}_r \varepsilon_r \longrightarrow E = \frac{V}{\pi^2 c^3} \int_0^\infty d\omega\, \omega^2 \times \underbrace{\frac{1}{e^{\beta\hbar\omega}-1}}_{\text{distb.'n fn.}} \times \underbrace{\hbar\omega}_{\text{photon energy.}}$$

$$\rightarrow \quad E = \frac{V\hbar}{\pi^2 c^3} \int_0^\infty d\omega\, \frac{\omega^3}{e^{\beta\hbar\omega}-1}.$$

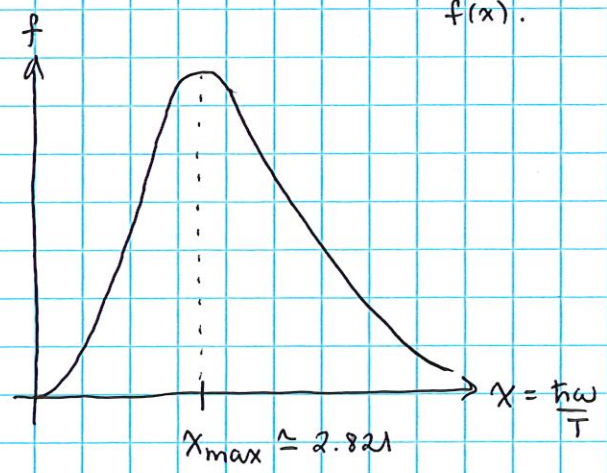
write this as $E = \int_0^\infty d\omega\, \frac{dE}{d\omega}$, where:

$$\boxed{\frac{dE}{d\omega}\, d\omega = \frac{V\hbar}{\pi^2 c^3} \frac{\omega^3 d\omega}{e^{\beta\hbar\omega}-1}}$$ = mean energy of photons w/ freq. $\in (\omega, \omega + d\omega)$.

"Planck's formula".

set $x = \beta\hbar\omega$:

$$\frac{dE}{d\omega}\, d\omega = \frac{V}{\pi^2(\hbar c)^3} T^4 \underbrace{\left(\frac{x^3}{e^x - 1}\right)}_{f(x).} dx$$



$\Rightarrow \hbar\omega_{max} \simeq 2.821\, T$ = max. of freq. distb.'n as fn. of T.

$\rightarrow$ as T increases, max is shifted to higher freq., in proportion to T "Wien's displacement law".

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For $\hbar\omega \ll T$ $(x \ll 1)$ $\quad f(x) \simeq \dfrac{x^3}{(1+x)-1} = x^2$

$e^x \simeq 1+x, \quad x \ll 1.$

$$\Rightarrow \frac{dE}{d\omega}\, d\omega \simeq \frac{T}{\pi^2 c^3}\, \omega^2 d\omega . \quad \text{"Rayleigh-Jeans formula".}$$

→ when $\hbar\omega \ll T$, $\hbar$ drops out & result is entirely <u>classical</u>.

The result follows from classical equipartition, as each mode contributes energy $\sim T$.

<u>Note</u>: The RJ formula predicts divergent energy density / unit freq. at high freq. ⇒ total (freq.-integrated) energy density diverges! → "ultraviolet catastrophe".

→ Planck's resolution of the UV catastrophe using quantized energies $\varepsilon = \hbar\omega$ was first success of quantum theory.

· Finally, compute the total energy:

$$E = \frac{T^4}{\pi^2 (\hbar c)^3} \underbrace{\int_0^\infty dx \, \frac{x^3}{e^x - 1}}_{= \frac{\pi^4}{15}} .$$

$$\Rightarrow \text{energy density} \quad \boxed{u = \frac{E}{V} = \frac{\pi^2}{15} \frac{T^4}{(\hbar c)^3}} \quad \text{"Stefan-Boltzmann law".}$$

= mean energy density of equil. rad. (photon gas) at temp. T.

