

1. A model thermodynamic system in which the allowed non-degenerate states have energies $0, \varepsilon, 2\varepsilon, 3\varepsilon, \dots$ consists of four particles with total energy $U = 6\varepsilon$. Identify the possible distribution of particles, evaluate $\Omega = \sum_k \omega_k$ and work out the average occupation numbers for the various energy levels. (i) When the particles are gaseous bosons; (ii) when the particles are gaseous fermions.

Solution: (i) For gaseous bosons,

$$\begin{aligned}
 U = 6\varepsilon &= 0\varepsilon \times 3 + 1\varepsilon \times 0 + 2\varepsilon \times 0 + 3\varepsilon \times 0 + 4\varepsilon \times 0 + 5\varepsilon \times 0 + 6\varepsilon \times 1 \\
 &= 0\varepsilon \times 2 + 1\varepsilon \times 1 + 2\varepsilon \times 0 + 3\varepsilon \times 0 + 4\varepsilon \times 0 + 5\varepsilon \times 1 + 6\varepsilon \times 0 \\
 &= 0\varepsilon \times 2 + 1\varepsilon \times 0 + 2\varepsilon \times 1 + 3\varepsilon \times 0 + 4\varepsilon \times 1 + 5\varepsilon \times 0 + 6\varepsilon \times 0 \\
 &= 0\varepsilon \times 1 + 1\varepsilon \times 2 + 2\varepsilon \times 0 + 3\varepsilon \times 0 + 4\varepsilon \times 1 + 5\varepsilon \times 0 + 6\varepsilon \times 0 \\
 &= 0\varepsilon \times 2 + 1\varepsilon \times 0 + 2\varepsilon \times 0 + 3\varepsilon \times 2 + 4\varepsilon \times 0 + 5\varepsilon \times 0 + 6\varepsilon \times 0 \\
 &= 0\varepsilon \times 1 + 1\varepsilon \times 1 + 2\varepsilon \times 1 + 3\varepsilon \times 1 + 4\varepsilon \times 0 + 5\varepsilon \times 0 + 6\varepsilon \times 0 \\
 &= 0\varepsilon \times 0 + 1\varepsilon \times 3 + 2\varepsilon \times 0 + 3\varepsilon \times 1 + 4\varepsilon \times 0 + 5\varepsilon \times 0 + 6\varepsilon \times 0 \\
 &= 0\varepsilon \times 1 + 1\varepsilon \times 0 + 2\varepsilon \times 3 + 3\varepsilon \times 0 + 4\varepsilon \times 0 + 5\varepsilon \times 0 + 6\varepsilon \times 0 \\
 &= 0\varepsilon \times 0 + 1\varepsilon \times 2 + 2\varepsilon \times 2 + 3\varepsilon \times 0 + 4\varepsilon \times 0 + 5\varepsilon \times 0 + 6\varepsilon \times 0
 \end{aligned} \tag{1}$$

$\omega_j = 1$; $\Omega = \sum \omega_j = 9$; $\bar{N}_i = \sum N_{ij} \frac{\omega_j}{\Omega}$; $\bar{N}_0 = \frac{4}{3}$, $\bar{N}_1 = 1$, $\bar{N}_2 = \frac{7}{9}$, $\bar{N}_3 = \frac{4}{9}$, $\bar{N}_4 = \frac{2}{9}$, $\bar{N}_5 = \frac{1}{9}$, $\bar{N}_6 = \frac{1}{9}$. (ii) For gaseous fermions, the occupation number cannot be larger than one for any state, $U = 6\varepsilon = 0\varepsilon \times 1 + 1\varepsilon \times 1 + 2\varepsilon \times 1 + 3\varepsilon \times 1 + 4\varepsilon \times 0 + 5\varepsilon \times 0 + 6\varepsilon \times 0$, $\Omega = 1$, $\bar{N}_- = \bar{N}_1 = \bar{N}_2 = \bar{N}_3 = 1$.

