

1. Problem 17-2 from McQuarrie & Simon:

Show that Equation 17.8 is equivalent to $f(x+y) = f(x)f(y)$. In this problem, we will prove that $f(x) \propto e^{ax}$. First, take the logarithm of the above equation to obtain

$$\ln f(x+y) = \ln f(x) + \ln f(y)$$

Differentiate both sides with respect to x (keeping y fixed) to get

$$\begin{aligned} \left[\frac{\partial \ln f(x+y)}{\partial x} \right]_y &= \frac{d \ln f(x+y)}{d(x+y)} \left[\frac{\partial (x+y)}{\partial x} \right]_y = \frac{d \ln f(x+y)}{d(x+y)} \\ &= \frac{d \ln f(x)}{dx} \end{aligned}$$

Now differentiate with respect to y (keeping x fixed) and show that

$$\frac{d \ln f(x)}{dx} = \frac{d \ln f(y)}{dy}$$

For this relation to be true for all x and y , each side must equal a constant, say a . Show that

$$f(x) \propto e^{ax} \quad \text{and} \quad f(y) \propto e^{ay}$$

2. Problem 17-5 from McQuarrie & Simon:

Show that the partition function in Example 17-1 can be written as

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

Use the fact that $d \cosh x / dx = \sinh x$ to show that

$$\langle E \rangle = -\frac{\hbar \gamma B_z}{2} \tanh \frac{\beta \hbar \gamma B_z}{2} = -\frac{\hbar \gamma B_z}{2} \tanh \frac{\hbar \gamma B_z}{2k_B T}$$

3. Problem 17-6 from McQuarrie & Simon:

Use either the expression for $\langle E \rangle$ in Example 17-1 or the one in Problem 17-5 to show that

$$\langle E \rangle \rightarrow -\frac{\hbar \gamma B_z}{2} \quad \text{as} \quad T \rightarrow 0$$

and that

$$\langle E \rangle \rightarrow 0 \quad \text{as} \quad T \rightarrow \infty$$

4. Problem 17-9 from McQuarrie & Simon:

In Section 17-3, we derived an expression for $\langle E \rangle$ for a monatomic ideal gas by applying Equation 17.20 to $Q(N, V, T)$ given by Equation 17.22. Apply Equation 17.21 to

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

to derive the same result. Note that this expression for $Q(N, V, T)$ is simply Equation 17.22 with β replaced by $1/k_B T$.

5. Problem 17-11 from McQuarrie & Simon:

Although we will not do so in this book, it is possible to derive the partition function for a monatomic van der Waals gas.

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

where a and b are the van der Waals constants. Derive an expression for the energy of a monatomic van der Waals gas.

6. Problem 17-20 from McQuarrie & Simon:

Deriving the partition function for an Einstein crystal is not difficult (see Example 17-3). Each of the N atoms of the crystal is assumed to vibrate independently about its lattice position, so that the crystal is pictured as N independent harmonic oscillators, each vibrating in three directions. The partition function of a harmonic oscillator is

$$\begin{aligned} q_{\text{ho}}(T) &= \sum_{v=0}^{\infty} e^{-\beta(v+\frac{1}{2})h\nu} \\ &= e^{-\beta h\nu/2} \sum_{v=0}^{\infty} e^{-\beta v h\nu} \end{aligned}$$

This summation is easy to evaluate if you recognize it as the so-called geometric series (MathChapter I)

$$\sum_{v=0}^{\infty} x^v = \frac{1}{1-x}$$

Show that

$$q_{\text{ho}}(T) = \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}}$$

and that

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

where U_0 simply represents the zero-of-energy, where all N atoms are infinitely separated.

Numbered equations:

$$f(E_1 - E_3) = f(E_1 - E_2)f(E_2 - E_3) \quad (17.8)$$

$$\langle E \rangle = - \left(\frac{\partial \ln Q}{\partial \beta} \right)_{N,V} \quad (17.20)$$

$$\langle E \rangle = k_B T^2 \left(\frac{\partial \ln Q}{\partial \beta} \right)_{N,V} \quad (17.21)$$

$$Q(N, V, \beta) = \frac{[q(V, \beta)]^N}{N!} \quad (17.22)$$

From Example 17-1:

$$\begin{aligned} Q(T, B_z) &= e^{\beta \hbar \gamma B_z / 2} + e^{-\beta \hbar \gamma B_z / 2} \\ &= e^{\hbar \gamma B_z / 2 k_B T} + e^{-\hbar \gamma B_z / 2 k_B T} \end{aligned}$$

$$\begin{aligned} \langle E \rangle &= - \left(\frac{\partial \ln Q}{\partial \beta} \right)_{B_z} = - \frac{1}{Q(\beta, B_z)} \left(\frac{\partial Q}{\partial \beta} \right)_{B_z} \\ &= - \frac{\hbar \gamma B_z}{2} \left(\frac{e^{\beta \hbar \gamma B_z / 2} - e^{-\beta \hbar \gamma B_z / 2}}{e^{\beta \hbar \gamma B_z / 2} + e^{-\beta \hbar \gamma B_z / 2}} \right) \\ &= - \frac{\hbar \gamma B_z}{2} \left(\frac{e^{\hbar \gamma B_z / 2 k_B T} - e^{-\hbar \gamma B_z / 2 k_B T}}{e^{\hbar \gamma B_z / 2 k_B T} + e^{-\hbar \gamma B_z / 2 k_B T}} \right) \end{aligned}$$