

Homework 5

Ravi Kini

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Exercise 1

An Introduction to Thermal Physics (Schroeder, 1e) Exercise 5.12

If S is held constant in the thermodynamic identity for U :

$$\begin{aligned} dU &= T dS - p dV = -p dV \\ \left(\frac{\partial U}{\partial V}\right)_S &= -p \end{aligned} \tag{1}$$

If V is held constant:

$$\begin{aligned} dU &= T dS - p dV = T dS \\ \left(\frac{\partial U}{\partial S}\right)_V &= T \end{aligned} \tag{2}$$

Then:

$$\begin{aligned} \frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S}\right)_V &= \frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V}\right)_S \\ \left(\frac{\partial T}{\partial V}\right)_S &= -\left(\frac{\partial p}{\partial S}\right)_V \end{aligned} \tag{3}$$

Exercise 2

An Introduction to Thermal Physics (Schroeder, 1e) Exercise 5.23 (partial)

Part (a)

Deriving the thermodynamic identity for Φ :

$$\begin{aligned}\Phi &= U - TS - \mu N \\ d\Phi &= dU - d(TS) - d(\mu N) \\ &= dU - T dS - S dT - \mu dN - N d\mu \\ &= (T dS - p dV + \mu dN) - T dS - S dT - \mu dN - N d\mu \\ &= -p dV - S dT - N d\mu\end{aligned}\tag{4}$$

If V and T are held constant in the thermodynamic identity for Φ :

$$\begin{aligned}d\Phi &= -p dV - S dT - N d\mu = -N d\mu \\ \left(\frac{\partial\Phi}{\partial\mu}\right)_{V,T} &= -N\end{aligned}\tag{5}$$

If V and μ are held constant:

$$\begin{aligned}d\Phi &= -p dV - S dT - N d\mu = -S dT \\ \left(\frac{\partial\Phi}{\partial\mu}\right)_{V,\mu} &= -S\end{aligned}\tag{6}$$

If T and μ are held constant:

$$\begin{aligned}d\Phi &= -p dV - S dT - N d\mu = -p dV \\ \left(\frac{\partial\Phi}{\partial\mu}\right)_{T,\mu} &= -p\end{aligned}\tag{7}$$

Part (b)

For a system in thermal equilibrium, T, μ remain constant and equal for the system and the reservoir. Further assume that the volume V_r remains fixed for the reservoir. Let the entropy of the universe (system and reservoir) increase by some $dS_u = dS + dS_r$ where dS is the change in entropy of the system and

dS_r the change in entropy of the reservoir. Then:

$$\begin{aligned}
dU_r &= T dS_r - P dV_r + \mu dN_r \\
dS_r &= \frac{1}{T} dU_r - \frac{\mu}{T} dN_r \\
&= -\frac{1}{T} dU + \frac{\mu}{T} dN \\
dS_u &= dS - \frac{1}{T} dU + \frac{\mu}{T} dN \\
&= -\frac{1}{T} (dU - T dS - \mu dN) = -\frac{1}{T} d\Phi
\end{aligned} \tag{8}$$

Since the entropy tends to increase spontaneously, dS_u is positive, and $d\Phi$ is negative, indicating that the grand free energy Φ tends to decrease.

Exercise 3

An Introduction to Thermal Physics (Schroeder, 1e) Exercise 6.5

Part (a)

The partition function of the particle Z is:

$$\begin{aligned} Z &= e^{-\frac{-0.05 \text{ J}}{k_B T}} + e^{-\frac{0 \text{ J}}{k_B T}} + e^{-\frac{0.05 \text{ J}}{k_B T}} \\ &= e^{-\frac{-0.05 \text{ J}}{8.617 \cdot 10^{-5} \text{ J/K} \cdot 300 \text{ J}}} + e^{-\frac{0 \text{ J}}{8.617 \cdot 10^{-5} \text{ J/K} \cdot 300 \text{ J}}} \\ &\quad + e^{-\frac{0.05 \text{ J}}{8.617 \cdot 10^{-5} \text{ J/K} \cdot 300 \text{ J}}} \approx 8.063 \end{aligned} \quad (9)$$

Part (b)