2. Consider a system of N distinguishable particles, at temperature T , with available energy levels ε_1 and $\varepsilon_2 > \varepsilon_1$ (only two available non-degenerate energy levels). (i) Determine the equilibrium values of the occupation numbers N_1 and N_2 , and the energy U of the system, as a function of temperature. (ii) Show that the specific heat is given by

$$C_V = Nk \left(\frac{\Delta}{kT} \right)^2 \frac{e^{-\Delta/kT}}{(1 + e^{-\Delta/kT})^2},$$

where $\Delta = \varepsilon_2 - \varepsilon_1$. Examine the low temperature and high temperature behavior of C_V/Nk , and sketch it as a function of kT/Δ .

Solution: From $N_i = N g_i \frac{e^{\varepsilon_i/kT}}{Z}$ it follows that $N_1 = N \frac{e^{-\varepsilon_1/kT}}{e^{-\varepsilon_1/kT} + e^{-\varepsilon_2/kT}}$ and $N_2 = N \frac{e^{-\varepsilon_2/kT}}{e^{-\varepsilon_1/kT} + e^{-\varepsilon_2/kT}}$
 $U = \sum \varepsilon_i = N \frac{\varepsilon_1 e^{-\varepsilon_1/kT} + \varepsilon_2 e^{-\varepsilon_2/kT}}{e^{-\varepsilon_1/kT} + e^{-\varepsilon_2/kT}} = N \frac{\varepsilon_1 e^{(\varepsilon_2 - \varepsilon_1)/kT} + \varepsilon_2}{e^{(\varepsilon_2 - \varepsilon_1)/kT} + 1} = N \frac{\varepsilon_1 + \varepsilon_2 e^{-(\varepsilon_2 - \varepsilon_1)/kT}}{1 + e^{-(\varepsilon_2 - \varepsilon_1)/kT}}$. See Fig. 1. (ii) $C_V = \left(\frac{\partial U}{\partial T} \right)_V = Nk \left(\frac{\Delta}{kT} \right)^2 \frac{e^{-\Delta/kT}}{(1 + e^{-\Delta/kT})^2}$.

3. Show that for a system of a large number N of bosons at very low temperatures (such that they are all in the non-degenerate lowest energy state $\varepsilon = 0$) the chemical potential varies with temperature according to

$$\lim_{T \rightarrow 0} \mu = -\frac{kT}{N}.$$

Solution: For $T \rightarrow 0$, almost all the particles are at the ground state for gaseous bosons, $N \approx N_0 = \frac{1}{e^{(0-\mu)/kT}-1} \approx \frac{1}{e^{-\mu/kT}-1}$. Then, $1 + \frac{1}{N} = e^{-\mu/kT}$ and so $\ln\left(1 + \frac{1}{N}\right) = -\frac{\mu}{kT}$, yielding $\frac{1}{N} \approx -\frac{\mu}{kT}$, or equivalently $\mu = -\frac{kT}{N}$.

4. (i) For a system of localized distinguishable oscillators, Boltzmann statistics applies. Show that the entropy S is given by

$$S = -k \sum_j N_j \ln \left(\frac{N_j}{N} \right).$$

(ii) Substitute the Boltzmann distribution in the previous result to show that

$$S = \frac{U}{T} + Nk \ln Z.$$

(iii) Show that

$$S = Nk \left[\frac{\theta/T}{e^{\theta/T} - 1} - \ln(1 - e^{-\theta/T}) \right],$$

where $\theta = \hbar\omega/k$. Examine the behavior of S as $T \rightarrow 0$ and $T \rightarrow \infty$. [Hint: For part (i), use $\omega = \omega_{\text{MB}}$ (keeping the $N!$ in the numerator) and use Stirling's approximation. Note that the result of part (i) can be written as $S = -Nk \sum_j f_j \ln f_j$, where $f_j = N_j/N$ is the probability of occupying level j .]

