Part V

- More applications of Canonical Ensemble Theory
- Classical Statistical Mechanics
    - Non-interacting Examples
    - Interacting example
      (not-so-ideal classical gas)
- More on interacting systems and phase transitions

IX. Classical Statistical Mechanics : Examples

- $Z(T,V,N) = \sum\limits_{\substack{\text{all } N\text{-particle}\\ \text{states } i}} e^{-E_i/kT}$ works
- In classical physics, $\sum\limits_{\substack{\text{all } N\text{-particle}\\ \text{states } i}}$ becomes an integration over Γ phase space
- This chapter puts together examples in classical stat. mech. (i.e. discrete energies not important & quantum nature of particles not important).
  Some of them are discussed in previous chapters, problem sets, and sample questions.
  E.g. classical ideal gas
  harmonic oscillators (high temp. behavior)
  classical theory of paramagnetism
- A discussion on not-so-ideal classical gas is included to illustrate the importance of interactions in real-world problems

IX. Classical Statistical Mechanics: Examples

A. The Partition Function

$$Z(T,V,N)=\sum_{\substack{\text{all states } i\\ \updownarrow \\ N\text{-particle states}}} e^{-\beta E_i}$$

- In classical mechanics, the key quantity is the Hamiltonian

$$H = H(\vec{p}_1, \vec{p}_2, \cdots \vec{p}_N ; \vec{x}_1, \vec{x}_2, \cdots, \vec{x}_N) \qquad (6N \text{ variables})^{\dagger}$$

The state of a N-particle system is characterized by the momentum and coordinates of each of the N particles

$$\sum_{\text{all states}} \rightarrow \int \frac{d^3x_1\, d^3p_1}{h^3} \cdot \frac{d^3x_2\, d^3p_2}{h^3} \cdots \frac{d^3x_N\, d^3p_N}{h^3}$$

$$= \frac{1}{h^{3N}} \int d^3x_1\, d^3x_2 \cdots d^3x_N\, d^3p_1\, d^3p_2 \cdots d^3p_N$$

$$= \frac{1}{(2\pi\hbar)^{3N}} \int d^3x_1\, d^3x_2 \cdots d^3x_N\, d^3p_1\, d^3p_2 \cdots d^3p_N$$

[The point is: Integrate over phase space (Γ-space)]

[†] Here, we only consider the translational degrees of freedom. If there are internal degrees of freedom, $\sum_{\text{all states } i}$ implies also integrating those variables.

For distinguishable particles:

$$Z(T,V,N) = \frac{1}{h^{3N}} \int d^3x_1\, d^3x_2 \cdots d^3x_N\, d^3p_1\, d^3p_2 \cdots d^3p_N\; e^{-\beta H(\{p,x\})}$$

- Note: This is good for interacting / non-interacting particles

- For indistinguishable particles (classical gas):
  - There is an "overcounting" of states in the 6N integrals

$$\begin{array}{ll} \text{A state:} & \{(\vec{x}_1, \vec{p}_1)\;;\; (\vec{x}_2, \vec{p}_2)\;;\; \cdots\;;\; (\vec{x}_N, \vec{p}_N)\} \\ & \quad\;\; \downarrow \qquad\quad\;\; \downarrow \qquad\qquad\quad\;\; \downarrow \\ \text{particle:} & \quad\;\; 1 \qquad\quad\;\; 2 \qquad\qquad\quad\;\; N \end{array}$$

Any permutation ⇒ Same state (∵ identical / indistinguishable

But they are included in $\int d^3x_1 \cdots d^3x_N\, d^3p_1 \cdots d^3p_N$

⇒ "Counted" the same state too many times

- To compensate this overcounting†:

$$\text{factor } \frac{1}{N!}$$

[†] Note: The factor $\frac{1}{N!}$ accounts only for overcounting of states. Including $\frac{1}{N!}$ is NOT helpful in treating quantum (fermions/bosons) gases, where we need to consider the symmetry of the N-particle wavefunctions when treating $\sum_{\text{all states } i}$. Also, the factor $1/N!$ over-corrects for some cases.

Classical Partition Function for indistinguishable particles:

$$Z(T,V,N) = \frac{1}{N!\,h^{3N}} \int d^3x_1 d^3x_2 \cdots d^3x_N \, d^3p_1 d^3p_2 \cdots d^3p_N \, e^{-\beta H(\{p,x\})}$$

- Good for interacting/noninteracting (depending on the form of $H(\{p,x\})$) classical gases
- Here, we considered only the translational degrees of freedom. If a gas of molecules, there may be internal (e.g. vibrational, rotational) degrees of freedom.
- This is the starting point to treat classical gases (fluids)

Then, $F = F(T,V,N) = -kT \ln Z$

$$S = -\frac{\partial F}{\partial T} \;;\; \langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z \;;\; \text{etc.}$$

and the thermodynamics of the system follows.

[$\langle E \rangle$ is U in thermodynamics]

B. Non-ideal ("Real") Gas: Setting up the Problem

- Gas particles interact through 2-body forces characterized by the 2-body potential energy

$$\mathcal{U}(\vec{x}_i - \vec{x}_j) = \mathcal{U}(\underbrace{|\vec{x}_i - \vec{x}_j|}_{\text{depends on separation}}) \qquad [\text{Ideal gas: } U=0]$$

N-particle system:

$$H(\{x,p\}) = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + \frac{1}{2} \sum_{\substack{i=1 \\ (i\neq j)}}^{N} \sum_{j=1}^{N} \mathcal{U}(\vec{x}_i - \vec{x}_j)$$

$$= \underset{\text{k.e.}}{\underset{\Uparrow}{K}} + \underset{\text{interacting p.e.}}{\underset{\Uparrow}{W(\vec{x}_1, \vec{x}_2, \cdots, \vec{x}_N)}}$$

$$Z = \frac{1}{N!\,h^{3N}} \int \underbrace{d^3p_1 \cdots d^3p_N}_{} \, \underbrace{d^3x_1 \cdots d^3x_N}_{} \, \underbrace{e^{-\frac{\beta}{2m}(\vec{p}_1^{\,2} + \cdots + \vec{p}_N^{\,2})}}_{} \, \underbrace{e^{-\beta W(\vec{x}_1, \cdots, \vec{x}_N)}}_{}$$

$$= \frac{1}{N!\,h^{3N}} \int d^3p_1 \cdots d^3p_N \, e^{-\frac{\beta}{2m}(\vec{p}_1^{\,2} + \cdots + \vec{p}_N^{\,2})} \underbrace{\int d^3x_1 \cdots d^3x_N \, e^{-\beta W}}_{\text{hard part } (Z_W(\beta))}$$

$$= \frac{1}{N!\,h^{3N}} \left(\int d^3p \, e^{-\frac{\beta}{2m}\vec{p}^{\,2}} \right)^N \cdot Z_W(\beta)$$

$$= \frac{1}{N!\,h^{3N}} \underbrace{\left(\int_{-\infty}^{\infty} dp \, e^{-\frac{\beta p^2}{2m}} \right)^{3N}}_{\text{we have done this integral!}} \cdot Z_W(\beta) \qquad \Bigg| \qquad \int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$$

$$Z = \frac{1}{N!\,h^{3N}}\left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}} \cdot Z_W(\beta)$$

$$= \frac{1}{N!}\left(\frac{\sqrt{2\pi m kT}}{h}\right)^{3N} \cdot \underbrace{Z_W(\beta)}$$

from $\sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m}$ in H

contains all the complications due to $U(\vec{x}_i - \vec{x}_j)$

(ideal gas has this term in H)

