

1. Last time we showed for a bare proton in a magnetic field B_z has energy $E_{\pm\frac{1}{2}} = \mp\frac{1}{2}\hbar\gamma B_z$ and partition function $Q = 2 \cosh\left(\frac{\beta\hbar\gamma B_z}{2}\right)$, where $\cosh x = \frac{e^x + e^{-x}}{2}$. Calculate the average energy for this system by method of partial derivatives.

$$\langle E \rangle = -\frac{\partial}{\partial\beta} \ln Q = -\frac{1}{Q} \frac{\partial Q}{\partial\beta}$$

Use the exponential form unless you remember trig identities:

$$Q = 2 \cosh\left(\frac{\beta\hbar\gamma B_z}{2}\right) = e^{\beta\hbar\gamma B_z/2} + e^{-\beta\hbar\gamma B_z/2}$$

$$\frac{\partial Q}{\partial\beta} = \frac{\hbar\gamma B_z}{2} (e^{\beta\hbar\gamma B_z/2} - e^{-\beta\hbar\gamma B_z/2})$$

$$\langle E \rangle = -\frac{1}{Q} \frac{\partial Q}{\partial\beta}$$

$$= \frac{\hbar\gamma B_z (e^{\beta\hbar\gamma B_z/2} - e^{-\beta\hbar\gamma B_z/2})}{2 (e^{\beta\hbar\gamma B_z/2} + e^{-\beta\hbar\gamma B_z/2})}$$

2. Given that the heat capacity at constant volume is defined as $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ and that the internal energy is given by $\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$, derive the following relationship:

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

For this class, mixed partial derivatives always commute (Clairaut's theorem):

$$\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y}\right) = \frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x}\right)$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Use Clairaut's theorem to change the order of partial differentiation:

$$\begin{aligned} \left(\frac{\partial C_V}{\partial V}\right)_T &= \frac{\partial}{\partial V} \left(\frac{\partial U}{\partial T}\right)_V = \frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V}\right)_T \\ &= \frac{\partial}{\partial T} \left[T \left(\frac{\partial P}{\partial T}\right)_V - P \right]_V \end{aligned}$$

The first term is simplified using the product rule:

$$\begin{aligned} &= \left(\frac{\partial P}{\partial T}\right)_V + T \left(\frac{\partial^2 P}{\partial T^2}\right)_V - \left(\frac{\partial P}{\partial T}\right)_V \\ C_V &= T \left(\frac{\partial^2 P}{\partial T^2}\right)_V \end{aligned}$$

3. In a few lectures we will learn that the partition function for a diatomic gas is $Q(N, V, \beta) = \frac{[q(V, \beta)]^N}{N!}$, where $q(V, \beta) = \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} V \cdot \frac{8\pi^2 I}{h^2\beta} \cdot \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}}$. Use this information to derive this expression for the average energy per mole of a diatomic ideal gas:

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

$$\langle E \rangle = -\frac{\partial \ln Q}{\partial \beta} \quad \text{where} \quad Q = \frac{[q(V, \beta)]^N}{N!}$$

$$\ln Q = N \ln q - \ln N!$$

There is no β dependence in $N!$, so we focus on the $N \ln q$ term:

$$\ln q = -\ln \beta - \frac{3}{2} \ln \beta - \frac{\beta h\nu}{2} - \ln(1 - e^{-\beta h\nu}) + (\text{constants})$$

$$\frac{\partial \ln q}{\partial \beta} = -\frac{3}{2\beta} - \frac{1}{\beta} - \frac{h\nu}{2} - \frac{\partial}{\partial \beta} \ln(1 - e^{-\beta h\nu})$$

$$\frac{\partial \ln q}{\partial \beta} = -\frac{5}{2\beta} - \frac{h\nu}{2} - \frac{h\nu e^{-\beta h\nu}}{1 - e^{-\beta h\nu}}$$

Substituting back in:

$$\begin{aligned} \langle E \rangle &= -\frac{\partial \ln Q}{\partial \beta} = -N \frac{\partial \ln q}{\partial \beta} \\ &= N \left(\frac{5}{2\beta} + \frac{h\nu}{2} + \frac{h\nu e^{-\beta h\nu}}{1 - e^{-\beta h\nu}} \right) \\ &= \frac{5}{2} N k_B T + \frac{N h\nu}{2} + \frac{N h\nu e^{-\beta h\nu}}{1 - e^{-\beta h\nu}} \end{aligned}$$

Using relations $R = N_A k_B$ and $N = n N_A$:

$$= \frac{5}{2} n R T + \frac{n N_A h\nu}{2} + \frac{n N_A h\nu e^{-\beta h\nu}}{1 - e^{-\beta h\nu}}$$

This is average energy of a single molecule, to get average energy per mol we divide by number of mols n :

$$\bar{U} = \frac{\langle E \rangle}{n} = \boxed{\frac{5}{2} R T + \frac{N_A h\nu}{2} + \frac{N_A h\nu e^{-\beta h\nu}}{1 - e^{-\beta h\nu}}}$$

Homework Problem 4

1. Consider a system of N identical, noninteracting particles with partition function $Q(N, V, T) = \frac{[q(V, T)]^N}{N!}$ where the single-particle partition function is given by $q(V, T) = f(T) \cdot V$. Using the thermodynamic relation $P = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_{T, N}$ show that the resulting equation of state is the ideal gas law.