Qualitatively: at temp. T, each photon contributes energy $\sim T$ to mean energy.

& # of photons $N_{ph} \sim V \int_{k<k_{max}} d^3\vec{k} \sim V k_{max}^3$, w/ $\hbar c k_{max} \sim T \Rightarrow N_{ph} \sim T^3$ & $E \sim N_{ph} \times T \sim T^4$

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Summary.

- Black-body radiation: equil. EM rad. $\leftrightarrow$ photon gas.

Single-particle photon state: $r \longrightarrow (\vec{k}\alpha)$, $\vec{k}$ = wave-vector, α = polarization $\perp \vec{k}$.

$$\varepsilon_r \longrightarrow \hbar c k = \hbar\omega$$

$$\longrightarrow \bar{n}_{\vec{k}\alpha} = \frac{1}{e^{\beta\hbar c k}-1}$$ = mean # of photon w/ wave-vector $\vec{k}$ & pol. α.

Counting photon states: $\sum_r \longrightarrow \frac{V}{\pi^2 c^3}\int \omega^2 d\omega$.

Planck formula: $\frac{dE}{d\omega}d\omega = \frac{V\hbar}{\pi^2 c^3}\frac{\omega^3 d\omega}{e^{\beta\hbar\omega}-1}$ = energy of photon gas in freq range $(\omega, \omega+d\omega)$.

$$\Rightarrow u = \frac{E}{V} = \frac{1}{V}\int_0^\infty \frac{dE}{d\omega}d\omega = \frac{\pi^2}{15}\frac{T^4}{(\hbar c)^3}.$$

Thermo. quantities for black-body radiation:

$$F = T\sum_r \ln(1-e^{-\beta\varepsilon_r}) \longrightarrow F = \frac{TV}{\pi^2 c^3}\int_0^\infty d\omega\, \omega^2 \ln(1-e^{-\beta\hbar\omega}).$$

$\downarrow x = \beta\hbar\omega$

$$= \frac{VT^4}{\pi^2(\hbar c)^3}\int_0^\infty dx\, x^2 \ln(1-e^{-x})$$

$\downarrow$ integration by parts.

$$= -\frac{VT^4}{3\pi^2(\hbar c)^3}\underbrace{\int_0^\infty dx \frac{x^3}{e^x-1}}_{=\frac{\pi^4}{15}}$$

$$\Rightarrow \boxed{F = -V\frac{\pi^2 T^4}{45(\hbar c)^3}}$$

- $E = -T^2\frac{\partial}{\partial T}\left(\frac{F}{T}\right) = V\frac{\pi^2}{15}\frac{T^4}{(\hbar c)^3}$ ✓

- pressure $p = -\left(\frac{\partial F}{\partial V}\right)_T \Rightarrow p = \frac{\pi^2 T^4}{45(\hbar c)^3} = \frac{1}{3}\frac{E}{V}$ "radiation pressure."

or $pV = \frac{1}{3}E$ (c.f. $pV = \frac{2}{3}E$ for FG & BG).

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- total # of photons:

$$N = \sum_r \bar{n}_r \longrightarrow N = \frac{V}{\pi^2 c^3} \int_0^\infty d\omega \frac{\omega^2}{e^{\beta\hbar\omega} - 1}$$