[Recall: $\frac{h}{\sqrt{2\pi mkT}} \equiv \lambda_{\text{thermal}}$; $\frac{\sqrt{2\pi mkT}}{h} = \frac{1}{\lambda_{th}}$]

- $Z_W(\beta)$ for $U(\vec{x}_i - \vec{x}_j)$ is in general hard to evaluate
- Many approximations (e.g. perturbation) have been developed to handle $Z_W(\beta)$ and one could derive the Van der Waals gas law AND MORE!

「 • Special and trivial case: (Non-interacting)

Ideal Classical Gas: $U=0 \Rightarrow Z_W = \int d^3x_1 \cdots d^3x_N \,(1) = \left(\int d^3x\right)^N = V^N$

$$\therefore Z = \frac{1}{N!}\Bigg(\underbrace{V\frac{(2\pi mkT)^{3/2}}{h^3}}_{z}\Bigg)^N = \frac{1}{N!}\left(\frac{V}{\lambda_{th}^3}\right)^N$$

z = single-particle partition function (classical)

$$= \frac{1}{N!}(z)^N$$ ┘

Non-interacting Examples

- Sections C, D, E, F, G, H are non-interacting exactly solvable examples of classical stat. mech.
- Sec C : Classical ideal gas
- Sec. D : Equipartition of energy
- Sec. E : Maxwell's distribution of molecular speeds
- Sec. F : $Z = \frac{(z_{trans})^N}{N!} \cdot z_{vib} \cdot z_{rot}$ in gas of molecules
- Sec. G : Classical (Langevin) Theory of Paramagnetism
- Sec. H : Classical Oscillators

C. Classical Ideal Gas

$$H = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} = H(\{\vec{p}\})$$ (3N kinetic energy terms)

↑ depends on $\vec{p}$'s only

$$Z = \frac{1}{N!\,h^{3N}} \int d^3x_1 \cdots d^3x_N \int d^3p_1 \cdots d^3p_N \, e^{-\frac{\beta}{2m}(\vec{p}_1^{\,2}+\cdots+\vec{p}_N^{\,2})}$$

$$= \frac{1}{N!}\left(\underbrace{\frac{1}{h^3}\int d^3x\, d^3p\; e^{-\frac{\beta}{2m}\vec{p}^{\,2}}}\right)^N$$

- this depends on $(\vec{x},\vec{p})$ of one particle only
- single-particle (classical) partition function z

$$= \frac{1}{N!}(z)^N$$ ("non-interacting + classical" gives factorization)

$$z = \frac{1}{h^3}\underbrace{\int d^3x}\int dp_x\, dp_y\, dp_z\; e^{-\beta\frac{p_x^2}{2m}}\, e^{-\beta\frac{p_y^2}{2m}}\, e^{-\beta\frac{p_z^2}{2m}}$$

$$= \frac{1}{h^3}V\left(\underbrace{\int_{-\infty}^{\infty} dp\; e^{-\beta\frac{p^2}{2m}}}\right)^3$$

$$= \frac{1}{h^3}V\left(\sqrt{\frac{2\pi m}{\beta}}\right)^3$$ (gaussian integral)

$$\therefore\; Z = \frac{1}{N!}\left(V\left(\underbrace{\frac{\sqrt{2\pi m kT}}{h}}_{\equiv\,\frac{1}{\lambda_{th}}}\right)^3\right)^N = \frac{1}{N!}\left(\frac{V}{\lambda_{th}^3}\right)^N$$ Done!

- We have discussed that for a gas to be considered as a classical ideal gas, we require $\lambda_{th} \ll V^{1/3}$ or $\frac{V}{\lambda_{th}^3} \gg 1$ (dilute, high T)

- $\ln Z = N\ln\left(\frac{V}{\lambda_{th}^3}\right) - \ln N!$ ↙ correct overcounting

$$\approx N\ln\left(\frac{V}{\lambda_{th}^3}\right) - N\ln N + N$$

$$= N\ln\left(\frac{V}{N\lambda_{th}^3}\right) + N$$

$$\lambda_{th} = \frac{h}{\sqrt{\frac{2\pi m}{\beta}}} = h\sqrt{\frac{\beta}{2\pi m}}$$

$$U = \langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z$$

Note: $\lambda(\beta)$

$$= -\frac{\partial}{\partial\beta}\left[N\ln\left(\frac{V}{N\lambda^3}\right)\right] = -\frac{N^2\lambda^3}{V}\cdot\frac{V}{N}\left(\frac{\partial}{\partial\beta}\frac{1}{\lambda^3}\right) = \frac{3N}{\lambda}\frac{\partial\lambda}{\partial\beta}$$

$$= \frac{3N}{\lambda}\cdot\frac{h}{\sqrt{2\pi m}}\cdot\frac{1}{2}\frac{1}{\sqrt{\beta}} = \frac{3N}{2\beta} = \underbrace{3N\left(\frac{1}{2}kT\right)}_{\text{equipartition theorem}} = \frac{3}{2}NkT$$

[3N quadratic terms in Hamiltonian]

$$C_v = \frac{\partial U}{\partial T} = \frac{3}{2}Nk$$

For one mole, $N = N_A$, $C_{mole} = \frac{3}{2}N_A k = \underbrace{\frac{3}{2}R}_{\text{contribution from k.e. (translational) term}}$

Pressure $p = \frac{1}{\beta}\frac{\partial \ln Z}{\partial V} = NkT\frac{\partial}{\partial V}\left(\ln\frac{V}{N\lambda^3}\right)$

$$= NkT\cdot\frac{N\lambda^3}{V}\cdot\frac{1}{N\lambda^3} = \frac{NkT}{V}$$

∴ Equation of state:

$$\boxed{pV = NkT}$$

"ideal gas law" [comes from $Z \propto V$]

Note that: $pV = NkT = \frac{2}{3}\left(\frac{3}{2}NkT\right)$

$$\Rightarrow \boxed{pV = \frac{2}{3}U}$$

Entropy $S = -\frac{\partial F}{\partial T} = k\left(\ln Z + \overset{\frac{3N}{2}}{\frac{U}{kT}}\right)$

$$= k\left(N\ln\left(\frac{V}{N\lambda^3}\right) + N + \frac{3N}{2}\right)$$

$$= Nk\left(\ln\left(\frac{V}{N}\right) + \frac{3}{2}\ln\left(\frac{mkT}{2\pi\hbar^2}\right) + \frac{5}{2}\right)$$

← same result as before [microcanonical]

which is called the Sacher-Tetrode formula.

