PHYSICS 140A : STATISTICAL PHYSICS
HW ASSIGNMENT #2 SOLUTIONS

(1) A box of volume V contains N_1 identical atoms of mass m_1 and N_2 identical atoms of mass m_2.

(a) Compute the density of states $D(E, V, N_1, N_2)$.

(b) Let $x_1 \equiv N_1/N$ be the fraction of particles of species #1. Compute the statistical entropy $S(E, V, N, x_1)$.

(c) Under what conditions does increasing the fraction x_1 result in an increase in statistical entropy of the system? Why?

Solution :

(a) Following the method outlined in §4.2.2 of the Lecture Notes, we rescale all the momenta $\boldsymbol{p}_i$ with $i \in \{1, \ldots, N_1\}$ as $p_i^\alpha = \sqrt{2m_1 E}\, u_i^\alpha$, and all the momenta p_j with $j \in \{N_1+1, \ldots, N_1+N_2\}$ as $p_j^\alpha = \sqrt{2m_2 E}\, u_j^\alpha$. We then have

$$D(E, V, N_1, N_2) = \frac{V^{N_1+N_2}}{N_1!\, N_2!} \left(\frac{\sqrt{2m_1 E}}{h}\right)^{N_1 d} \left(\frac{\sqrt{2m_2 E}}{h}\right)^{N_2 d} E^{-1} \cdot \tfrac{1}{2}\Omega_{(N_1+N_2)d} \,.$$

Thus,

$$D(E, V, N_1, N_2) = \frac{V^N}{N_1!\, N_2!} \left(\frac{m}{2\pi\hbar^2}\right)^{\frac{1}{2}Nd} \frac{E^{\frac{1}{2}Nd-1}}{\Gamma(Nd/2)} \,,$$

where $N = N_1 + N_2$ and $m \equiv m_1^{N_1/N} m_2^{N_2/N}$ has dimensions of mass. Note that the $N_1!\, N_2!$ term in the denominator, in contrast to $N!$, appears because only particles of the same species are identical.

(b) Using Stirling's approximation $\ln K! \simeq K \ln K - K + \mathcal{O}(\ln K)$, we find

$$\frac{S}{k_B} = \ln D = N \ln\!\left(\frac{V}{N}\right) + \tfrac{1}{2}Nd \ln\!\left(\frac{2E}{Nd}\right) - N\big(x_1 \ln x_1 + x_2 \ln x_2\big) + \tfrac{1}{2}Nd \ln\!\left(\frac{m_1^{x_1} m_2^{x_2}}{2\pi\hbar^2}\right) + N\big(1 + \tfrac{1}{2}d\big) \,,$$

where $x_2 = 1 - x_1$.

(c) Using $x_2 = 1 - x_1$, we have

$$\frac{\partial S}{\partial x_1} = N \ln\!\left(\frac{1 - x_1}{x_1}\right) + \tfrac{1}{2}Nd \ln\!\left(\frac{m_1}{m_2}\right) .$$

Setting $\partial S/\partial x_1$ to zero at the solution $x = x_1^*$, we obtain

$$x_1^* = \frac{m_1^{d/2}}{m_1^{d/2} + m_2^{d/2}} \quad , \quad x_2^* = \frac{m_2^{d/2}}{m_1^{d/2} + m_2^{d/2}} \,.$$

Thus, an increase of x_1 will result in an increase in statistical entropy if $x_1 < x_1^*$. The reason is that $x_1 = x_1^*$ is optimal in terms of maximizing S.

(2) Two chambers containing Argon gas at $p = 1.0\,\text{atm}$ and $T = 300\,\text{K}$ are connected via a narrow tube. One chamber has volume $V_1 = 1.0\,\text{L}$ and the other has volume $V_2 = r\,V_1$.

(a) Compute the RMS energy fluctuations of the particles in the smaller chamber when the volume ration is $r = 2$.

(b) Compute the RMS energy fluctuations of the particles in the smaller chamber when the volume ration is $r = \infty$.

Solution :

For two systems in thermal contact (see Lecture Notes §4.5), the RMS energy fluctuation of system #1 is $\Delta E_1 = \sqrt{k_{\text{B}} T^2\, \bar{C}_V}$, where

$$\bar{C}_V = \frac{C_{V,1}\, C_{V,2}}{C_{V,1} + C_{V,2}} = \frac{r}{r+1}\, C_{V,1}\ .$$

Thus, with $C_V = \frac{3}{2} N k_{\text{B}} = 3pV/T$, we have

$$\Delta E_1 = \sqrt{\frac{r}{r+1}} \cdot \sqrt{\tfrac{3}{2}\, pV k_{\text{B}} T} = \sqrt{\frac{r}{r+1}} \cdot 7.93 \times 10^{-10}\,\text{J}\ .$$

Thus, (a) for $r = 2$ we have $\Delta E_1 = 648\,\text{pJ}$, and (b) for $r = \infty$ we have $\Delta E_1 = 793\,\text{pJ}$, where $1\,\text{pJ} = 10^{-12}\,\text{J}$.

(3) Consider a system of N identical but distinguishable particles, each of which has a nondegenerate ground state with energy zero, and a g-fold degenerate excited state with energy $\varepsilon > 0$.

(a) Let the total energy of the system be fixed at $E = M\varepsilon$, where M is the number of particles in an excited state. What is the total number of states $\Omega(E, N)$?

(b) What is the entropy $S(E, N)$? Assume the system is thermodynamically large. You may find it convenient to define $\nu \equiv M/N$, which is the fraction of particles in an excited state.

(c) Find the temperature $T(\nu)$. Invert this relation to find $\nu(T)$.

(d) Show that there is a region where the temperature is negative.