$x = \beta\hbar\omega$

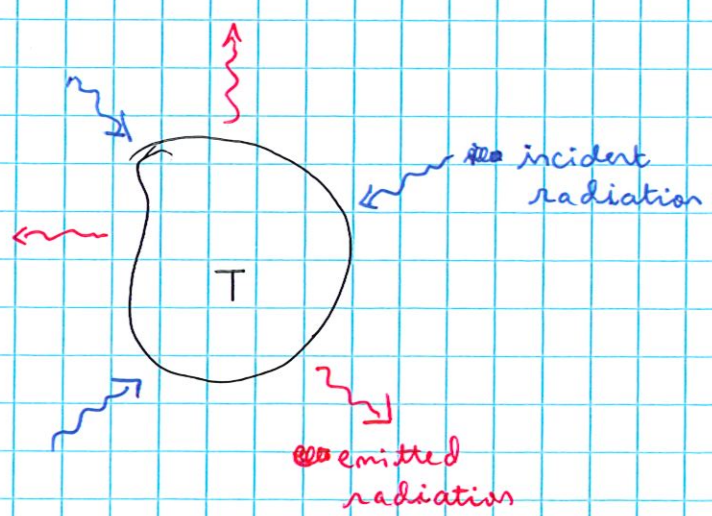
$$= \frac{V T^3}{\pi^2 (\hbar c)^3} \underbrace{\int_0^\infty dx \frac{x^2}{e^x - 1}}_{2\zeta(3) \simeq 2.404}$$

$\Rightarrow$ # of photons per unit vol. $n = \frac{N}{V} \simeq 0.244 \left(\frac{T}{\hbar c}\right)^3$

$\rightarrow$ in equil., density of photons determined solely by temp. T.

- ~~Thus~~ <u>Radiation emitted by a body at temp. T</u>
- Thus far, considered problem of equil. EM rad. in an enclosure at temp. T.

$\rightarrow$ now consider problem of a body in thermal equil. w/ black-body rad. around it. $\Rightarrow$ body continually reflects & absorbs incident photons & also emits new photons. In equil., these processes balance & photon distb.'n $\bar{n}_{\vec{k}\alpha}$ unchanged.



<u>Q</u>: How much power does the body emit by radiation as a fn. of freq. ω?

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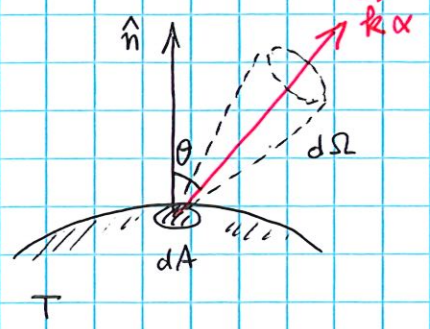
· emission of radiation :

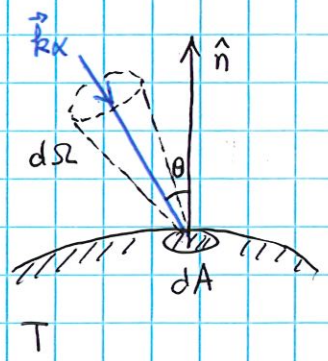


$k = |\vec{k}| = \omega/c$, $\hat{k} = \frac{\vec{k}}{k}$, $\hat{k}\cdot\hat{n} = \cos\theta$.

→ $J(\omega, \theta, \alpha)\, d\omega\, d\Omega$ = power emitted per unit area dA by the body into a small solid angle $d\Omega$ about $\hat{k}$ w/ freq. $\in (\omega, \omega+d\omega)$ (summed over polarization α).

· absorption of radiation:

→ first consider rad. incident on the body.



· Let $u_\omega d\omega = \frac{1}{V}\frac{dE}{d\omega}d\omega = \frac{\hbar}{\pi^2 c^3}\frac{\omega^3 d\omega}{e^{\beta\hbar\omega}-1}$

= energy density of photon w/ freq. $\in (\omega, \omega+d\omega)$.

→ (in time dt, energy incident on dA from photon w/ freq $\in (\omega, \omega+d\omega)$)

$$= u_\omega d\omega \times \underbrace{\left(\frac{d\Omega}{4\pi}\right)}_{\substack{\text{fraction of photon} \\ \text{in solid angle } d\Omega \\ \text{about } \hat{k}.}} \times \underbrace{(\text{spatial vol. containing incident photon})}_{= c\,dt \times dA \times \cos\theta.}$$

→ dividing by dt & dA gives incident power per unit area:

$$dP_i = c\, u_\omega d\omega \frac{d\Omega}{4\pi}\cos\theta = \frac{\hbar}{4\pi^3 c^2}\frac{\omega^3}{e^{\beta\hbar\omega}-1}\cos\theta\, d\omega\, d\Omega.$$

In general, only a fraction $a(\omega,\theta)$ of incident rad. is absorbed, the rest being reflected (assume no rad. transmitted through body).

