Lecture 26

Friday, October 27, 2023 9:54 AM

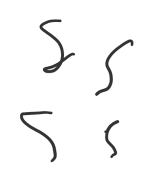
Last Time = $Z(T)$ counts microstates @ const T.

$$P_j = W(E_j)\, e^{-E_j/RT} \Big/ Z(T)$$

Microworld — Macroworld

$$Z(T) = \sum_j W(E_j)\, e^{-E_j/RT} = e^{-F/RT} \quad (F = \text{Free energy})$$

Folded state "F" — Unfolded State "U"

ex.  $\underset{}{\overset{K_{eq}}{\rightleftharpoons}}$ 

$E_j = E_F = 0$ — $E_j = E_U = \varepsilon$

$$\Rightarrow P_f = \frac{1}{Z} \qquad P_u = \frac{W_u\, e^{-E_u/RT}}{Z} \qquad K_{eq} = \frac{P_u}{P_F} = W_u\, e^{-\varepsilon/RT}$$

Once we know P_j, we can calculate the average of any quantity as $A = \sum_j P_j A_j$ e.g. $E = \sum_j P_j E_j$

Today = one more "law", this time using $Z(T)$

Q: What is the energy E & heat capacity C_v of a gas?

A: (1) system eq. + (2) postulates eq. = (3) combine

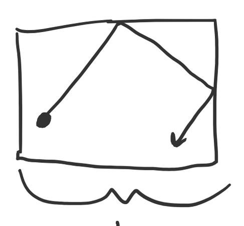
First, another method for calculating E directly from $Z(T)$

(HW S4.2) $\left(\beta = \frac{1}{k_B T} = \frac{1}{RT}\right)$

$$Z = e^{-F/RT} = e^{-\beta F} = e^{-\beta(E - TS)} = e^{-\beta E + S/R}$$

$$-\frac{\partial Z}{\partial \beta} = E\, e^{-\beta E + S/R} = E \cdot Z \Rightarrow E = \frac{-1}{Z}\frac{\partial Z}{\partial \beta} = \frac{-\partial \ln Z}{\partial \beta}$$

(1) What are the E_j? or, E_n? $E_n = \frac{h^2 n^2}{8mL^2}$ from QM

 ; in 3-D $E_{n_x}, E_{n_y}, E_{n_z} = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2)$

L

$V = L^3$

$$\Rightarrow Z(T) = \sum_{n_x, n_y, n_z} 1 \cdot e^{-\beta E_{n_x, n_y, n_z}}$$

$$= \sum_{n_x, n_y, n_z} e^{-\beta\left(\frac{h^2}{8mL^2}\right)(n_x^2 + n_y^2 + n_z^2)}$$

$$\approx \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z\, e^{-\beta \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2)}$$

$$Z(T) = \int_0^\infty dn_x \int_0^\infty dn_y \int_0^\infty dn_z\, e^{-\beta\frac{h^2}{8mL^2} n_x^2} \cdot e^{-\beta\frac{h^2}{8mL^2} n_y^2} \cdot \ldots$$

$$= \int_0^\infty dn_x\, e^{-\beta\frac{h^2}{8mL^2} n_x^2} \int_0^\infty dn_y\, e^{-\beta\frac{h^2}{8mL^2} n_y^2} \cdot \int \ldots$$

$$= \left(\int_0^\infty dx\, e^{-\frac{\beta h^2}{8mL^2} x^2}\right)^3 = \left\{\left(\frac{2\pi m}{\beta h^2}\right)^{1/2} \cdot L\right\}^3$$

$$\text{So} \Rightarrow Z(T) = \left(\frac{2\pi m}{\beta h^2}\right)^{3/2} \cdot V$$

For N particles, since Z (like ω) is multiplicative

$$Z(T) = \left(\frac{2\pi m}{\beta h^2}\right)^{3N/2} \cdot V^N$$

Take log, $\ln(Z(T)) = \frac{3}{2}N \ln\beta + \frac{3}{2}N \ln\left(\frac{2\pi m}{h^2}\right) + N \ln V$

$$E = -\frac{\partial \ln Z}{\partial \beta} = \frac{-\partial}{\partial \beta}\left(\frac{-3}{2}N \cdot \ln\beta\right)$$

$$= \frac{3}{2}N \cdot \frac{1}{\beta}$$

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

$$E = \frac{3}{2} nRT$$

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v = \frac{3}{2}nR = \frac{3}{2}Nk_B$$