MSAE3111, Thermodynamics and Statistical Mechanics

Prof. William Bailey

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Partition function

- Recall the energy for a particle in a box,

$$\epsilon_{n_x,n_y,n_z} = \frac{\hbar^2}{2m_e}\left(\frac{\pi}{L}\right)^2\left(n_x^2 + n_y^2 + n_z^2\right) \quad (1)$$

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- Our partition function is

$$Z = \sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} \exp -\frac{\epsilon_s}{\tau} \tag{4}$$

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- Since for a large box, the energy spacings are small, we can replace the summation with an integral

$$\sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \rightarrow \int_1^{\infty} \int_1^{\infty} \int_1^{\infty} dn_x dn_y dn_z \simeq \left(\frac{1}{8}\right) 4\pi \int_0^{\infty} n^2 d \quad (6)$$

where in the latter two steps we neglect the discretization of energy and make use of the fact that the properties in n are isotropic (independent of direction.)

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- The integration by parts evaluates as

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$$Z = \left(\frac{\pi\tau}{4\pi^2 \frac{\hbar^2}{2m}}\right)^{\frac{3}{2}} n^{-1} = \left(\frac{1}{4\pi} \frac{\tau}{\frac{\hbar^2}{2m}}\right)^{\frac{3}{2}} n^{-1} \tag{14}$$

Where $n = L^{-3}$ is the volume.

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$$\frac{\tau}{2} = \frac{p_i^2}{2m} \tag{21}$$

$$p_i = \sqrt{m\tau} \tag{22}$$

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$$Z = \frac{n_Q}{n} \equiv Z_1 \tag{26}$$

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$$F = -\tau \ln Z \tag{27}$$

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$$R \equiv k_B N_A = 8.314 \text{ J/mol/K} \tag{37}$$

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- Since $n_Q \propto \tau^{3/2}$,

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$$U = \frac{3}{2} \tau \qquad U = \frac{3}{2} k_B T \tag{42}$$

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  - Each term in Z is overcounted by $N!$

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$$\sigma = -\left(\frac{\partial F}{\partial \tau} \right)_V \quad (48)$$