

You are graded on your work (with partial credit where it is deserved) so please do not just write down answers with no explanation (or skip important steps)!

Please give clear, well-organized, understandable solutions.

$$\begin{aligned}
 h &= 6.63 \times 10^{-34} \text{ J s} && \text{[Planck's constant]} && k &= 1.38 \times 10^{-23} \text{ J/K} && \text{[Boltzmann constant]} \\
 c &= 3.00 \times 10^8 \text{ m/s} && \text{[speed of light]} && m_e &= 9.11 \times 10^{-31} \text{ kg} && \text{[mass of electron]} \\
 1 \text{ eV} &= 1.60 \times 10^{-19} \text{ J} && \text{and} && \frac{1 \text{ eV}}{k} &= 11,600 \text{ K}
 \end{aligned}$$

**See back page for small integral table.**

The variables have their usual meanings:  $E$  = energy,  $S$  = entropy,  $V$  = volume,  $N$  = number of particles,  $T$  = temperature,  $P$  = pressure,  $\mu$  = chemical potential,  $B$  = applied magnetic field,  $C_V$  = heat capacity at constant volume,  $k$  = Boltzmann constant. Also,  $\langle \dots \rangle$  represents an average.

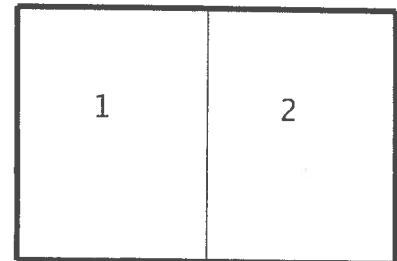
1. Two systems, 1 and 2, are separated by a partition that permits energy and particles to flow through, and which is also movable. Then we have

$$E = E_1 + E_2, \quad V = V_1 + V_2, \quad N = N_1 + N_2, \quad S = S_1 + S_2$$

where the total energy  $E$ , total volume  $V$ , and total number of particles  $N$  are constant, but  $E_i$ ,  $V_i$ , and  $N_i$  can vary. Recall that

$$dS_i = \frac{1}{T_i} dE_i + \frac{P_i}{T_i} dV_i - \frac{\mu_i}{T_i} dN_i \quad (i=1,2)$$

where  $T$  is the temperature,  $P$  the pressure, and  $\mu$  the chemical potential.



Initially  $T_2 > T_1$ ,  $P_2 > P_1$ , and  $\mu_2 > \mu_1$ . But assume that the processes in parts (a), (b), and (c) can be treated independently, and after part (a) assume that the temperatures have become equal.

Use the second law of thermodynamics to **clearly** demonstrate the following.

(a) (4) Energy flows from one system to the other - i.e.,  $dE_i/dt > 0$  (where you determine  $i$  in the calculation).

$$\begin{aligned}
 \frac{dS}{dt} &= \frac{dS_1}{dt} + \frac{dS_2}{dt} = \frac{\partial S_1}{\partial E_1} \frac{dE_1}{dt} + \frac{\partial S_2}{\partial E_2} \frac{dE_2}{dt} = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \frac{dE_1}{dt} \\
 &\quad \text{since } E_2 = E - E_1 \text{ so } \frac{dE_2}{dt} = -\frac{dE_1}{dt} \\
 \frac{dS}{dt} &> 0 \quad \text{and} \quad \frac{1}{T_1} - \frac{1}{T_2} > 0 \Rightarrow \frac{dE_1}{dt} > 0
 \end{aligned}$$

In the following parts, assume that the temperatures have become equal:  $T_1 = T_2$  in parts (b) and (c).

(b) (4) One system expands and the other contracts - i.e.,  $dV_i/dt > 0$  (where you determine  $i$  in the calculation).

$$\frac{dS}{dt} = \frac{\partial S_1}{\partial V_1} \frac{dV_1}{dt} + \frac{\partial S_2}{\partial V_2} \frac{dV_2}{dt} = \left( \frac{P_1}{T} - \frac{P_2}{T} \right) \frac{dV_1}{dt}$$

$$\frac{dS}{dt} > 0 \text{ and } P_1 - P_2 < 0 \Rightarrow \frac{dV_1}{dt} < 0 \Rightarrow \boxed{\frac{dV_2}{dt} > 0}$$

(c) (4) Particles flow from one system to the other - i.e.,  $dN_i/dt > 0$  (where you determine  $i$  in the calculation).

$$\frac{dS}{dt} = \frac{\partial S_1}{\partial N_1} \frac{dN_1}{dt} + \frac{\partial S_2}{\partial N_2} \frac{dN_2}{dt} = - \left( \frac{\mu_1}{T} - \frac{\mu_2}{T} \right) \frac{dN_1}{dt}$$

$$\frac{dS}{dt} > 0 \text{ and } -(\mu_1 - \mu_2) > 0 \Rightarrow \boxed{\frac{dN_1}{dt} > 0}$$

2. The  $N$  identical atoms in an ideal gas each have a magnetic dipole moment  $\mu$  which can be aligned parallel or antiparallel to an applied magnetic field  $B$ .