$\Rightarrow$ power absorbed per unit area in freq. range $(\omega, \omega+d\omega)$:

$$= a(\omega,\theta) \times \frac{c}{4\pi} u_\omega \cos\theta \, d\omega \, d\Omega.$$

- In equil., when energy of the body is unchanged, radiated power must balance absorbed power:

$$\Rightarrow \quad J(\omega,\theta) = a(\omega,\theta) \times \frac{c}{4\pi} u_\omega \cos\theta$$

- Fn.'s $J(\omega,\theta)$ & $a(\omega,\theta)$ are determined solely by prop.'s of the body at temp. T. But we see that their ratio is a universal fn. of ω, θ, T; indep of prop.'s of the body:

$$\rightarrow \boxed{\frac{J(\omega,\theta)}{a(\omega,\theta)} = \frac{c}{4\pi} u_\omega = \frac{\hbar}{4\pi^3 c^2} \frac{\omega^3}{e^{\beta\hbar\omega}-1} \cos\theta}$$

$\Rightarrow$ "Kirchoff's law": good emitter of rad. = good absorber of rad. (& vice-versa)

- Important special case: $a(\omega,\theta)=1 \Rightarrow$ body absorbs all incident radiation. Such a body is called a "black body". (At $T=0$, such a body would look black). For a black body:

$$J(\omega,\theta) = \frac{c}{4\pi} u_\omega \cos\theta = \frac{\hbar}{4\pi^3 c^2} \frac{\omega^3}{e^{\beta\hbar\omega}-1} \cos\theta.$$

$\Rightarrow$ emitted power entirely determined by equil. rad. at temp. T of the body. In particular, emitted power is the same for all black bodies.

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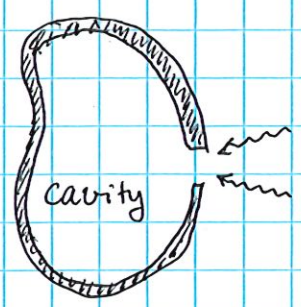
Model of a black body:



· cavity w/ highly absorbing walls & a small hole in the wall.

→ any rad. incident on the ~~whole~~ hole has negligible prob. of escaping, after repeated reflections from cavity walls.

⇒ sufficiently small hole will absorb essentially all incident rad. & so the hole acts as a black body

· Finally, compute total power per unit area radiated in freq. range $(\omega, \omega + d\omega)$

$$\rightarrow \quad J_\omega d\omega = \int d\Omega \; J(\omega,\theta)\, d\omega.$$

$$= \frac{c\, u_\omega d\omega}{4\pi} \underbrace{\int d\Omega \cos\theta}_{\int_0^{2\pi} d\varphi_k \int_0^{\pi/2} d\theta_k \sin\theta \cos\theta}$$

only outgoing photons.

$$= 2\pi \times \frac{1}{2}$$

$$= \pi$$

$$\Rightarrow \boxed{J_\omega = \frac{c}{4} u_\omega}$$

or $J_\omega = \dfrac{\hbar}{4\pi^2 c^2} \dfrac{\omega^3}{e^{\beta\hbar\omega} - 1}$, Planck law for spectral distb.'n of black-body rad.

· Total power/area over all freq: $J = \int_0^\infty d\omega\, J_\omega = \frac{\pi^2}{60} \frac{1}{c^2\hbar^3} T^4$.

→ when T in deg. K: $J = \frac{\pi^2}{60} \frac{k_B^4}{c^2\hbar^3} T^4 \equiv \sigma T^4$, $\sigma = \frac{\pi^2}{60} \frac{k_B^4}{c^2\hbar^3}$ Stefan-Boltzmann Const.