Equipartition Theorem

classical phase space variables: (q_α, p_α), $\alpha = 1, \ldots, N$

OR z_i, $i = 1, \ldots, 2N$

integral over phase space

$$\int d\omega = \int dz_1 \cdots dz_{2N}$$

$$= \int d\omega_j \int dz_j$$

integral over remaining $2N-1$ variables

average over canonical ensemble

$$\left\langle z_i \frac{\partial H}{\partial z_j} \right\rangle = \frac{1}{Z} \int d\omega \, z_i \frac{\partial H}{\partial z_j} e^{-\beta H}$$

$$Z = \int d\omega \, e^{-\beta H}$$

numerator: $\displaystyle \int d\omega \, z_i \frac{\partial H}{\partial z_j} e^{-\beta H} = -\frac{1}{\beta} \int d\omega \, z_i \left(\frac{\partial}{\partial z_j} e^{-\beta H} \right)$

$$= -\frac{1}{\beta} \int d\omega \left[\frac{\partial}{\partial z_j} \left(z_i e^{-\beta H} \right) - \frac{\partial z_i}{\partial z_j} e^{-\beta H} \right]$$

$$= -\frac{1}{\beta} \int d\omega \left[\frac{\partial}{\partial z_j} \left(z_i e^{-\beta H} \right) - \delta_{ij} e^{-\beta H} \right]$$

$$= -\frac{1}{\beta} \int d\omega \frac{\partial}{\partial z_j} \left(z_i e^{-\beta H} \right) + \frac{1}{\beta} \delta_{ij} Z$$

last term: $\int d\omega \frac{\partial}{\partial z_j}\left(z_i e^{-\beta H}\right) = \int d\omega_j \int dz_j \frac{\partial}{\partial z_j}\left(z_i e^{-\beta H}\right)$

$$= \int d\omega_j \, z_i e^{-\beta H}\Big|_{z_j = z_{j,min}}^{z_j = z_{j,max}}$$

$$= 0 \quad \text{if } H \to +\infty \text{ as } z_j \to z_{j,max} \text{ or } z_{j,min}$$

$$\Longrightarrow \quad \left\langle z_i \frac{\partial H}{\partial z_j}\right\rangle = \delta_{ij}\frac{1}{\beta} = \delta_{ij} T$$

set $j = i$: $\boxed{\left\langle z_i \frac{\partial H}{\partial z_i}\right\rangle = T}$

If H includes a quadratic term $C z_i^2$ $\qquad z_i \frac{\partial}{\partial z_i}(C z_i^2) = 2(C z_i^2)$

its average value is $\langle C z_i^2\rangle = \frac{1}{2}T$

Equipartition

If all terms in H are quadratic in momenta or coordinates, then the average energy in the classical limit is

$$U \equiv \langle H \rangle = \frac{1}{2}T \times (\text{number of quadratic terms in } H)$$

ideal gas of N atoms: $H = \sum_{n=1}^{N} \frac{1}{2m}\vec{p}_n^{\,2} \Longrightarrow U = \frac{1}{2}T(3N)$

N harmonic oscillators: $H = \sum_{n=1}^{N}\left(\frac{1}{2m}p_n^2 + \frac{1}{2}m\omega^2 x_n^2\right) \Longrightarrow U = \frac{1}{2}T(2N)$

Suppose Hamiltonian has the form $H(p,q) = K(p) + V(q)$

where V is homogeneous function of coordinates q
of degree n

$$\sum_\alpha q_\alpha \frac{\partial}{\partial q_\alpha} V = nV$$

equipartition: $\displaystyle\sum_{\alpha=1}^{N} \left\langle q_\alpha \frac{\partial H}{\partial q_\alpha} \right\rangle = \sum_{\alpha=1}^{N} \delta_{\alpha\alpha} T = NT$

$$\Longrightarrow \quad n\langle V \rangle = NT$$

average potential energy: $\langle V \rangle = N\left(\frac{1}{n}T\right)$

example

linear potential between particle: $n = +1$

$$V = \sum_{n_1 < n_2} \sigma \left| \vec{r}_{n_1} - \vec{r}_{n_2} \right| \qquad \langle U \rangle = 3N \cdot T$$

gravitational potential: $n = -1$

$$V = \sum_{n_1 < n_2} \frac{Gm^2}{\left| \vec{r}_{n_1} - \vec{r}_{n_2} \right|} \qquad \langle U \rangle = 3N(-T)$$

Virial: $\mathcal{V} = \left\langle \sum_\alpha q_\alpha \dot{p}_\alpha \right\rangle = - \left\langle \sum_\alpha q_\alpha \frac{\partial H}{\partial q_\alpha} \right\rangle$

<u>Ideal gas</u>: N particles in volume V

$$H = \sum_{n=1}^{N} \left(\frac{1}{2m} \vec{p}_n^{\,2} + U_{ext}(\vec{r}_n) \right)$$

where $U_{ext}(\vec{r})$ is potential confining particle to volume V

$U(\vec{r}) = 0$ if $\vec{r}$ is inside

$U(\vec{r}) \to \infty$ if $\vec{r}$ is outside

equipartition: $\left\langle \vec{r} \cdot \nabla U_{ext} \right\rangle = \left\langle x \frac{\partial H}{\partial x} + y \frac{\partial H}{\partial y} + z \frac{\partial H}{\partial z} \right\rangle = 3kT$

$$\sum_{n=1}^{N} \left\langle \vec{r}_n \cdot \vec{\nabla} U_{ext}(\vec{r}) \right\rangle = 3NkT$$

$$\sum_{n=1}^{N} \left\langle \vec{r}_n \cdot \nabla U_{ext}(\vec{r}_n) \right\rangle = -\sum_{n=1}^{N} \left\langle \vec{r}_n \cdot \vec{F}(\vec{r}_n) \right\rangle$$

$\vec{F}(\vec{r}) = 0$ inside

$\propto \hat{n}$ at boundary

sum of normal force on all particles near boundary
= integral of pressure over surface

$$= + \int \vec{r} \cdot P\hat{n}\, dS = + P \int \vec{r} \cdot \hat{n}\, dS$$

divergence theorem

$$= + P \int \nabla \cdot \vec{r}\, dV = + P \int 3\, dV$$

$N(3kT) = P \cdot 3V \implies$ ideal gas law $PV = NkT$