Phys. 528 Lecture 7

Canonical Ensemble (cont.)

1) Alternative expression for Z

$$Z = \sum_s e^{-\beta E_s}$$

Define the density of states

$$g(E) \equiv \sum_s \delta(E - E_s).$$

$$Z = \int dE\, g(E)\, e^{-\beta E}.$$

For a quantum system, the spectrum of $\hat{H}$ is bounded below. Choose the energy scale s.t. $E_0 \geq 0$.

Then

$$Z(\beta) = \int_0^\infty dE\, g(E)\, e^{-\beta E}$$

Laplace transform of $g(E)$.

Inverse laplace transform:

$$g(E) = \frac{1}{2\pi i} \int_{\beta'-i\infty}^{\beta'+i\infty} d\beta \; e^{\beta E} Z(\beta). \qquad (\beta' > 0)$$

$$\langle f \rangle \equiv \sum_s P_s f_s = \frac{\sum_s f_s e^{-\beta E_s}}{\sum_s e^{-\beta E_s}}$$

$$= \frac{\int dE \; g(E) e^{-\beta E} f(E)}{\int dE \; g(E) e^{-\beta E}}$$

2) Energy fluctuations

$$E \equiv \langle E_r \rangle = \frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

$$\frac{\partial E}{\partial \beta} = -\frac{\sum_r E_r^2 e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} + \frac{\left(\sum_r E_r e^{-\beta E_r}\right)^2}{\left(\sum_r e^{-\beta E_r}\right)^2}$$

$$= -\langle E_r^2 \rangle + \langle E_r \rangle^2$$

$$\langle (\Delta E)^2 \rangle \equiv \langle E_r^2 \rangle - \langle E_r \rangle^2 = -\left.\frac{\partial E}{\partial \beta}\right|_V$$

$$= -\left.\frac{\partial E}{\partial T}\right|_V \frac{\partial T}{\partial \beta} = k_B T^2 \left.\frac{\partial E}{\partial T}\right|_V$$

$$= k_B T^2 C_V$$

$$\frac{\langle (\Delta E)^2 \rangle}{\langle E \rangle^2} = \frac{k_B T^2 C_V}{\langle E \rangle^2} \sim \frac{1}{N} \quad \text{(negligible)}$$

$$p(E)\, dE \propto e^{-\beta E} g(E)\, dE$$

most probable energy E^* determined by

$$\frac{\partial}{\partial E}\left(e^{-\beta E} g(E)\right)\Big|_{E^*} = 0$$

$$\frac{\partial \ln g}{\partial E}\Big|_{E^*} = \beta$$

equiv $$\frac{\partial S}{\partial E}\Big|_{E=\langle E\rangle} = \frac{1}{T}$$

$\Rightarrow \langle E \rangle = E^*$

irrespective of the nature of the system.

3) <u>Classical systems</u>

$$Z_N(V,T) = \frac{1}{N!\,h^{3N}} \int d^{3N}q\, d^{3N}p\; e^{-\beta H(q,p)}$$

<u>Free particles</u> (ideal gas)

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

$$Z_N(V,T) = \frac{V^N}{N!\,h^{3N}} \int d^{3N}p\; e^{-\frac{\beta}{2m}\sum_i \vec{p}_i^{\,2}}$$

$$= \frac{V^N}{N!\,h^{3N}} \left[\int_0^\infty e^{-\frac{p^2}{2mk_BT}}\, 4\pi p^2\, dp \right]^N$$

$$= \frac{1}{N!} \left[\frac{V}{h^3} (2\pi m k_B T)^{3/2} \right]^N$$

$$= \frac{Z_1^N}{N!}$$

$$F(N,V,T) = -k_B T \ln Z_N(V,T)$$

$$= N k_B T \left[\ln \left\{ \frac{N}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} \right\} - 1 \right]$$

$$\mu = \left. \frac{\partial F}{\partial N} \right|_{V,T} = k_B T \ln \left\{ \frac{N}{V} \left(\frac{h^2}{2\pi m k_B T} \right)^{3/2} \right\}$$

$$P = -\left. \frac{\partial F}{\partial V} \right|_{N,T} = \frac{N k_B T}{V}$$

$$S = -\left. \frac{\partial F}{\partial T} \right|_{N,V} = N k_B \left[\ln \left\{ \frac{V}{N} \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right\} + \frac{5}{2} \right]$$

$$E = -\frac{\partial \ln Z}{\partial \beta} = \frac{3}{2} N k_B T$$

$$\frac{\langle (\Delta E)^2 \rangle}{\langle E \rangle^2} = \frac{k_B T^2 \, \frac{3}{2} N k_B}{\left(\frac{3}{2} N k_B T \right)^2} = \frac{2}{3N} \xrightarrow[N \to \infty]{} 0$$