- Note that S is extensive
- In particular, by including a factor of $1/N!$, we get the term $\ln\left(\frac{V}{N}\right)$ only, which gives the extensivity of S.

$$\frac{V}{N} \uparrow \quad \frac{1}{\text{number density}} = \frac{1}{(N/V)}$$

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

To prepare for taking the derivative, write

$$S = Nk\left[\ln\left(\frac{kT}{p}\right) + \frac{3}{2}\ln\left(\frac{mkT}{2\pi\hbar^2}\right) + \frac{5}{2}\right],$$

← Eq. of state used

then $\left(\frac{\partial S}{\partial T}\right)_{p,N} = Nk\cdot\frac{1}{\left(\frac{kT}{p}\right)}\cdot\frac{k}{p} + \frac{3Nk}{2}\cdot\frac{1}{\frac{mkT}{2\pi\hbar^2}}\cdot\frac{mk}{2\pi\hbar^2}$

$$= \frac{Nk}{T} + \frac{3Nk}{2T} = \frac{5}{2}\frac{Nk}{T}$$

∴ $C_p = T\left(\frac{\partial S}{\partial T}\right)_{p,N} = \frac{5}{2}Nk = C_V + Nk$

For one mole, $C_p = C_V + R$ (a well known result)

Fluctuations in U:

$$\frac{\sqrt{\langle(\Delta E)^2\rangle}}{U} = \frac{\sqrt{kT^2C_V}}{U} = \sqrt{\frac{2}{3N}} \sim \frac{1}{\sqrt{N}}$$

(as discussed)

[All results are well known and now evaluated by the canonical ensemble theory.]

What does $1/N!$ do in $Z(T,V,N)$?

- Using $Z = \frac{V^N}{h^{3N}}(2\pi mkT)^{3N/2}$ instead of $\frac{V^N}{N!\,h^{3N}}(2\pi mkT)^{3N/2}$,

$$S = k\left[\underbrace{N\ln N}_{\text{cause problem!}} + N\ln\frac{V}{N} + \frac{3N}{2}\ln\left(\frac{mkT}{2\pi\hbar^2}\right) + \frac{3}{2}N\right]$$

[S is ~~not~~ extensive! But S should be extensive]

Including $\frac{1}{N!}$ makes S extensive, as it should be!

[Note: The wrong Z (without $1/N!$) still gives $p = \frac{NkT}{V}$ and $\langle E\rangle = \frac{3}{2}NkT$, which are correct.]

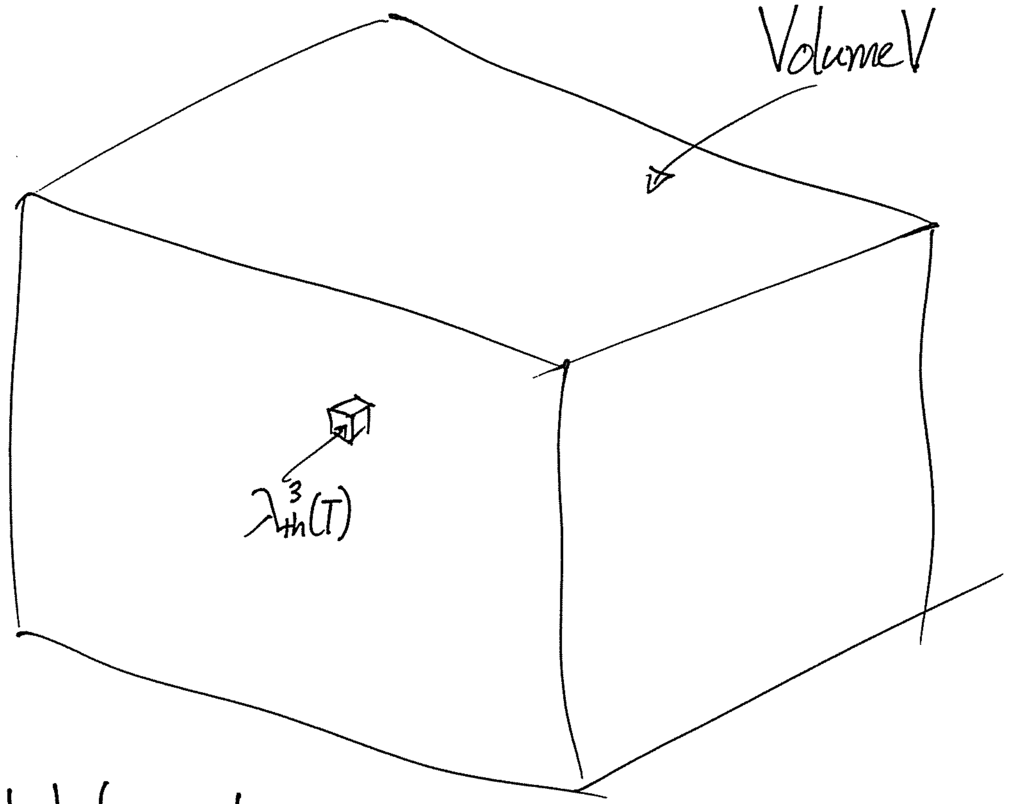
Think like a physicist!

$$Z = \frac{z^N}{N!} = \frac{1}{N!}\left(\frac{V}{\lambda_{th}^3}\right)^N$$ Classical ideal gas

For classical ideal gas, $V \gg \lambda_{th}^3$

[recall: particle separation $\gg \lambda_{th}$]

- Meaning of $\left(\frac{V}{\lambda_{th}^3}\right)^N$?
  - Use $\lambda_{th}(T)$ to divide whole volume V into boxes



$$\lambda_{th} = \frac{h}{\sqrt{2\pi mkT}}$$

High-temperature: $\underbrace{\frac{V}{\lambda_{th}^3}}_{\text{many boxes}}$ is huge $\gg N$

[# boxes $\gg N$]

- Take particle 1, fill in a box: $\left(\frac{V}{\lambda_{th}^3}\right)$ choices
- Take particle 2, fill in a box...

