Virial Theorem: 10/3

Last time:

$$\mathcal{V} = -\left\langle \sum_{i=1}^{3N} q_i \dot{p}_i \right\rangle = 3NkT$$

$$\therefore \boxed{\mathcal{V} = -3NkT} \quad (*)$$

$$= -\left\langle \sum_{i=1}^{3N} q_i \underbrace{\frac{\partial (m v_i)}{\partial t}}_{} \right\rangle$$

$m a_i = F_i$ generalize force.

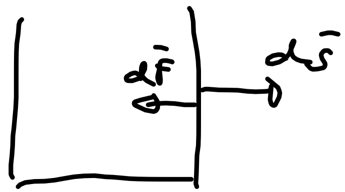
$+\mathcal{V}$ is called the Virial of a system.

What is the relationship between Virial and other physical quantities?

$$\bar{F} = \oint_S -P\,d\bar{S}$$

- Ideal gas: (non-interacting).

$$d\bar{F} = -P\,d\bar{S}$$



$$\mathcal{V}_0 = \left\langle \sum_{i=1}^{3N} q_i \cdot F_i \right\rangle_0 = -P \oint_S \bar{r} \cdot d\bar{S} \underset{\text{divergence theorem}}{=} -P \int_V \bar{\nabla} \cdot \bar{r}\, dV =$$

$$= -P \int_V \underbrace{\left(\frac{dx}{dx} + \frac{dy}{dy} + \frac{dz}{dz} \right)}_{3} dV =$$

$$= -3P \int_V dV = -3PV \overset{(*)}{=} -3NkT \Rightarrow \underbrace{\boxed{PV = NkT}}_{\text{eq. of state}}$$

$$\frac{PV}{V} = \frac{NkT}{V}$$

$$P = nkT \qquad n = \frac{N}{V}$$

$$\boxed{\frac{P}{nkT} = 1}$$ true for the ideal gas.

Notice that for the ideal gas:

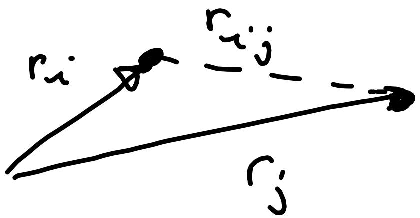
$$U = \frac{3}{2} NkT \equiv K \text{ (kinetic)}$$

↳ equipartition

$$\therefore \boxed{\mathcal{V}_0 = -3NkT = -2K}$$

Non-ideal gas:

molecules interact with each other via a potential $u(r_{ij})$



$$\mathcal{V} = \underbrace{\left\langle \sum_i q_i F_i \right\rangle_0}_{\text{contribution from } P \text{ on the walls}} + \left\langle \sum_{i<j} q_{ij} F_{ij} \right\rangle$$

$$F_{ij} \to -\frac{\partial u(r_{ij})}{\partial r_{ij}}$$

$=$

$$= \underbrace{-3PV}_{\text{contribution from collision of molecules versus wall}} - \left\langle \sum_{i<j} \frac{\partial u(r_{ij})}{\partial r_{ij}} r_{ij} \right\rangle = -3NkT$$

virial

$\therefore$ Solving for P:

$$P = \frac{\cancel{3}NkT}{\cancel{3}V} - \frac{1}{3V}\left\langle \sum_{i<j} \frac{\partial u(r_{ij})}{\partial r_{ij}} r_{ij} \right\rangle =$$

$$= nkT - \frac{1}{3V}\left\langle \sum_{i<j} \frac{\partial u}{\partial r_{ij}} r_{ij} \right\rangle \quad \text{or}$$

$$\frac{P}{nkT} = 1 - \frac{1}{3NkT}\left\langle \sum_{i<j} \frac{\partial u}{\partial r_{ij}} r_{ij} \right\rangle$$

modified eq. of state.

Virial's theorem is useful to obtain equations of state for interacting systems.

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Harmonic oscillator in the canonical formalism: (N non-interacting oscillators).

- classical case in 1D.

$$H(q_i, p_i) = \frac{1}{2} m \omega^2 q_i^2 + \frac{1}{2m} p_i^2$$

$i = 1, 2, \ldots N$

\# of oscillators.

We need to find $Z_1(\beta)$ since

$$Z_N(\beta) = (Z_1)^N$$

(no $N!$ needed because the oscillators are localized and distinguishable).

$$Z_1(\beta) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\beta\left(\frac{1}{2}m\omega^2 q^2 + \frac{1}{2m}p^2\right)} \frac{dp\,dq}{h} =$$

$$= \frac{1}{h}\sqrt{\frac{2\pi}{\beta m\omega^2}}\sqrt{\frac{2\pi m}{\beta}} = \frac{2\pi}{h\beta\omega} = \frac{1}{\hbar\beta\omega} =$$

gaussian integrals

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

counts how many accessible states the oscillator has since $kT \propto E_{\text{available}}$ and $\hbar\omega \propto$ quantum energy.

$$Z_N(\beta) = [Z_1(\beta)]^N = \left(\frac{kT}{\hbar\omega}\right)^N$$

$$F = -kT \ln Z_N = +NkT \ln\left(\frac{\hbar\omega}{kT}\right)$$

But

$$dF = -S\,dT - P\,dV + \mu\,dN$$

$$\therefore \mu = \left.\frac{\partial F}{\partial N}\right|_{T,V} = kT \ln\left(\frac{\hbar\omega}{kT}\right)$$

$$P = -\left.\frac{\partial F}{\partial V}\right|_{N,T} = 0 \qquad \text{since } Z_N \neq Z_N(V)$$

$$S = -\left.\frac{\partial F}{\partial T}\right|_{V,N} = Nk\left[\ln\left(\frac{kT}{\hbar\omega}\right) + 1\right]$$

