Theorem of equipartition of the energy:

Let's find

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle$$

$H(q,p)$ Hamiltonian

classical systems

x_i, x_j are 2 of the $6N$ generalized coordinates.

Canonical:

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \frac{\int x_i \frac{\partial H}{\partial x_j} e^{-\beta H} d\omega}{\int e^{-\beta H} d\omega} \quad (1)$$

Notice that

$$\frac{\partial}{\partial x_j}\left(x_i e^{-\beta H}\right) = \frac{\partial x_i}{\partial x_j} e^{-\beta H} + x_i(-\beta)\frac{\partial H}{\partial x_j} e^{-\beta H}$$

$$\therefore \quad x_i \frac{\partial H}{\partial x_j} e^{-\beta H} = \frac{1}{\beta}\frac{\partial x_i}{\partial x_j} e^{-\beta H} - \frac{1}{\beta}\frac{\partial}{\partial x_j}\left(x_i e^{-\beta H}\right)$$

Then

$$\int x_i \frac{\partial H}{\partial x_j} e^{-\beta H} d\omega = \int x_i \frac{\partial H}{\partial x_j} e^{-\beta H} dx_j \, d\omega'(j) =$$

$$= \frac{1}{\beta}\int \underbrace{\frac{\partial x_i}{\partial x_j}}_{\delta_{ij}} e^{-\beta H} dx_j \, d\omega'(j) - \frac{1}{\beta}\int \frac{\partial}{\partial x_j}\left(x_i e^{-\beta H}\right) dx_j \, d\omega'(j)$$

$$= \frac{1}{\beta}\left[\int \delta_{ij} e^{-\beta H} dx_j - \underbrace{x_i e^{-\beta H}\Big|_{x_{j1}}^{x_{j2}}}_{\text{boundaries}}\right] d\omega'(j) =$$

$H \to \infty$ at the "boundary" of phase space so this term vanishes.

$$= \frac{1}{\beta}\delta_{ij}\int e^{-\beta H} d\omega$$

$\therefore$ (1)

$$\boxed{\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle} = \frac{1}{\beta}\delta_{ij}\frac{\int e^{-\beta H} d\omega}{\int e^{-\beta H} d\omega} = \frac{\delta_{ij}}{\beta} = \boxed{\delta_{ij} kT} \quad (2)$$

Examples:

1) If $x_i = x_j = p_i$

$$\left\langle p_i \frac{\partial H}{\partial p_i} \right\rangle \overset{\text{Hamilton}}{=} \langle p_i \dot{q}_i \rangle \overset{(2)}{=} kT$$

$$\left\langle p_i \frac{\partial H}{\partial p_i} \right\rangle \overset{\to \text{Ham}}{\equiv} \left\langle p_i \dot{q}_i \right\rangle \overset{(2)}{=} kT$$

2) If $x_i = x_j = q_i$

$$\left\langle q_i \frac{\partial H}{\partial q_i} \right\rangle \overset{\to \text{Hamilton}}{\equiv} - \left\langle q_i \dot{p}_i \right\rangle \overset{(2)}{=} kT$$

$3N$

$i=1$ ∂p_i

and

$$\left\langle \sum_{i=1}^{3N} q_i \frac{\partial H}{\partial q_i} \right\rangle \equiv - \left\langle \sum_{i=1} q_i \dot{p}_i \right\rangle = 3NkT$$

Consider a hamiltonian that is a quadratic function of its coordinates. We always can write:

$$H = \sum_j \left(A_j P_j^2 + B_j Q_j^2 \right) \qquad (3)$$

P_j and Q_j may be the result of a canonical transformation of the original generalized coordinates.