When $\left(\frac{V}{\lambda_{th}^3}\right) \gg N \gg 1$, $\left(\frac{V}{\lambda_{th}^3}\right)$ choices without worrying having two particles too close (in the same box) to each other (as the chance for it to happen is too tiny)

⋮

- $$\underbrace{\frac{1}{N!}}\left(\frac{V}{\lambda_{th}^3}\right)^N = \text{\# ways to put N particles into the many boxes}$$

correct over-counting

As T decreases, λ_{th} increases ⇒ box size increases

⇒ # boxes decreases

⇒ Soon or later; $\underbrace{\frac{V}{\lambda_{th}^3} = \#\text{ boxes} \approx N}$

Need to consider quantum nature of particles

[Not a classical gas any more]

Criteria for the validity of classical description

- Quantum effect $\lambda_{th} \cong$ de Broglie thermal wavelength

$$\lambda_{th} \ll \underbrace{\left(\frac{V}{N}\right)^{1/3}}$$

average separation between particles

⇒ quantum nature of particles is not important

thermal energy ~ kT ~ k.e. per particle ~ $\frac{p^2}{2m}$

⇒ $p \sim \sqrt{mkT}$

∴ $\lambda_{th} \sim \frac{h}{\sqrt{mkT}}$

$$\boxed{\lambda_{th}(T) = \frac{h}{\sqrt{2\pi mkT}}}$$

- Classical description is valid when†:

$$\frac{h}{\sqrt{mkT}} \ll \left(\frac{V}{N}\right)^{1/3}$$

∴ need
- number density: small (dilute)
- temperature: high
- mass of particles: not so small

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† Recall that this condition also implies $n_i \ll g_i$ in the previous discussion on the most probable distributions.

Examples

(i) Helium Gas at T~300K

$T \sim 300\text{K}$, $m \sim \frac{4}{6\times10^{23}}\text{g} \sim 7\times10^{-23}\text{g}$, $p \sim 760\text{mmHg}$

$\lambda_{th} = \frac{h}{\sqrt{2\pi mkT}} \sim 0.7\times10^{-8}\text{cm}$

$\frac{N}{V} \sim 10^{19}\text{-}10^{20}/\text{cm}^3 \Rightarrow \left(\frac{V}{N}\right)^{1/3} \sim 3\times10^{-7}\text{cm}$

∴ can use classical description

[this is why all other gases give $C_V = \frac{3}{2}R$ per mole at 300K]

(ii) Liquid Helium (T ~ a few K)

Denser than gas $\left(\frac{V}{N}\right)^{1/3} \sim 4\times10^{-8}\text{cm}$

Liquid He exists below 4.2K

At $T \sim 3\text{K}$, $\lambda_{th} \sim 0.7\times10^{-7}\text{cm}$

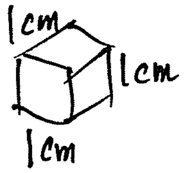
$\lambda_{th} \approx \left(\frac{V}{N}\right)^{1/3}$

∴ Cannot ignore quantum effects in studying liquid helium

Liquid Helium is a $\underbrace{\text{Quantum Liquid.}}_{\text{small mass and low-temperature make } \lambda_{th} \gtrsim \left(\frac{V}{N}\right)^{1/3}}$

Below 2K, liquid ^{4}He is a superfluid.

(iii) Metal (conduction electron) Physics at room temperature



$N \sim 10^{23}\text{-}10^{24}/\text{cm}^3$ electrons in Metal

$\frac{N}{V} \sim 10^{23}\text{-}10^{24}\,\text{cm}^{-3} \Rightarrow \left(\frac{V}{N}\right)^{1/3} \sim 2\times10^{-8}\text{cm}$

(dense gas!)

$\lambda_{th} = \frac{h}{\sqrt{2\pi mkT}}$

↖ electron mass is tiny (makes λ_{th} "big")

$T \sim \underbrace{300\text{K}}_{\text{which is not "low" in ordinary sense}}$, $\lambda_{th} \sim 2\times10^{-7}\text{cm}$

∴ $\lambda_{th}(300\text{K}) > \left(\frac{V}{N}\right)^{1/3}$ for electrons in Metals

⇒ Must consider Quantum effects (electrons are fermions) in the physics of metals

[Need Fermi gas and Fermi-Dirac distribution] in free-electron model of metals

Remarks: See p. IX-⑥

For classical ideal Gas, the single-particle partition function can also be viewed as: [particle-in-a-big-box]

$$z = \underbrace{\sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty}}_{\text{sum over single-particle states}} e^{-\beta\frac{\hbar^2}{2m}\left(k_{x,n_x}^2+k_{y,n_y}^2+k_{z,n_z}^2\right)};$$

where $k_{x,n_x} = n_x\frac{\pi}{L}$

$k_{y,n_y} = n_y\frac{\pi}{L}$

$k_{z,n_z} = n_z\frac{\pi}{L}$

- From Ch. VIII, we could turn the sum into an integral over $\vec{k}$

$$z = \frac{V}{(2\pi)^3}\int_{\text{all }\vec{k}\text{-space}} d^3k\; e^{-\beta\frac{\hbar^2k^2}{2m}} \qquad (*)$$

$$= \frac{1}{(2\pi)^3}\int_V d^3x \iiint_{\text{all }\vec{k}\text{-space}} dk_x\, dk_y\, dk_z\; e^{-\beta\frac{\hbar^2}{2m}\left(k_x^2+k_y^2+k_z^2\right)}$$

$$= \frac{1}{(2\pi)^3}\int_V d^3x \iiint_{\text{all }\vec{p}\text{-space}} \frac{dp_x}{\hbar}\cdot\frac{dp_y}{\hbar}\cdot\frac{dp_z}{\hbar}\; e^{-\beta\frac{1}{2m}\left(p_x^2+p_y^2+p_z^2\right)}$$

$$= \frac{1}{(2\pi\hbar)^3}\int_V d^3x \int_{\text{all }\vec{p}\text{-space}} d^3p\; e^{-\beta\varepsilon(p)}$$

$$= \frac{1}{h^3}\int_V d^3x \int d^3p\; e^{-\beta\frac{p^2}{2m}}$$

Note: $\frac{1}{h^3}$ appears!

[This justifies the prefactor $\frac{1}{h^{3N}}$ in evaluating Z in classical stat. mech.]

