Lecture 5: Thermodynamic Properties, but harder

Average Energy, Heat Capacity, Pressure

Flow Chart

Direct enumeration of particles

Direct enumeration of system (for small N)

q → Q

distinguishable

$$Q = q^N$$

indistinguishable

$$Q = \frac{q^N}{N!}$$

$$\langle E \rangle = -\frac{\partial \ln Q}{\partial \beta} = k_B T^2 \frac{\partial \ln Q}{\partial T} = -\frac{1}{Q}\frac{\partial Q}{\partial \beta} = k_B T^2 \frac{1}{Q}\frac{\partial Q}{\partial T}$$

(at constant N, V)

$$C_V = \frac{\partial \langle E \rangle}{\partial T} = -\frac{1}{k_B T^2}\frac{\partial \langle E \rangle}{\partial \beta}$$

(at constant N, V)

$$\langle P \rangle = \frac{1}{\beta}\frac{\partial \ln Q}{\partial V}$$

(at constant β, N)

$$n = \frac{N}{N_A} \quad R = N_A k_B \quad \beta = \frac{1}{k_B T} \quad \overline{C}_V = \frac{C_V}{n}$$

Problem Solving Strategy: Think before you math

When to use $\langle E\rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V}$ vs $\langle E\rangle = -\frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_{N,V}$

Product of terms with exponentials $\implies \langle E\rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V}$:

$$Q(N,V,\beta) = \frac{V^N}{N!}\left(\frac{2\pi m}{h^2\beta}\right)^{3N/2}\left(\frac{8\pi^2 I}{h^2\beta}\right)^N \frac{e^{-N\beta h\nu/2}}{\left(1-e^{-\beta h\nu}\right)^N}$$

Expression with easy derivative $\implies \langle E\rangle = -\frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_{N,V}$:

$$Q = 2\cosh\left(\frac{\beta\hbar\gamma B_z}{2}\right)$$

Generally preserve the variables in the problem: $\frac{\partial f}{\partial \beta} = -k_B T^2 \frac{\partial f}{\partial T}$

Example: Heat Capacity per mol of diatomic ideal gas

Activity 4: Average energy per mol of diatomic ideal gas

$$\bar{U} = \frac{5}{2}RT + \frac{N_A h\nu}{2} + \frac{N_A h\nu e^{-\beta h\nu}}{1 - e^{-\beta h\nu}}$$

$$\bar{C}_V = \left(\frac{\partial \bar{U}}{\partial T}\right)_{N,V}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V}$$

$$\bar{C}_V = \frac{\partial}{\partial T}\left(\frac{5}{2}RT + \frac{N_A h\nu}{2} + \frac{N_A h\nu e^{-\beta h\nu}}{1 - e^{-\beta h\nu}}\right)_{N,V}$$

$$\frac{\partial f}{\partial \beta} = -k_B T^2 \frac{\partial f}{\partial T}$$

$$= \frac{5}{2}R + N_A h\nu \frac{\partial}{\partial T}\left(\frac{e^{-\beta h\nu}}{1 - e^{-\beta h\nu}}\right)$$

Convert the partial wrt T to β:

$$= \frac{5}{2}R - \frac{N_A h\nu}{k_B T^2}\frac{\partial}{\partial \beta}\left(\frac{e^{-\beta h\nu}}{1 - e^{-\beta h\nu}}\right)$$

Example: Heat Capacity per mol of diatomic ideal gas

Recognize quotient rule: $\frac{d}{dx}\left[\frac{f(x)}{g(x)}\right] = \frac{f'(x)g(x) - f(x)g'(x)}{g(x)^2}$

$$= \frac{5}{2}R - \frac{N_A h\nu}{k_B T^2}\frac{\partial}{\partial\beta}\left(\frac{e^{-\beta h\nu}}{1 - e^{-\beta h\nu}}\right)$$

$$= \frac{5}{2}R - \frac{N_A h\nu}{k_B T^2} \cdot \frac{(-h\nu e^{-\beta h\nu})(1 - e^{-\beta h\nu}) - e^{-\beta h\nu}(h\nu e^{-\beta h\nu})}{(1 - e^{-\beta h\nu})^2}$$

$$= \frac{5}{2}R - \frac{N_A h\nu}{k_B T^2} \cdot \frac{-h\nu e^{-\beta h\nu} + h\nu e^{-2\beta h\nu} - h\nu e^{-2\beta h\nu}}{(1 - e^{-\beta h\nu})^2}$$

$$= \boxed{\frac{5}{2}R + \frac{N_A (h\nu)^2}{k_B T^2}\frac{e^{-\beta h\nu}}{(1 - e^{-\beta h\nu})^2}}$$