Now

$$\sum_j \left(P_j \underbrace{\frac{\partial H}{\partial P_j}}_{2A_jP_j} + Q_j \underbrace{\frac{\partial H}{\partial Q_j}}_{2B_jQ_j} \right) \sum_j 2A_j P_j^2 + 2B_j Q_j^2 \overset{(3)}{=}$$

$$= 2 \sum_j A_j P_j^2 + B_j Q_j^2 = 2H$$

$$\therefore \quad 2\langle H \rangle = \sum_j \left[\left\langle P_j \frac{\partial H}{\partial P_j} \right\rangle + \left\langle Q_j \frac{\partial H}{\partial Q_j} \right\rangle \right]$$

$$= kTf \qquad f = \text{\# of degrees of freedom}$$

$$\therefore \quad \boxed{\langle H \rangle = \frac{1}{2} f kT}$$

Theorem of equipartition of energy.

Valid for quadratic coordinates in a classical Hamiltonian

We will see that in quantum systems quadratic degrees of freedom in H only get $\frac{1}{2}kT$ when T is sufficiently large.

— x —

Virial Theorem

$$-\left\langle \sum_{i=1}^{3N} q_i \dot{p}_i \right\rangle \qquad \text{Virial of a system.}$$

Using the previous results we know that

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

Notice that

$$\dot{p}_i = \frac{\partial (mv)}{\partial t} = m a_i = F_i$$

force associated to the p_i coordinate.

Virial theorem says that

$$\mathcal{V} \equiv -3NKT \qquad (4)$$

This will be useful to obtain equations of state for interacting systems.

Ideal gas: P resulting from collisions of molecules against container's walls is the only "force".

$$d\bar{F} = -P\,d\bar{S} \qquad \overset{\bar{r}}{\bar{q}} \cdot \bar{F}$$

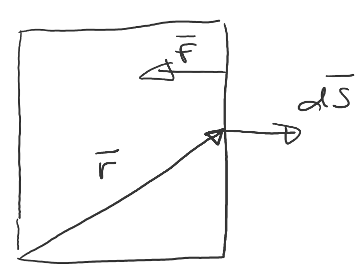
force inwards while $d\bar{S}$ outwards

divergence theorem

$$\mathcal{V}_0 = \left(\sum_i q_i F_i \right)_0 = -P \oint_S \bar{r} \cdot d\bar{S}$$

non-interacting gas

$$= -P \int_V \bar{\nabla} \cdot \bar{r} \, dV = -P \int_V \underbrace{\left(\frac{\partial x}{\partial x} + \frac{\partial y}{\partial y} + \frac{\partial z}{\partial z} \right)}_{3} dV = -3PV$$



$\therefore$ since $\mathcal{V}_0 = -3NKT$ we get

$$-3NKT = -3PV \implies \boxed{PV = NKT}$$

equation of state for the ideal gas.

Notice that

$$P = nKT \quad \text{or} \quad \boxed{\frac{P}{nKT} = 1} \quad \text{for ideal gas.}$$

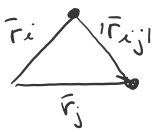
Since $U = \frac{3}{2} NKT = K$ (all kinetic)

equipartition

$K = -\frac{\mathcal{V}_0}{2}$ or $\boxed{\mathcal{V} = -2K}$

Application: gas with interacting particles.

Consider a potential $u(r_{ij})$ between pairs of molecules.



$$\mathcal{V} = \underbrace{\left(\sum_i q_i F_i\right)_0}_{-3PV} + \left\langle \sum_{i<j} \underbrace{q_{ij}}_{r_{ij}} \underbrace{F_{ij}}_{-\frac{\partial U(r_{ij})}{\partial r_{ij}}} \right\rangle =$$

$$= -3PV - \left\langle \sum_{i<j} \frac{\partial u}{\partial r_{ij}} r_{ij} \right\rangle \equiv -3NKT$$

Virial theorem

$\therefore$ solving for P to get eq. of state:

$$P = \frac{NKT}{V} - \frac{1}{3V} \left\langle \sum_{i<j} \frac{\partial U}{\partial r_{ij}} r_{ij} \right\rangle$$

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

Virial equation of state

we will see later how to calculate these.

Harmonic Oscillators: 1D

- black-body radiation
- lattice vibrations

Classical case

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

number of 1D oscillators.