Solution: (i) For distinguishable particles it follows that $S = k \ln \left(\frac{N}{\prod N_i!} \right) \approx k[N \ln N - N - \sum_i (N_i \ln N_i - N_i)] = -k \sum_i N_i \ln \frac{N_i}{N}$. (ii) For Boltzmann distribution, $N_i = N \frac{1}{e^{(\varepsilon_i - \mu)/kT}}$; $S = k \sum_i N_i \ln \frac{N_i}{N} = k \sum_i \left[N_i \ln \frac{1}{e^{(\varepsilon_i - \mu)/kT}} \right] = k \sum_i \left[N_i \left(\frac{\varepsilon_i - \mu}{kT} \right) \right] = \frac{1}{T} \sum_i N_i \varepsilon_i - k \frac{\mu}{kT} \sum_i N_i = \frac{U}{T} - k(-\ln Z)N = \frac{U}{T} + Nk \ln Z$. (iii) $U = Nk\theta \left(\frac{1}{2} + \frac{1}{e^{\theta/T} - 1} \right)$; $Z = \frac{e^{-\theta/2T}}{1 - e^{-\theta/T}}$; $S = \frac{U}{T} + Nk \ln Z = \frac{Nk\theta}{T} \left(\frac{1}{2} + \frac{1}{e^{\theta/T} - 1} \right) + Nk \ln \left(\frac{e^{-\theta/2T}}{1 - e^{-\theta/T}} \right) = Nk \left[\frac{\theta/T}{e^{\theta/T} - 1} - \ln(1 - e^{-\theta/T}) \right]$.

5. The partition function of an Einstein solid is

$$Z = \frac{e^{-\theta_E/2T}}{1 - e^{-\theta_E/T}},$$

where θ_E is the Einstein temperature. Treat the crystalline lattice as an assembly of $3N$ distinguishable oscillators. (i) Calculate the Helmholtz function F . (ii) Calculate the entropy S . Show that the entropy approaches zero as the temperature goes to absolute zero. Show that at high temperatures, $S \approx 3Nk[1 + \ln(T/\theta_E)]$. Sketch $S/3Nk$ as a function of T/θ_E .

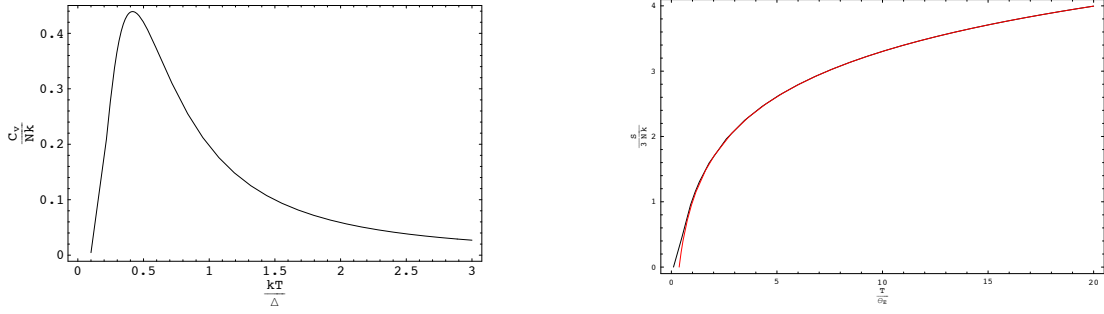


Figure 1: Problem 2 (i) (left) and problem 5 (ii) (right).

Solution: (i) $Z_{3N} = z^{3N}$; $F = -kT \ln Z_{3N} = -3NkT \ln z = -3NkT \left[-\frac{\theta_E}{2T} - \ln(1 - e^{-\theta_E/T}) \right]$.
(ii) $S = -\left(\frac{\partial F}{\partial T}\right)_V = -3Nk \ln(1 - e^{-\theta_E/T}) + 3NkT \frac{\theta_E}{T} \frac{e^{-\theta_E/T}}{1 - e^{-\theta_E/T}}$, as the black line in Fig. 1. (iii) For $T \rightarrow 0$, $e^{-\theta_E/T} \ll 1$, and so $S = -3Nk \ln(1 - e^{-\theta_E/T}) + 3NkT \frac{\theta_E}{T^2} \frac{e^{-\theta_E/T}}{1 - e^{-\theta_E/T}} \rightarrow -3Nk \ln 1 + 3Nk \frac{\theta_E}{T} e^{-\theta_E/T} \rightarrow 0$. For high temperature, $T \gg \theta_E$ and $e^{-\theta_E/T} \rightarrow 1 - \frac{\theta_E}{T}$, yielding $S = -3Nk \ln(1 - e^{-\theta_E/T}) + 3NkT \frac{\theta_E}{T^2} \frac{e^{-\theta_E/T}}{1 - e^{-\theta_E/T}} \rightarrow -3Nk \ln(\theta_E/T) + 3Nk$, as the red line in Fig. 1.