Also

from $U = F + TS$

$$U = -\frac{\partial \ln Z_N}{\partial \beta} = -T^2\left(\frac{\partial}{\partial T}\left(\frac{F}{T}\right)\right]_{N,V} = F + TS \Rightarrow$$

$$U = NkT \cancel{\ln}\left(\frac{\hbar\omega}{kT}\right) - NkT \cancel{\ln}\frac{\hbar\omega}{kT} + NkT = NkT$$

in agreement with equipartition of energy

$$c_V = \frac{\partial U}{\partial T}\Big|_V = Nk$$

Hw: $\langle K \rangle, \ \langle V \rangle$

$$\langle K \rangle = \left\langle \frac{p^2}{2m} \right\rangle$$

Density of states $g(E)$:

$g(E)$ is the anti-Laplace transform of $Z_N(\beta)$.

$$Z_N(\beta) = \frac{1}{\hbar^N \omega^N \beta^N} \quad \therefore$$

we want to anti-laplace transform β^{-N}:

From table: $f(s) = \frac{1}{s^n} \Rightarrow F(t) = \frac{t^{n-1}}{(n-1)!}$

$\mathcal{L}$. transform of $F(t)$

if $t \to E$

$s \to \beta$

$n \to N$

$$g(E) = \begin{cases} \frac{1}{(\hbar\omega)^N} \frac{E^{N-1}}{(N-1)!} & \text{for } E > 0 \\ 0 & \text{for } E \leq 0. \end{cases}$$

Now consider the quantum mechanical case:-

$$\varepsilon_n = (n+\tfrac{1}{2})\hbar\omega \qquad n = 0, 1, 2, \ldots$$

$$Z_1(\beta) = \sum_{n=0}^{\infty} e^{-\beta(n+\frac{1}{2})\hbar\omega} \underset{\text{geometric sum}}{=} \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} =$$

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

$$\therefore \quad Z_N(\beta) = [Z_1(\beta)]^N = \left[2\sinh\frac{\beta\hbar\omega}{2}\right]^{-N} =$$

$$= \left[e^{\frac{\beta\hbar\omega}{2}} - e^{-\frac{\beta\hbar\omega}{2}}\right]^{-N} = e^{-\frac{N}{2}\beta\hbar\omega}\left[1-e^{-\beta\hbar\omega}\right]^{-N}$$

$$U = -\frac{\partial \ln Z_N}{\partial \beta} = \frac{1}{2} N \hbar\omega \coth\left(\frac{\beta\hbar\omega}{2}\right) =$$

$$= N\left[\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right] \neq NkT$$

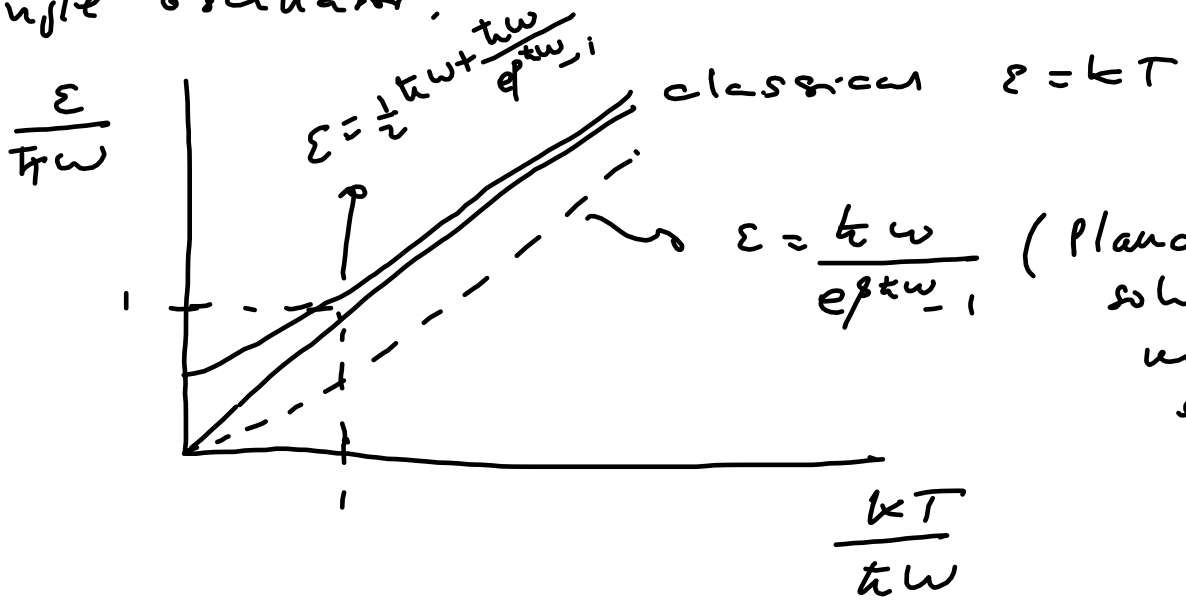
it does not satisfy equipartition.

However, if $\hbar\omega << kT$ (high T)

$$U \approx N\left[\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{1+\beta\hbar\omega+\dots}\right] = N\left[\frac{1}{2}\hbar\omega + \frac{\cancel{\hbar\omega}\, kT}{\cancel{\hbar\omega}}\right]$$

$\approx NkT$ now equipartition is satisfied.

Single oscillator:



(Planck's original solution with no zero point energy).