Similarly, in evaluating z (see Eq. (*)), we could turn the "sum over single-particle states" into an integral over single-particle energies (see Ch. VIII), i.e.

$$z = \sum_{\text{s.p. states } i} e^{-\beta\varepsilon_i} = \int_0^{\infty} g(\varepsilon)\, e^{-\beta\varepsilon}\, d\varepsilon$$

For non-interacting particles (3D), the DOS $g(\varepsilon)$ is

$$g(\varepsilon) = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\varepsilon^{1/2}$$

(apart from a spin-degeneracy factor g_s)

$$z = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\int_0^{\infty}\varepsilon^{1/2}e^{-\beta\varepsilon}\,d\varepsilon$$

$$= \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\frac{1}{\beta^{3/2}}\int_0^{\infty}x^{1/2}e^{-x}\,dx \qquad (x=\beta\varepsilon)$$

$$= \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}(kT)^{3/2}\,\underbrace{\Gamma\left(\frac{3}{2}\right)}_{\frac{\sqrt{\pi}}{2}}$$

[Gamma function]

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

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

$$= \frac{V}{\lambda_{th}^3} \;\#$$

(same as before)

D. Equipartition "Theorem"

Look at some previous results:

- classical ideal gas $\sum_i \frac{\vec{p}_i^{\,2}}{2m} = \sum_{i=1}^{N}\left(\frac{p_{ix}^2}{2m}+\frac{p_{iy}^2}{2m}+\frac{p_{iz}^2}{2m}\right)$

$$\langle E\rangle = \frac{3}{2}NkT = \underbrace{3N}_{\substack{\uparrow\\ \text{3N quadratic}\\ \text{terms in Hamiltonian}}}\cdot\left[\frac{1}{2}kT\right]$$

- 3N harmonic oscillators $\sum_{i=1}^{3N}\left(\frac{p_i^2}{2m}+\frac{1}{2}m\omega^2x_i^2\right)$

$$\langle E\rangle = 3NkT = 3N\cdot\left[\frac{1}{2}kT+\frac{1}{2}kT\right]$$
$$= \underbrace{6N}_{\substack{\uparrow\\ \text{6N quadratic terms in Hamiltonian}}}\cdot\left[\frac{1}{2}kT\right]$$

[Recall: $C = 3Nk$ (Dulong & Petit limit)]

- In classical limit, each quadratic term in Hamiltonian contributes $\frac{1}{2}kT$ to $\langle E\rangle$, when the system is in equilibrium at temperature T.

This is what the "Equipartition Theorem" says.

D. Equipartition Theorem

> • For a system in equilibrium at absolute temperature T, the mean value of each independent quadratic term in the energy is equal to $\frac{1}{2}kT$.

- Consider a classical system with f degrees of freedom and assume that the energy can be written as

$$E(p_1,p_2,\dots,p_f;\,x_1,x_2,\dots,x_f) = \underbrace{b p_i^2}_{\substack{\uparrow\\ \text{quadratic in } p_i}} + \mathcal{E}(p_1,\dots,p_f;\,x_1,\dots,x_f)$$

where $b>0$ and $\mathcal{E}$ does not depend on p_i

When the system is in equilibrium at T:

$$\langle b p_i^2\rangle = \frac{\int dp_1\cdots dp_f\,dx_1\cdots dx_f\; e^{-\beta E}\, b p_i^2}{\int dp_1\cdots dp_f\,dx_1\cdots dx_f\; e^{-\beta E}}$$

$$= \frac{\int dp_1\cdots dp_i\cdots dp_f\,dx_1\cdots dx_f\; e^{-\beta\mathcal{E}}\, e^{-\beta b p_i^2}\, b p_i^2}{\int dp_1\cdots dp_i\cdots dp_f\,dx_1\cdots dx_f\; e^{-\beta\mathcal{E}}\, e^{-\beta b p_i^2}}$$

$$\langle b p_i^2\rangle = \frac{\int_{-\infty}^{\infty} dp_i\, e^{-\beta b p_i^2}\, b p_i^2}{\int_{-\infty}^{\infty} dp_i\, e^{-\beta b p_i^2}}$$

(these integrals can be done separately, they are related to Gaussian integrals)

$$= -\frac{\partial}{\partial\beta}\left(\ln\left[\underbrace{\int_{-\infty}^{\infty} dp\, e^{-\beta b p^2}}_{\sqrt{\frac{\pi}{\beta b}}}\right]\right)$$

$$= -\frac{\partial}{\partial\beta}\left(\ln\sqrt{\frac{\pi}{\beta b}}\right)$$

$$= \frac{1}{2\beta} = \frac{1}{2}kT \quad *$$

Obviously, this result works† for $\begin{cases} E = \sum_i b_i p_i^2 \\ E = \sum_i c_i x_i^2 \\ E = \sum_i b_i p_i^2 + \sum_j c_j x_j^2 \end{cases}$

and each quadratic term contributes $\frac{1}{2}kT$ to $\langle E\rangle$ (or U in thermodynamics)

⌈† The result is <u>much more general</u>!

It works for terms of the form: $x_i x_j$, $p_i p_j$, $x_i p_j$!

Why?
$$\underset{\substack{\uparrow\\ \text{Hamiltonian}}}{H} = \frac{1}{2}\sum_{i,j=1}^{M} \underset{\substack{\uparrow\\ \text{real symmetric matrix}}}{\alpha_{ij}}\; \underset{\substack{\uparrow\quad\uparrow\\ \text{could be coordinates or momenta}}}{y_i y_j} \qquad \text{(quadratic terms)}$$

$$\langle E\rangle = \frac{\int_{-\infty}^{\infty} dy_1\, dy_2 \cdots dy_M\; H\, e^{-\beta H}}{\int_{-\infty}^{\infty} dy_1\, dy_2 \cdots dy_M\; e^{-\beta H}}$$

The point is: We can always <u>diagonalize the Hamiltonian</u> by performing a suitable transformation.

i.e., Construct $\overleftrightarrow{A}$ such that $\qquad \overleftrightarrow{A} \leftarrow$ matrix A

$$y_i = \sum_l A_{il}\, x_l$$

new variables $\qquad$ generalized coordinates/momenta

Construct/choose $\overleftrightarrow{A}$: $\overleftrightarrow{A}^{-1}\overleftrightarrow{\alpha}\overleftrightarrow{A}$ is diagonal with elements λ_k (eigenvalues of $\overleftrightarrow{\alpha}$)

i.e. diagonalize $\overleftrightarrow{\alpha}$

Then
$$\boxed{H = \frac{1}{2}\sum_{k=1}^{M} \lambda_k x_k^2} \qquad (*)$$

The Jacobian involved in changing $\int dy_1 \cdots dy_M$ to $\int dx_1 \cdots dx_M$ is $\det \overleftrightarrow{A} = \underline{1}$

Using $(*)$, the equipartition theorem $\Rightarrow \langle E\rangle = \frac{1}{2}MkT$

⌋

E. Maxwell Distribution of molecular speeds

$n(v)dv$ = # particles with speeds ($v = |\vec{v}|$) between v and $v+dv$ in a N-particle gas at temperature T