(a) (5) Obtain the partition function  $Z_{mag}$  associated with the magnetic dipole of a single atom at temperature  $T$  in magnetic field  $B$ .

$$\begin{aligned} \epsilon_{\uparrow} &= -\mu B, \quad \epsilon_{\downarrow} = +\mu B \\ Z_{mag} &= e^{-\epsilon_{\uparrow}/kT} + e^{-\epsilon_{\downarrow}/kT} = e^{+\mu B/kT} + e^{-\mu B/kT} \end{aligned}$$

$\uparrow \vec{B}$

(b) (5) Calculate the average magnetic dipole moment  $\langle M \rangle$  for one atom.

$$\begin{aligned} \langle M \rangle &= \frac{\mu e^{+\mu B/kT} + (-\mu) e^{-\mu B/kT}}{e^{+\mu B/kT} + e^{-\mu B/kT}} \\ &= \frac{e^{+\mu B/kT} - e^{-\mu B/kT}}{e^{+\mu B/kT} + e^{-\mu B/kT}} \mu \\ &= \mu \tanh\left(\frac{\mu B}{kT}\right) \end{aligned}$$

(c) (5) Given that the density of states for translational (center-of-mass) motion of a single atom is

$$D(\epsilon) = A\epsilon^{1/2}, \quad A = \frac{2\pi(2m)^{3/2}}{h^3} V, \quad \epsilon = \text{energy}, \quad V = \text{volume}$$

calculate the partition function  $Z_{trans}$  for the translational motion of a single atom. (You can use substitution of variables and the integral table on the last page.)

$$Z_{trans} = \int_0^{\infty} e^{-\epsilon/kT} D(\epsilon) d\epsilon = A \int_0^{\infty} e^{-\epsilon/kT} \epsilon^{1/2} d\epsilon$$

Let  $\epsilon = x^2$ , so  $d\epsilon = 2x dx$  and  $\epsilon^{1/2} = x$ ; also,  $a \equiv \frac{1}{kT}$ :

$$\begin{aligned} Z_{trans} &= A \int_0^{\infty} e^{-ax^2} x \cdot 2x dx \\ &= 2A \int_0^{\infty} e^{-ax^2} x^2 dx \\ &= \frac{1}{4} \sqrt{\frac{\pi}{a^3}} \text{ from last page} \\ &= \frac{1}{2} A \sqrt{\pi (kT)^3} \end{aligned}$$

(d) (5) Show that  $Z_{trans} = \frac{V}{\lambda_{th}^3}$  while at the same time defining the thermal de Broglie wavelength  $\lambda_{th}$ .

$$\begin{aligned} Z_{trans} &= \frac{V}{\lambda_{th}^3} \frac{2\pi(2m)^{3/2}}{h^3} V \cdot \pi^{1/2} (kT)^{3/2} \\ &= \frac{(2\pi m kT)^{3/2}}{h^3} V = \frac{V}{\lambda_{th}^3}, \quad \lambda_{th} = \frac{h}{(2\pi m kT)^{1/2}} \end{aligned}$$

(e) (5) Bearing in mind that the atoms are indistinguishable, write down the partition function  $Z = Z_{trans} Z_{mag}$  for the whole gas.

$$Z = \frac{Z_{trans}^N Z_{mag}^N}{N!}$$

(f) (5) Show that the average energy  $\langle E \rangle$  of a general physical system is given by (function of  $T$ )  $\times \frac{\partial}{\partial T} \ln Z$ , while determining the function of  $T$ .

$$Z = \sum_j e^{-E_j/kT}$$

$$\frac{\partial}{\partial T} \ln Z = \frac{1}{Z} \sum_j e^{-E_j/kT} \left(-\frac{E_j}{k}\right) \left(-\frac{1}{T^2}\right)$$

$$= \frac{1}{kT^2} \sum_j p_j E_j \quad , \quad p_j = \frac{e^{-E_j/kT}}{Z}$$

$$= \frac{1}{kT^2} \langle E \rangle \Rightarrow \langle E \rangle = kT^2 \frac{\partial}{\partial T} \ln Z$$

(g) (5) Using the result of part (f), calculate the average translational kinetic energy.

$$\langle E_{trans} \rangle = kT^2 \frac{\partial}{\partial T} (N \ln Z_{trans}) \quad [ \text{since } \frac{\partial}{\partial T} (\ln N!) = 0 ]$$

$$= kT^2 N \frac{\partial}{\partial T} (\ln T^{3/2} + \text{function of } V + \text{constant})$$

$$= kT^2 N \cdot \frac{3}{2} \frac{1}{T}$$

$$= \left[ \frac{3}{2} NkT \right]$$

(h) (5) Using the result of part (f), calculate the average magnetic energy of these atoms for strong magnetic fields or low temperatures,  $\frac{\mu B}{kT} \gg 1$ .