Canonical formalism:

non-interacting so we know that $Z_N = (Z_1)^N$

no Gibb's correction ($1/N_1!$) because they are distinguishable.

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

distinguishable.

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

$$= \frac{1}{h}\int_{-\infty}^{\infty} dq \; e^{-\frac{\beta m\omega^2 q^2}{2}} \int_{-\infty}^{\infty} dp \; e^{-\frac{\beta p^2}{2m}} =$$

Gaussians

table

$$= \frac{1}{h}\sqrt{\left(\frac{2\pi}{\beta m\omega^2}\right)}\sqrt{\frac{2\pi m}{\beta}} =$$

$$= \frac{1}{h}\sqrt{\frac{(2\pi)^2}{\beta^2\omega^2}} = \frac{2\pi}{h\beta\omega} = \frac{kT}{\hbar\omega}$$

this basically gives the # of allowed microstates for the oscillator

Then for N oscillators:

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

$$\therefore \quad F = -kT \ln Z_N = -kTN \ln\left(\frac{kT}{\hbar\omega}\right) =$$

$$= kTN \ln\left(\frac{\hbar\omega}{kT}\right)$$

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

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

$$P = -\left.\frac{\partial F}{\partial V}\right|_{N,T} = 0 \qquad \text{no } V \text{ dependence on } F.$$

$$S = -\left.\frac{\partial F}{\partial T}\right|_{V,N} = -kN\ln\left(\frac{\hbar\omega}{kT}\right) - \frac{kTN}{\frac{\hbar\omega}{kT}}\frac{\hbar\omega}{k}(-T^{-2}) =$$

$$= Nk\left[\ln\frac{kT}{\hbar\omega} + 1\right]$$

$$\boxed{U} = -\frac{\partial \ln Z_N}{\partial\beta} = \frac{\partial(F/kT)}{\partial\beta} = \frac{\partial(F/kT)}{\partial T}\underbrace{\frac{\partial T}{\partial\beta}}_{-\frac{1}{k\beta^2}} = \qquad T = \frac{1}{k\beta}$$

$$= -\frac{1}{\cancel{k}}\frac{\partial F/T}{\partial T}\cancel{k}T^2 = -T^2\left(\frac{\partial(F/T)}{\partial T}\right)\Bigg|_{N,V} = \qquad \underbrace{-\frac{1}{k\beta^2}}_{-\frac{k^2T^2}{k}}$$

$$= F + TS = \boxed{NkT}$$

in agreement with $\frac{1}{2}kT$ per degree of freedom. $(\mathcal{N} = 2N)$

$$\therefore \quad c_V = \left.\frac{\partial U}{\partial T}\right|_V = Nk$$

We also can get $g(\epsilon)$:

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

$g(\epsilon)$ is the anti Laplace transform of β^{-N}

From table: $\quad f(s) = \frac{1}{s^n} \Rightarrow F(t) = \frac{t^{n-1}}{(n-1)!} \qquad t \to \epsilon,\ s \to \beta,\ n \to N$

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

Quantum case: $\quad \varepsilon_n = (n+\frac{1}{2})\hbar\omega \qquad n = 0, 1, \dots$

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

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

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

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

Now

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

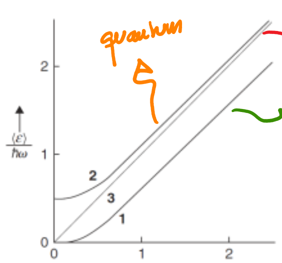
but if $kT \gg \hbar\omega$

$$U \simeq N\left[\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{\cancel{1} + \frac{\hbar\omega}{kT} - \cancel{1}}\right] = N\left[\frac{1}{2}\hbar\omega + kT\right]$$

$$\approx NkT$$ equipartition is now valid.

quantum

classical $\varepsilon = NkT$



$\varepsilon = \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}$ (no zero energy point original Planck's proposal)

q: $\varepsilon = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}$