Aim: Obtain an expression for $n(v)$

$$\epsilon(k) = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2(k_x^2+k_y^2+k_z^2)}{2m} = \frac{p_x^2+p_y^2+p_z^2}{2m} = \underset{\overset{\|}{\epsilon(p)}}{\frac{p^2}{2m}} = \frac{1}{2}mv^2$$

Ideas: (i) Look for # particles with k or p $(=|\vec{p}|)$

$k \rightarrow k+dk$ $\quad$ $p \rightarrow p+dp$

(ii) change variable from k (or p) to v

(*)

$$n(v)dv = \underbrace{\frac{V}{(2\pi)^3} 4\pi k^2}_{\text{number of states in } k\rightarrow k+dk} \left(\frac{Ne^{-\beta\frac{\hbar^2k^2}{2m}}}{Z}\right) dk$$

← # particles per single-particle state

$\hbar k = p = mv$

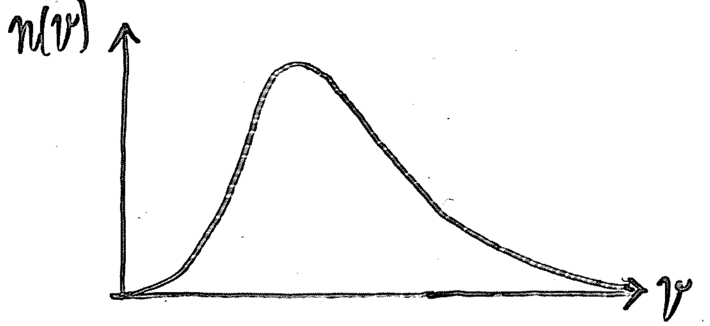
$$= \frac{\frac{V}{(2\pi\hbar)^3} 4\pi p^2 \, N e^{-\beta p^2/2m} dp}{\frac{1}{(2\pi\hbar)^3}\int d^3x \int d^3p \, e^{-\beta p^2/2m}} = \frac{N 4\pi p^2 e^{-\beta\frac{p^2}{2m}} dp}{\left(\int dp \, e^{-\beta\frac{p^2}{2m}}\right)^3}$$

(*) This follows from (Ch. VII, classical limit): $\frac{n_i}{g_i} = N\frac{e^{-\beta\epsilon_i}}{Z} \Rightarrow n_i = g_i \cdot \left(\frac{Ne^{-\beta\epsilon_i}}{Z}\right)$

$$n(v)dv = \frac{N 4\pi m^2 v^2 e^{-\frac{mv^2}{2kT}} m dv}{(2\pi m kT)^{3/2}} \qquad (\because p = mv)$$

$$\therefore \boxed{n(v) = N\frac{4\pi m^3}{(2\pi m kT)^{3/2}} \underbrace{v^2 e^{-\frac{mv^2}{2kT}}}_{v\text{-dependence}}}$$

[Maxwell distribution of molecular speeds (~1859)]



Behaviour:

- small v, increases as v^2
- large v, drops exponentially

$\int_0^\infty n(v)dv = N$ by definition

(i) Mean square speed: $\langle v^2\rangle$

$$n(v) = B v^2 e^{-\frac{mv^2}{2kT}}$$

$$\langle v^2\rangle = \frac{\int_0^\infty v^2 n(v)dv}{\int_0^\infty n(v)dv} = \frac{\int_0^\infty v^4 e^{-\frac{mv^2}{2kT}}dv}{\int_0^\infty v^2 e^{-\frac{mv^2}{2kT}}dv}$$

$$= \frac{\left(\frac{2kT}{m}\right)^{5/2}\int_0^\infty y^4 e^{-y^2}dy}{\left(\frac{2kT}{m}\right)^{3/2}\int_0^\infty y^2 e^{-y^2}dy} \qquad \Big| \; y = \sqrt{\frac{m}{2kT}}\,v$$

[recall: Gaussian integrals]

⌜ ∴ Need $I_n = \int_0^\infty x^n e^{-x^2} dx$; $\left(I_0 = \frac{\sqrt{\pi}}{2} ;\ I_1 = \frac{1}{2} \right)$

$$= -\frac{1}{2} \int_0^\infty x^{n-1} \frac{d(e^{-x^2})}{dx}\, dx$$

$$= -\frac{1}{2} \left[x^{n-1} e^{-x^2} \Big|_0^\infty - \int_0^\infty e^{-x^2} \frac{d}{dx} x^{n-1} dx \right] \quad \text{(by parts)}$$

$$= \frac{1}{2} \int_0^\infty (n-1)\, x^{n-2} e^{-x^2} dx$$

$$\Rightarrow I_n = \left(\frac{n-1}{2} \right) I_{n-2} \quad ⌟$$

(a property of gaussian integrals)

$$\therefore \langle v^2 \rangle = \frac{2kT}{m} \cdot \frac{I_4}{I_2} = \frac{2kT}{m} \cdot \frac{\frac{3}{2} \cdot \frac{1}{2} \cdot I_0}{\frac{1}{2} \cdot I_0}$$

$$= \frac{3kT}{m}$$

Note: $\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} kT$

$$\sqrt{\langle v^2 \rangle} \equiv v_{rms} = \sqrt{\frac{3kT}{m}} = 1.73 \sqrt{\frac{kT}{m}}$$

(ii) Mean speed $\langle v \rangle$

$$\langle v \rangle = \frac{\int_0^\infty v\, n(v) dv}{\int_0^\infty n(v)\, dv} = \frac{\int_0^\infty v^3 e^{-\frac{mv^2}{2kT}} dv}{\int_0^\infty v^2 e^{-\frac{mv^2}{2kT}} dv} = \sqrt{\frac{2kT}{m}} \frac{\int_0^\infty y^3 e^{-y^2} dy}{\int_0^\infty y^2 e^{-y^2} dy}$$

$$\langle v \rangle = \sqrt{\frac{2kT}{m}} \frac{I_3}{I_2} = \sqrt{\frac{2kT}{m}} \frac{1 \cdot I_1}{\frac{1}{2} \cdot I_0}$$

$$= \sqrt{\frac{2kT}{m}}\, 2 \cdot \frac{1}{2} \frac{1}{\frac{\sqrt{\pi}}{2}} = \sqrt{\frac{kT}{m}}\, 2\sqrt{\frac{2}{\pi}}$$