$$\langle E_{mag} \rangle = kT^2 \frac{\partial}{\partial T} \ln Z_{mag}^N = kT^2 \cdot N \frac{\frac{\partial}{\partial T} (e^{\mu B/kT} + e^{-\mu B/kT})}{Z_{mag}}$$

$$= kT^2 \cdot N \frac{e^{\mu B/kT} \left(\frac{\mu B}{k}\right) \left(-\frac{1}{T^2}\right) + e^{-\mu B/kT} \left(-\frac{\mu B}{k}\right) \left(-\frac{1}{T^2}\right)}{e^{\mu B/kT} + e^{-\mu B/kT}}$$

$$= \left[ -N\mu B \tanh\left(\frac{\mu B}{kT}\right) \right] \rightarrow -N\mu B \text{ as } \frac{\mu B}{kT} \rightarrow \infty$$

[All dipole moments line up]

(i) (5) Using the result of part (f), calculate the average magnetic energy of these atoms for weak magnetic fields or high temperatures,  $\frac{\mu B}{kT} \ll 1$ .

$$\langle E_{mag} \rangle = -N\mu B \tanh\left(\frac{\mu B}{kT}\right)$$

$$\rightarrow -N\mu B \cdot \frac{\mu B}{kT}$$

$$\rightarrow 0 \text{ as } \frac{\mu B}{kT} \rightarrow 0$$

since  $\tanh x = \frac{e^x - e^{-x}}{e^x + e^{-x}} \approx \frac{(1+x) - (1-x)}{(1+x) + (1-x)} = x \text{ as } x \rightarrow 0$

[Spins - i.e. magnetic dipoles - do not line up.]

3. Consider a photon gas in 2 dimensions with only one polarization allowed. (One can imagine a cavity so thin that the system is effectively 2-dimensional.) The thermodynamic properties can be calculated just as in 3 dimensions, but first we need the appropriate 2-dimensional density of states.

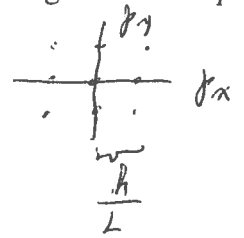
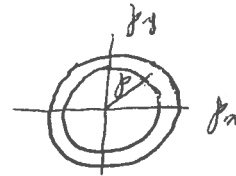
(a) (3) Using periodic boundary conditions, so that  $n_x \lambda_x = L$  where  $\lambda_x$  is the de Broglie wavelength of a particle and  $L$  is the periodicity length, obtain the allowed values of the momenta  $p_x$  in terms of  $n_x$ ,  $L$ , and Planck's constant  $h$ . Then calculate

$D(p)dp$  = number of allowed momenta in  $dp$  at  $p$

= number of allowed momenta in momentum space between ring with radius  $p$  and ring with radius  $p+dp$

$$n_x \lambda_x = L \Rightarrow \lambda_x = \frac{L}{n_x} \Rightarrow p_x = \frac{h}{\lambda_x} = n_x \frac{h}{L}$$

$$D(p)dp = \frac{2\pi p dp}{(h/L)^2} = \frac{2\pi L^2}{h^2} p dp$$



(b) (3) Next calculate the density of states for photons in 2 dimensions,  $D(\epsilon)$ .

$$\epsilon = cp \Rightarrow D(\epsilon)d\epsilon = D(p)dp = \frac{2\pi L^2}{h^2} \left(\frac{\epsilon}{c}\right) d\left(\frac{\epsilon}{c}\right)$$

& 1 polarization

$$\Rightarrow D(\epsilon) = \frac{2\pi L^2}{h^2 c^2} \epsilon$$

(c) (8) Calculate the average energy  $\langle E \rangle$  in terms of the various constants, and show that it is proportional to  $T^n$ , with  $n$  determined in the calculation. (See the integral table on the last page.)

$$\langle E \rangle = \int_0^\infty \epsilon \frac{1}{e^{\epsilon/kT} - 1} \frac{2\pi L^2}{h^2 c^2} \epsilon d\epsilon$$

$$= \frac{2\pi L^2}{h^2 c^2} (kT)^3 \int_0^\infty \frac{x^2}{e^x - 1} dx$$

$\int_0^\infty \frac{x^2}{e^x - 1} dx = 2\zeta(3)$  from last page [or 2.40]

$$= \frac{4\pi L^2}{h^2 c^2} \zeta(3) (kT)^3$$

4. (15) According to Stirling's approximation,  $\ln N! = N \ln N - N + \ln(\sqrt{2\pi N})$ , but you may ignore the last  $O(\ln N)$  term here as we normally do.