Example: Heat Capacity Atomic Crystal

Partition function for an atomic crystal:

$$Q = e^{-\beta U_0} \left(\frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} \right)^{3N}$$

$$Q = e^{-\beta U_0} \cdot e^{-3N\beta h\nu/2} \cdot \left(1 - e^{-\beta h\nu}\right)^{-3N}$$

$$\ln Q = -\beta U_0 - \frac{3N}{2}\beta h\nu - 3N \ln(1 - e^{-\beta h\nu})$$

$$U = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V}$$

$$= U_0 + \frac{3Nh\nu}{2} + \frac{3N}{1 - e^{-\beta h\nu}} \frac{d}{d\beta}\left(1 - e^{-\beta h\nu}\right)$$

$$= U_0 + \frac{3Nh\nu}{2} + \frac{3Nh\nu e^{-\beta h\nu}}{1 - e^{-\beta h\nu}}$$

$$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V}$$

$$= -\frac{1}{Q}\left(\frac{\partial Q}{\partial \beta}\right)_{N,V}$$

$$C_v = \left(\frac{\partial U}{\partial T}\right)_{N,V}$$

Example: Heat Capacity Atomic Crystal

$$C_V = \frac{\partial}{\partial T}\left(\cancel{U_0} + \cancel{\frac{3Nh\nu}{2}} + \frac{3Nh\nu e^{-\beta h\nu}}{1-e^{-\beta h\nu}}\right)_{N,V}$$

$$= 3Nh\nu\frac{\partial}{\partial T}\left(\frac{e^{-\beta h\nu}}{1-e^{-\beta h\nu}}\right)$$

Convert the partial wrt T to β:

$$= -\frac{3Nh\nu}{k_B T^2}\frac{\partial}{\partial \beta}\left(\frac{e^{-\beta h\nu}}{1-e^{-\beta h\nu}}\right)$$

$$= \frac{3Nh\nu}{k_B T^2}\cdot\frac{h\nu e^{-\beta h\nu}}{(1-e^{-\beta h\nu})^2}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V}$$

$$\frac{\partial f}{\partial \beta} = -k_B T^2\frac{\partial f}{\partial T}$$

$$\frac{\partial}{\partial \beta}\left(\frac{e^{-\beta h\nu}}{1-e^{-\beta h\nu}}\right) = \frac{-h\nu e^{-\beta h\nu}}{(1-e^{-\beta h\nu})^2}$$

Example: Pressure of van der Waals Equation

Partition function of vdW:

$$Q(N,V,\beta) = \frac{1}{N!}\left(\frac{2\pi m}{h^2\beta}\right)^{3N/2}(V-Nb)^N e^{\beta a N^2/V}$$

$$\langle P\rangle = \frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}$$

$$\ln Q = -\ln(N!) + \frac{3N}{2}\ln\left(\frac{2\pi m}{h^2\beta}\right) + N\ln(V-Nb) + \frac{\beta a N^2}{V}$$

$$\ln Q = N\ln(V-Nb) + \frac{\beta a N^2}{V} + \text{non-}V\text{ terms}$$

Example: Pressure of van der Waals Equation

$$\ln Q = N \ln(V - Nb) + \frac{\beta a N^2}{V} + \text{non-}V \text{ terms}$$

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta} = \frac{N}{V - Nb} - \frac{\beta a N^2}{V^2}$$

$$P = \frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta} = \frac{N k_{\mathrm{B}} T}{V - Nb} - \frac{a N^2}{V^2}$$

$$P + \frac{a N^2}{V^2} = \frac{N k_{\mathrm{B}} T}{V - Nb}$$

$$\boxed{\left(P + \frac{a N^2}{V^2}\right)(V - Nb) = N k_{\mathrm{B}} T}$$ This is van der Waal's!