(e) What happens when a system at negative temperature is placed in thermal contact with a heat bath at positive temperature?

Solution :

(a) Since each excited particle can be in any of g degenerate energy states, we have

$$\Omega(E,N) = \binom{N}{M} g^M = \frac{N!\, g^M}{M!\,(N-M)!} \ .$$

(b) Using Stirling's approximation, we have

$$S(E,N) = k_\mathrm{B} \ln \Omega(E,N) = -N k_\mathrm{B} \Big\{ \nu \ln \nu + (1-\nu) \ln(1-\nu) - \nu \ln g \Big\} \ ,$$

where $\nu = M/N = E/N\varepsilon$.

(c) The inverse temperature is

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{\!N} = \frac{1}{N\varepsilon} \left(\frac{\partial S}{\partial \nu}\right)_{\!N} = \frac{k_\mathrm{B}}{\varepsilon} \cdot \left\{ \ln\!\left(\frac{1-\nu}{\nu}\right) + \ln g \right\} \ ,$$

hence

$$k_\mathrm{B} T = \frac{\varepsilon}{\ln\!\big(\frac{1-\nu}{\nu}\big) + \ln g} \ .$$

Inverting,

$$\nu(T) = \frac{g\, e^{-\varepsilon/k_\mathrm{B}T}}{1 + g\, e^{-\varepsilon/k_\mathrm{B}T}} \ .$$

(d) The temperature diverges when the denominator in the above expression for $T(\nu)$ vanishes. This occurs at $\nu = \nu^* \equiv g/(g+1)$. For $\nu \in (\nu^*, 1)$, the temperature is negative! This is technically correct, and a consequence of the fact that the energy is bounded for this system: $E \in [0, N\varepsilon]$. The entropy as a function of ν therefore has a maximum at $\nu = \nu^*$. The model is unphysical though in that it neglects various excitations such as kinetic energy (*e.g.* lattice vibrations) for which the energy can be arbitrarily large.

(e) When a system at negative temperature is placed in contact with a heat bath at positive temperature, heat flows from the system to the bath. The energy of the system therefore decreases, and since $\frac{\partial S}{\partial E} < 0$, this results in a net entropy increase, which is what is demanded by the Second Law of Thermodynamics.

(4) Solve for the model in problem 3 using the ordinary canonical ensemble. The Hamiltonian is

$$\hat{H} = \varepsilon \sum_{i=1}^{N} \left(1 - \delta_{\sigma_i,1}\right) \ ,$$

where $\sigma_i \in \{1, \ldots, g+1\}$.

(a) Find the partition function $Z(T,N)$ and the Helmholtz free energy $F(T,N)$.

(b) Show that $\hat{M} = \frac{\partial \hat{H}}{\partial \varepsilon}$ counts the number of particles in an excited state. Evaluate the thermodynamic average $\nu(T) = \langle \hat{M} \rangle / N$.

(c) Show that the entropy $S = -\left(\frac{\partial F}{\partial T}\right)_N$ agrees with your result from problem 3.

Solution :

(a) We have

$$Z(T,N) = \mathsf{Tr}\, e^{-\beta \hat{H}} = \left(1 + g\, e^{-\varepsilon/k_{\mathrm{B}}T}\right)^N .$$

The free energy is

$$F(T,N) = -k_{\mathrm{B}} T \ln F(T,N) = -N k_{\mathrm{B}} T \ln\left(1 + g\, e^{-\varepsilon/k_{\mathrm{B}}T}\right) .$$

(b) We have

$$\hat{M} = \frac{\partial \hat{H}}{\partial \varepsilon} = \sum_{i=1}^{N} \left(1 - \delta_{\sigma_i,1}\right) .$$

Clearly this counts all the excited particles, since the expression $1 - \delta_{\sigma_i,1}$ vanishes if $i = 1$, which is the ground state, and yields 1 if $i \neq 1$, *i.e.* if particle i is in any of the g excited states. The thermodynamic average of $\hat{M}$ is $\langle \hat{M} \rangle = \left(\frac{\partial F}{\partial \varepsilon}\right)_{T,N}$, hence

$$\nu = \frac{\langle \hat{M} \rangle}{N} = \frac{g\, e^{-\varepsilon/k_{\mathrm{B}}T}}{1 + g\, e^{-\varepsilon/k_{\mathrm{B}}T}} ,$$

which agrees with the result in problem 3c.

(c) The entropy is

$$S = -\left(\frac{\partial F}{\partial T}\right)_N = N k_{\mathrm{B}} \ln\left(1 + g\, e^{-\varepsilon/k_{\mathrm{B}}T}\right) + \frac{N\varepsilon}{T} \, \frac{g\, e^{-\varepsilon/k_{\mathrm{B}}T}}{1 + g\, e^{-\varepsilon/k_{\mathrm{B}}T}} .$$

Working with our result for $\nu(T)$, we derive

$$\begin{aligned} 1 + g\, e^{-\varepsilon/k_{\mathrm{B}}T} &= \frac{1}{1-\nu} \\ \frac{\varepsilon}{k_{\mathrm{B}}T} &= \ln\left(\frac{g(1-\nu)}{\nu}\right) . \end{aligned}$$

Inserting these results into the above expression for S, we verify

$$\begin{aligned} S &= -N k_{\mathrm{B}} \ln(1-\nu) + N k_{\mathrm{B}}\, \nu \ln\left(\frac{g(1-\nu)}{\nu}\right) \\ &= -N k_{\mathrm{B}} \Big\{ \nu \ln \nu + (1-\nu) \ln(1-\nu) - \nu \ln g \Big\} , \end{aligned}$$

as we found in problem 3b.