Using this approximation and a Taylor series to second order, show that

$$f(N_1) \equiv \frac{N!}{N_1! N_2!} \approx \text{constant} \times e^{-\left(N_1 - \frac{N}{2}\right)^2 / 2\sigma^2}, \quad N_2 = N - N_1$$

while at the same time determining  $\sigma$ .

This shows that deviations from the most probable state become extremely small for large  $N$ . (And it is interesting that the binomial distribution becomes a Gaussian.)

$$\frac{d}{dx} (x \ln x - x) = \ln x \quad \left[ \text{we used } \int \ln x \, dx = x \ln x - x \right]$$

$$\begin{aligned} \text{so } \frac{d \ln f}{d N_1} &= - \frac{d}{d N_1} (\ln N_1!) - \frac{d}{d N_1} (\ln N_2!) \\ &\approx - \frac{d}{d N_1} (N_1 \ln N_1 - N_1) - \frac{d}{d N_2} (N_2 \ln N_2 - N_2) \cdot \frac{d N_2}{d N_1} \\ &= - \ln N_1 + \ln N_2 \end{aligned}$$

$$\Rightarrow \left[ \frac{d \ln f}{d N_1} \right]_{N_1 = \frac{1}{2} N} = 0$$

$$\begin{aligned} \frac{d^2 \ln f}{d N_1^2} &= - \frac{1}{N_1} + \frac{1}{N_2} \frac{d N_2}{d N_1} \\ &= - \frac{2}{N_1} \end{aligned}$$

$$\Rightarrow \left[ \frac{d^2 \ln f}{d N_1^2} \right]_{N_1 = \frac{1}{2} N} = - \frac{2}{\frac{1}{2} N} = - \frac{4}{N}$$

$$\therefore \ln f \approx \ln f\left(\frac{1}{2} N\right) + 0 + \frac{1}{2} \left(-\frac{4}{N}\right) \left(N_1 - \frac{1}{2} N\right)^2$$

$$\Rightarrow \boxed{f} = e^{\ln f} = \boxed{\text{constant} \times e^{-\frac{2}{N} \left(N_1 - \frac{1}{2} N\right)^2}}$$

$$\text{so } \frac{1}{2\sigma^2} = \frac{2}{N} \quad \text{or} \quad \boxed{\sigma = \frac{\sqrt{N}}{2}}$$

5. The Carnot cycle is shown on the next page. **Be complete and clear in your arguments** while obtaining the answers to the following questions.

(a) (3) For any heat engine, use the first law of thermodynamics to obtain the efficiency  $e$  in terms of the heat  $Q_h$  received (ideally from a hot reservoir) and the heat  $Q_c$  expelled (ideally to a cold reservoir).

$$\boxed{e} \equiv \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$$

(b) (5) For a Carnot engine, obtain the relation between the heats  $Q_h$  and  $Q_c$  and the associated temperatures  $T_h$  and  $T_c$ .

$$\Delta S_{\text{cycle}} = 0 \Rightarrow \frac{Q_h}{T_h} - \frac{Q_c}{T_c} = 0 \Rightarrow \boxed{\frac{Q_c}{Q_h} = \frac{T_c}{T_h}}$$

(c) (3) Then obtain the efficiency of a Carnot engine in terms of  $T_h$  and  $T_c$ .

$$\boxed{e_{\text{Carnot}} = 1 - \frac{T_c}{T_h}}$$

(c) (3) What is the essential difference between the Otto or Diesel cycle and the Carnot cycle which makes the Carnot cycle the most efficient possible? Address the one specific step (process) where the cycles differ. (Here, and elsewhere, be clear: score  $\propto$  clarity and specificity.)

In the Carnot cycle, the working substance receives  $Q_h$  in an isothermal rather than constant volume or constant pressure process.

This means that the change in entropy is  $+\frac{Q_h}{T_h}$  for the substance and  $-\frac{Q_h}{T_h}$  for the reservoir, so the total entropy does not change during the entire cycle — the best that one can do.

$$\int_0^{\infty} \frac{x^2}{e^x - 1} dx = 2\zeta(3) \simeq 2.40$$

$$\int_0^{\infty} \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}$$

$$\int_0^{\infty} e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{a}} \text{ for } a > 0 \text{ (the Gaussian integral)}$$

$$\int_0^{\infty} x^2 e^{-ax^2} dx = \frac{1}{4} \sqrt{\frac{\pi}{a^3}} \text{ for } a > 0$$

$$\int_0^{\infty} x^{2n} e^{-ax^2} dx = \frac{2n-1}{2a} \int_0^{\infty} x^{2(n-1)} e^{-ax^2} dx$$

$$\int_0^{\infty} x^3 e^{-ax^2} dx = \frac{1}{2a^2} \text{ when } a > 0$$