Z from d.o.s. $g(E)$:

For $N=1$, $\Sigma(E) = \frac{4\pi}{3}\frac{p^3 V}{h^3} = \frac{4\pi}{3}\frac{V}{h^3}(2mE)^{3/2}$

$$g(E) = \frac{d\Sigma}{dE} = \frac{2\pi V}{h^3}(2m)^{3/2} E^{1/2}$$

$$Z_1(\beta) = \int_0^\infty e^{-\beta E} g(E)\, dE = \frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}$$

4) Equipartition theorem

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

$$d\omega = \frac{d^{3N}q\, d^{3N}p}{h^{3N}} \qquad x_i, x_j \in (q, p)$$

Integrate by parts over x_j:

$$\int \left(x_i \frac{\partial H}{\partial x_j}\right) e^{-\beta H}\, dx_j = -\frac{x_i}{\beta} e^{-\beta H}\Bigg|_{x_j=-\infty}^{x_j=+\infty} + \frac{1}{\beta}\int \frac{\partial x_i}{\partial x_j} e^{-\beta H}\, dx_j$$

0

$$= \frac{\delta_{ij}}{\beta} \int e^{-\beta H} \, dx_j$$

Putting it all together, we get

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = \delta_{ij} k_B T$$

i) $x_i = p_i \qquad \frac{\partial H}{\partial p_i} = \dot{q}_i$

$$\langle p_i \dot{q}_i \rangle = k_B T$$

ii) $x_i = q_i \qquad \frac{\partial H}{\partial q_i} = -\dot{p}_i$

$$-\langle q_i \dot{p}_i \rangle = k_B T$$

iii) $\sum_{i=1}^{3N} p_i \dot{q}_i = 3N k_B T = 2K$

$$K = \frac{3}{2} N k_B T$$

iv) $\dot{p}_i = -\dfrac{\partial U}{\partial q_i}$

If $U = U(q_1, \dots q_{3N})$ is a homogeneous function of degree α:

$$U(\lambda q) = \lambda^\alpha U(q)$$

then $$\sum_i q_i \frac{\partial U}{\partial q_i} = \alpha U$$

$$\alpha U = 3N k_B T$$

$$U = \frac{3N}{\alpha} k_B T$$

Also $\alpha U = K$ (virial theorem).

5) <u>Harmonic oscillator</u>

$$H = \frac{p^2}{2m} + \frac{m\omega^2 q^2}{2}, \qquad E_n = \hbar\omega(n + 1/2),$$

$$n = 0, 1, 2, \dots, \infty$$

$$Z = \sum_{n=0}^{\infty} e^{-\beta E_n}$$

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

$$E = -\frac{\partial \ln Z}{\partial \beta} = -\frac{\partial}{\partial\beta}\left[-\beta\frac{\hbar\omega}{2} - \ln\left(1-e^{-\beta\hbar\omega}\right)\right]$$

$$E = \frac{\hbar\omega}{2} + \frac{\hbar\omega\, e^{-\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}$$

$$\boxed{E = \hbar\omega\left(\langle n\rangle + \frac{1}{2}\right) \qquad \langle n\rangle = \frac{1}{e^{\beta\hbar\omega}-1} \quad \text{Planck distribution}}$$

High-temperature limit $\beta\hbar\omega \ll 1$:

$$\langle n \rangle \simeq \frac{1}{1+\beta\hbar\omega+\dots-1} = \frac{k_B T}{\hbar\omega}$$

$$E \cong \hbar\omega\left(\frac{k_B T}{\hbar\omega} + \frac{1}{2}\right) \cong k_B T$$

c.f. equipartition theorem

$$\left\langle p\frac{\partial H}{\partial p} + q\frac{\partial H}{\partial q}\right\rangle = 2k_B T$$

$$\parallel$$

$$\langle 2H \rangle$$

For $k_B T \lesssim \hbar\omega$, quantum effects are important, and equipartition breaks down.