$$= 1.59 \sqrt{\frac{kT}{m}} \#$$

(iii) Most probable speed v_{mp}

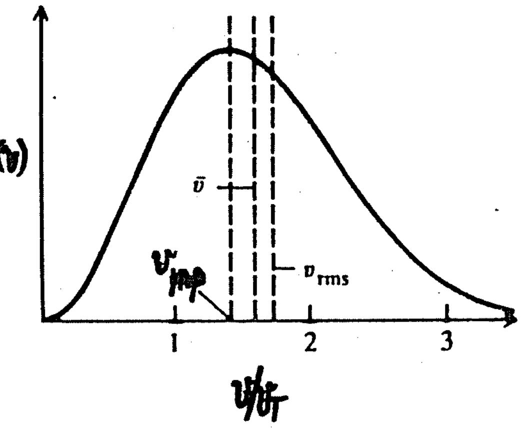
$$\left. \frac{dn(v)}{dv} \right|_{v = v_{mp}} = 0 \quad \text{(peaks at } v_{mp})$$

$$\Rightarrow v_{mp} = \sqrt{\frac{2kT}{m}} = 1.41 \sqrt{\frac{kT}{m}} \#$$

$$\therefore v_{mp} = \sqrt{2} \sqrt{\frac{kT}{m}} \cong 1.41 \sqrt{\frac{kT}{m}}$$

$$\langle v \rangle = \sqrt{\frac{8}{\pi}} \sqrt{\frac{kT}{m}} \approx 1.59 \sqrt{\frac{kT}{m}}$$

$$v_{rms} = \sqrt{\langle v^2 \rangle} = \sqrt{3} \sqrt{\frac{kT}{m}} \approx 1.73 \sqrt{\frac{kT}{m}}$$



$$v_T = \sqrt{\frac{kT}{m}}$$

Alternatively

- $$\underset{\uparrow \text{ wave vector}}{\vec{k}} \xrightarrow{\hbar k} \underset{\uparrow \text{ momentum}}{\vec{p}} \longrightarrow m\vec{v}$$

- Two key points: $\underbrace{\text{speed } v \text{ to } v+dv}_{\text{those } \vec{k}\text{'s in } k \text{ to } k+dk}$

(1) 3D system: $\sim k^2 dk \sim v^2 dv$

(2) Boltzmann factor: $e^{-\frac{\varepsilon_i}{kT}} \rightarrow e^{-\frac{mv^2}{2kT}}$

$$\therefore\ n(v) = \overset{\text{a constant}}{C}\ v^2 e^{-\frac{mv^2}{2kT}}$$

- To get the complete form:

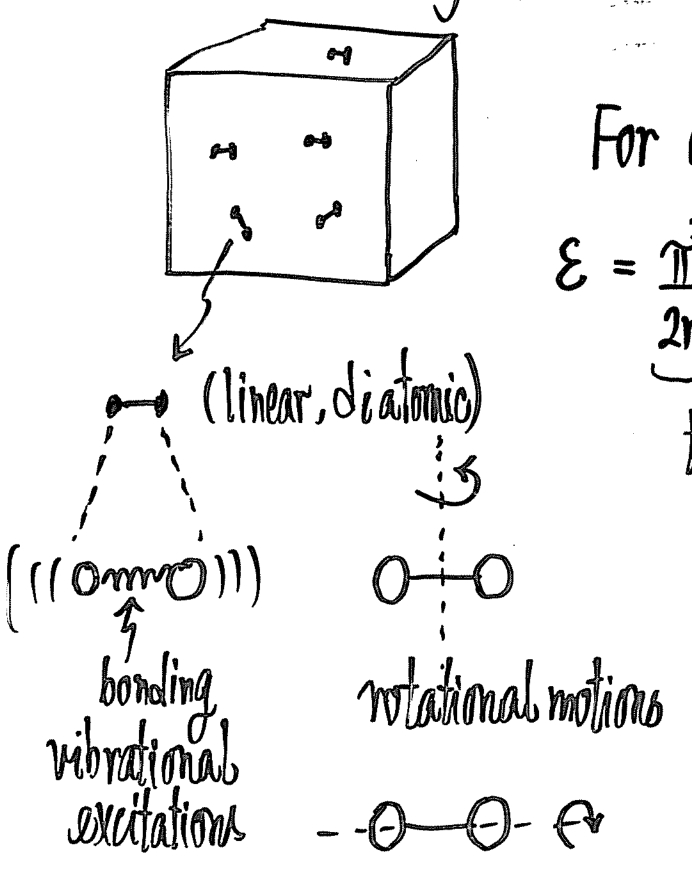
Require $$\int_0^\infty n(v)\,dv = \underbrace{C\int_0^\infty v^2 e^{-\frac{mv^2}{2kT}}\,dv}_{\text{determines the constant } C} = \overset{\substack{\text{total \#} \\ \text{particles}}}{N}$$

Also give

$$n(v) = N \frac{4\pi m^3}{(2\pi mkT)^{3/2}}\, v^2 e^{-\frac{mv^2}{2kT}}$$

(same result)

F. A Gas of molecules (diatomic)



For each molecule†,

$$\varepsilon = \underbrace{\frac{\pi^2\hbar^2}{2mL^2}(n_x^2+n_y^2+n_z^2)}_{\substack{\text{translational} \\ \text{(CM motion)}}} + \overbrace{\underbrace{\left(n+\frac{1}{2}\right)\hbar\omega}_{\substack{\text{vibrational} \\ (n)}} + \underbrace{\frac{l(l+1)\hbar^2}{2I}}_{\substack{\text{rotational} \\ (l,m)}}}^{\text{internal degrees of freedom}^{+}}$$

- For such a classical ideal gas,

$$Z = \frac{1}{N!}(z)^N$$

Here,

$$z = \sum_{\substack{\text{single-particle} \\ \text{states}}} e^{-\beta\varepsilon_i} = \text{single-molecule partition function}$$

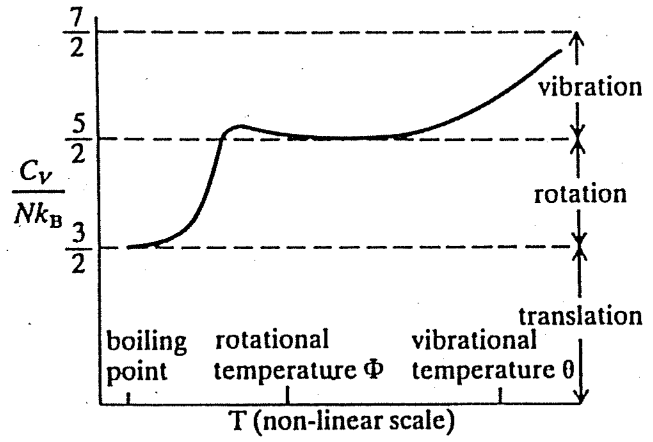
Assume the degrees of freedom $\underbrace{\text{are independent}}_{\text{one motion is not affecting another}}$