The probabilities of the particle being in each of the states is:

$$\begin{aligned} P(E = -0.05 \text{ J}) &= \frac{e^{-\frac{-0.05 \text{ J}}{8.617 \cdot 10^{-5} \text{ J/K} \cdot 300 \text{ J}}}}{Z} \approx 0.858 \\ P(E = 0 \text{ J}) &= \frac{e^{-\frac{0 \text{ J}}{8.617 \cdot 10^{-5} \text{ J/K} \cdot 300 \text{ J}}}}{Z} \approx 0.124 \\ P(E = 0.05 \text{ J}) &= \frac{e^{-\frac{0.05 \text{ J}}{8.617 \cdot 10^{-5} \text{ J/K} \cdot 300 \text{ J}}}}{Z} \approx 0.018 \end{aligned} \quad (10)$$

Part (c)

Shifting the zero point and repeating the calculations:

$$\begin{aligned} Z &= e^{-\frac{0 \text{ J}}{k_B T}} + e^{-\frac{0.05 \text{ J}}{k_B T}} + e^{-\frac{0.10 \text{ J}}{k_B T}} \\ &= e^{-\frac{0 \text{ J}}{8.617 \cdot 10^{-5} \text{ J/K} \cdot 300 \text{ J}}} + e^{-\frac{0.05 \text{ J}}{8.617 \cdot 10^{-5} \text{ J/K} \cdot 300 \text{ J}}} \\ &\quad + e^{-\frac{0.10 \text{ J}}{8.617 \cdot 10^{-5} \text{ J/K} \cdot 300 \text{ J}}} \approx 1.165 \\ P(E = 0 \text{ J}) &= \frac{e^{-\frac{0 \text{ J}}{8.617 \cdot 10^{-5} \text{ J/K} \cdot 300 \text{ J}}}}{Z} \approx 0.858 \\ P(E = 0.05 \text{ J}) &= \frac{e^{-\frac{0.05 \text{ J}}{8.617 \cdot 10^{-5} \text{ J/K} \cdot 300 \text{ J}}}}{Z} \approx 0.124 \\ P(E = 0.10 \text{ J}) &= \frac{e^{-\frac{0.10 \text{ J}}{8.617 \cdot 10^{-5} \text{ J/K} \cdot 300 \text{ J}}}}{Z} \approx 0.018 \end{aligned} \quad (11)$$

The partition function changes, but the probabilities remain the same, since the zero for measuring energy is arbitrary.

Exercise 4

An Introduction to Thermal Physics (Schroeder, 1e) Exercise 6.11

The partition function of a lithium nucleus is:

$$\begin{aligned}
 Z &= e^{-\frac{\frac{3}{2}\mu_B}{k_B T}} + e^{-\frac{-\frac{1}{2}\mu_B}{k_B T}} + e^{-\frac{\frac{1}{2}\mu_B}{k_B T}} + e^{-\frac{\frac{3}{2}\mu_B}{k_B T}} \\
 &= e^{-\frac{\frac{3}{2} \cdot 1.03 \cdot 10^{-7} \text{ eV/T} \cdot 0.63 \text{ T}}{8.617 \cdot 10^{-5} \text{ eV/K} \cdot 300 \text{ K}}} + e^{-\frac{-\frac{1}{2} \cdot 1.03 \cdot 10^{-7} \text{ eV/T} \cdot 0.63 \text{ T}}{8.617 \cdot 10^{-5} \text{ eV/K} \cdot 300 \text{ K}}} \\
 &\quad + e^{-\frac{\frac{1}{2} \cdot 1.03 \cdot 10^{-7} \text{ eV/T} \cdot 0.63 \text{ T}}{8.617 \cdot 10^{-5} \text{ eV/K} \cdot 300 \text{ K}}} + e^{-\frac{\frac{3}{2} \cdot 1.03 \cdot 10^{-7} \text{ eV/T} \cdot 0.63 \text{ T}}{8.617 \cdot 10^{-5} \text{ eV/K} \cdot 300 \text{ K}}} \approx 4
 \end{aligned} \tag{12}$$

The probability of the nucleus being in each of the spin orientations is then:

$$\begin{aligned}
 P\left(m = -\frac{3}{2}\right) &= \frac{e^{-\frac{\frac{3}{2} \cdot 1.03 \cdot 10^{-7} \text{ eV/T} \cdot 0.63 \text{ T}}{8.617 \cdot 10^{-5} \text{ eV/K} \cdot 300 \text{ K}}}}{Z} \approx 0.25 \\
 P\left(m = -\frac{1}{2}\right) &= \frac{e^{-\frac{-\frac{1}{2} \cdot 1.03 \cdot 10^{-7} \text{ eV/T} \cdot 0.63 \text{ T}}{8.617 \cdot 10^{-5} \text{ eV/K} \cdot 300 \text{ K}}}}{Z} \approx 0.25 \\
 P\left(m = \frac{1}{2}\right) &= \frac{e^{-\frac{\frac{1}{2} \cdot 1.03 \cdot 10^{-7} \text{ eV/T} \cdot 0.63 \text{ T}}{8.617 \cdot 10^{-5} \text{ eV/K} \cdot 300 \text{ K}}}}{Z} \approx 0.25 \\
 P\left(m = \frac{3}{2}\right) &= \frac{e^{-\frac{\frac{3}{2} \cdot 1.03 \cdot 10^{-7} \text{ eV/T} \cdot 0.63 \text{ T}}{8.617 \cdot 10^{-5} \text{ eV/K} \cdot 300 \text{ K}}}}{Z} \approx 0.25
 \end{aligned} \tag{13}$$

If both B and T change sign, $\frac{m\mu_B}{k_B T}$ does not change sign, so the expression for the probability remains the same. Consequently, the particles obey the Boltzmann distribution for $T = -300\text{K}$.

Exercise 5

An Introduction to Thermal Physics (Schroeder, 1e) Exercise 6.14

For a single air molecule, with s_1 being the state where the molecule is at sea level and s_2 being the state where the molecule is at height z :

$$\begin{aligned} E(s_1) &= E(s_2) + mgz \\ \frac{P(s=s_1)}{P(s=s_2)} &= \frac{e^{-\frac{E(s_1)}{k_B T}}}{e^{-\frac{E(s_2)}{k_B T}}} = e^{-\frac{E(s_1)-E(s_2)}{k_B T}} = e^{-\frac{mgz}{k_B T}} \\ P(s=s_1) &= P(s=s_2) e^{-\frac{mgz}{k_B T}} \\ P(z) &= P(0) e^{-\frac{mgz}{k_B T}} \\ \rho(z) &= \rho(0) e^{-\frac{mgz}{k_B T}} \end{aligned} \tag{14}$$

Exercise 6

An Introduction to Thermal Physics (Schroeder, 1e) Exercise 6.16

For a system in equilibrium with a reservoir at temperature T , where $\beta = \frac{1}{k_B T}$:

$$\begin{aligned} -\frac{d}{d\beta} \ln Z &= -\frac{\frac{dZ}{d\beta}}{Z} = -\frac{\frac{d}{d\beta} \sum_s e^{-\beta E(s)}}{Z} \\ &= -\frac{\sum_s \frac{d}{d\beta} e^{-\beta E(s)}}{Z} \\ &= -\frac{\sum_s -E(s) e^{-\beta E(s)}}{Z} = \frac{\sum_s E(s) e^{-\beta E(s)}}{Z} = \overline{E} \end{aligned} \tag{15}$$

Exercise 7

An Introduction to Thermal Physics (Schroeder, 1e) Exercise 6.20 (partial)

Part (a)

The partition function of a single harmonic oscillator Z is:

$$\begin{aligned} Z &= \sum_s e^{-E(s)\beta} \\ &= \sum_{n=0}^{\infty} e^{-n h f \beta} \\ &= \sum_{n=0}^{\infty} (e^{-h f \beta})^n \\ &= \frac{1}{1 - e^{-h f \beta}} \end{aligned} \tag{16}$$

Part (b)

At temperature T , the average energy of a single harmonic oscillator \bar{E} is:

$$\begin{aligned} \bar{E} &= -\frac{d}{d\beta} \ln Z \\ &= -\frac{d}{d\beta} \ln \left(\frac{1}{1 - e^{-h f \beta}} \right) \\ &= \frac{d}{d\beta} \ln (1 - e^{-h f \beta}) \\ &= \frac{h f e^{-h f \beta}}{1 - e^{-h f \beta}} \\ &= \frac{h f}{e^{h f \beta} - 1} = \frac{h f}{e^{\frac{h f}{k_B T}} - 1} \end{aligned} \tag{17}$$