↪ ε = sum of contributions from independent modes

$$z = \sum_{n_x,n_y,n_z} \overset{\text{vib.}}{\sum_{n=0}^{\infty}} \overset{\text{rot.}}{\sum_{l,m}} e^{-\beta\varepsilon_{n_x,n_y,n_z,n,l,m}}$$

$$= \underbrace{z_{\text{translation}}}_{V\left(\frac{\sqrt{2\pi mkT}}{h}\right)^3} \cdot \underbrace{z_{\text{vib}} \cdot z_{\text{rot}}}_{\text{(see Ch. VI) [need quantum treatment for } z_{\text{vib}}]} \qquad \text{(factorized)}$$

- And the free energies from each part <u>add</u>.
- This is why at very high temperatures $kT \gg \hbar\omega \gg \frac{\hbar^2}{2I}$, vibrational, rotational, translational excitations all contribute to the heat capacity.
- As temperature is lowered $\hbar\omega \gg kT \gg \frac{\hbar^2}{2I}$, vibrational excitations cannot be excited $\Rightarrow$ no vibrational contribution to U and thus C $\Rightarrow$ C drops by R per mole.
- At even lower temp., rotational contribution may be frozen, and only translational contribution to U and thus C remains.



(Schematic) C_V vs T for a diatomic gas

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† One may also include electronic excitations in ε. These excitations require a few eV or more to be excited, and thus the excitation energy $\gg kT$.

G. Classical Theory of Paramagnetism

Done! See Chapter VI.

H. Harmonic Oscillators: Classical Version

- Consider N localized (distinguishable) <u>classical 3D</u> harmonic oscillators

$$H = \sum_{i=1}^{N}\left(\frac{\vec{p}_i^{\,2}}{2m} + \frac{1}{2}m\omega^2 x_i^2\right)$$

$p_{ix}^2 + p_{iy}^2 + p_{iz}^2$

$x_i^2 + y_i^2 + z_i^2$

$$Z = \frac{1}{h^{3N}}\int d^3p_1 \cdots d^3p_N \, d^3x_1 \cdots d^3x_N \, e^{-\beta H}$$

$$= \left[\frac{1}{h^3}\int d^3p\, d^3x\, e^{-\beta\left(\frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2\right)}\right]^N$$

$$= (z)^N$$

$$z = \frac{1}{h^3}\int_{-\infty}^{\infty}dp_x\int_{-\infty}^{\infty}dp_y\int_{-\infty}^{\infty}dp_z\int_{-\infty}^{\infty}dx\int_{-\infty}^{\infty}dy\int_{-\infty}^{\infty}dz\; e^{-\beta\left(\frac{p_x^2+p_y^2+p_z^2}{2m} + \frac{1}{2}m\omega^2(x^2+y^2+z^2)\right)}$$

$$= \left(\frac{1}{h}\underbrace{\int_{-\infty}^{\infty}dp\; e^{-\beta\frac{p^2}{2m}}}\;\underbrace{\int_{-\infty}^{\infty}dx\; e^{-\frac{\beta}{2}m\omega^2x^2}}\right)^3$$

Gaussian integrals again!

$$= \left(\frac{1}{2\pi\hbar}\sqrt{\frac{2m\pi}{\beta}}\;\sqrt{\frac{2\pi}{\beta m\omega^2}}\right)^3 = \left(\frac{kT}{\hbar\omega}\right)^3$$

$$Z = \left(\frac{kT}{\hbar\omega}\right)^{3N}$$

$$\therefore\ F = -kT\ln Z = -3NkT\ln\left(\frac{kT}{\hbar\omega}\right)$$

$$S = -\frac{\partial F}{\partial T} = 3Nk\left(1+\ln\left(\frac{kT}{\hbar\omega}\right)\right)$$

$\langle E\rangle = 3NkT$ (as expected from the <u>equipartition theorem</u>)

$C_V = 3Nk$ (a constant, doesn't → 0 as $T \to 0$!)

[▪ Compare results with quantum oscillators
▪ The results here are those in the limit $kT \gg \hbar\omega$.]

▪ When $kT < \hbar\omega$, we need to consider the discreteness of the harmonic oscillator energy spectrum, as the low-lying states now dominate the physics.

▪ For a 1D harmonic oscillator, z_{1D}(classical)

$$= \frac{1}{h}\int_{-\infty}^{\infty} dp\, e^{-\beta\frac{p^2}{2m}} \int_{-\infty}^{\infty} dx\, e^{-\beta\frac{m\omega^2 x^2}{2}}$$

$$= \frac{kT}{\hbar\omega}$$

Alternative approaches:

We could have started formally with: for a 1D harmonic oscillator

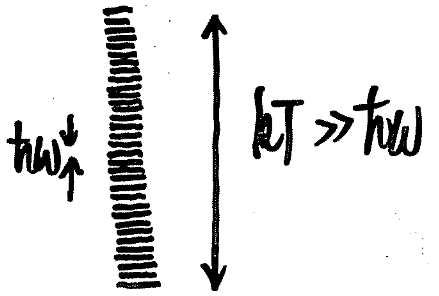
$$z_{1D} = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega}$$

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

• This comes from the zero-point (ground state) energy. No one who only knows classical physical would have anticipated the presence of this factor (constant factor).

Consider $z_{1D} = \sum_{n=0}^{\infty} e^{-\beta n\hbar\omega}$

When $kT \gg \hbar\omega$, <u>discreteness</u> of allowed energies is <u>not important.</u>



(a) <u>Treat n as continuous</u>

$$z_{1D} \approx \int_0^{\infty} dn\, e^{-n\beta\hbar\omega} = \frac{1}{\beta\hbar\omega}\int_0^{\infty} dy\, e^{-y}$$

$$= \frac{1}{\beta\hbar\omega}$$

$$= \frac{kT}{\hbar\omega}$$ (same as before)

(b) Invoking density of states

$$Z_{1D} = \sum_n e^{-\beta\varepsilon_n} \qquad \text{where } \varepsilon_n = n\hbar\omega$$

$g(\varepsilon)\,d\varepsilon$ = number of 1D oscillator states with energy between ε and $\varepsilon + d\varepsilon$

$$= \frac{d\varepsilon}{\hbar\omega} \qquad \therefore\ g(\varepsilon) = \frac{1}{\hbar\omega}$$

= constant for 1D oscillator

$$Z_{1D} = \int_0^\infty g(\varepsilon)\, e^{-\beta\varepsilon}\, d\varepsilon$$

$$= \frac{1}{\hbar\omega}\int_0^\infty e^{-\beta\varepsilon}\, d\varepsilon$$

$$= \frac{1}{\beta\hbar\omega} = \frac{kT}{\hbar\omega}$$

(same as before)