Part (c)

The total energy of a system with N oscillators U is then:

$$\begin{aligned} U &= N \bar{E} \\ &= \frac{N h f}{e^{\frac{h f}{k_B T}} - 1} \end{aligned} \tag{18}$$

Part (d)

The heat capacity of this system C is:

$$\begin{aligned}
 C &= \frac{\partial U}{\partial T} = -Nhf \frac{-\frac{hf}{k_B T^2} e^{\frac{hf}{k_B T}}}{\left(e^{\frac{hf}{k_B T}} - 1\right)^2} \\
 &= \frac{Nh^2 f^2}{k_B T^2} \frac{e^{\frac{hf}{k_B T}}}{\left(e^{\frac{hf}{k_B T}} - 1\right)^2}
 \end{aligned} \tag{19}$$

In the low-temperature limit:

$$\lim_{T \rightarrow 0} C = \lim_{T \rightarrow 0} \frac{Nh^2 f^2}{k_B T^2} \frac{e^{\frac{hf}{k_B T}}}{\left(e^{\frac{hf}{k_B T}} - 1\right)^2} = 0 \tag{20}$$

In the high-temperature limit:

$$\begin{aligned}
 \lim_{T \rightarrow \infty} C &= \lim_{T \rightarrow \infty} \frac{Nh^2 f^2}{k_B T^2} \frac{e^{\frac{hf}{k_B T}}}{\left(e^{\frac{hf}{k_B T}} - 1\right)^2} \\
 &= \lim_{T \rightarrow \infty} \frac{Nh^2 f^2}{k_B T^2} \frac{1 + \frac{hf}{k_B T} + \dots}{\left(\frac{hf}{k_B T} + \frac{1}{2} \left(\frac{hf}{k_B T}\right)^2 + \dots\right)^2} \\
 &= \lim_{T \rightarrow \infty} \frac{Nh^2 f^2}{k_B T^2} \frac{1 + \dots}{\left(\frac{hf}{k_B T}\right)^2 + \dots} \\
 &= Nk_B
 \end{aligned} \tag{21}$$

Exercise 8

An Introduction to Thermal Physics (Schroeder, 1e) Exercise 6.26

Approximating the rotational partition function Z_{rot} :

$$Z_{\text{rot}} = \sum_{j=0}^{\infty} (2j+1) e^{-\frac{j(j+1)\epsilon}{k_B T}} \approx 1 + 3e^{-\frac{2\epsilon}{k_B T}} = 1 + 3e^{-2\epsilon\beta} \quad (22)$$

Using this approximation to find the average energy $\overline{E}_{\text{rot}}$ and heat capacity C :

$$\begin{aligned} \overline{E}_{\text{rot}} &= -\frac{d}{d\beta} \ln Z_{\text{rot}} \approx -\frac{d}{d\beta} \ln(1 + 3e^{-2\epsilon\beta}) = \frac{6\epsilon e^{-2\epsilon\beta}}{1 + 3e^{-2\epsilon\beta}} \\ &\approx 6\epsilon e^{-2\epsilon\beta} = 6\epsilon e^{-\frac{2\epsilon}{k_B T}} \\ C &= \frac{\partial \overline{E}}{\partial T} \approx \frac{\partial}{\partial T} 6\epsilon e^{-\frac{2\epsilon}{k_B T}} \\ &\approx 6\epsilon \frac{2\epsilon}{k_B T^2} e^{-\frac{2\epsilon}{k_B T}} = \frac{12\epsilon^2}{k_B T^2} e^{-\frac{2\epsilon}{k_B T}} \\ \lim_{T \rightarrow 0} c &= \lim_{T \rightarrow 0} \frac{12\epsilon^2}{k_B T^2} e^{-\frac{2\epsilon}{k_B T}} = 0 \end{aligned} \quad (23)$$

This result is consistent with the third law, as the heat capacity goes to 0 as the temperature goes to 0.

