

PHY5524 Problem Set 3: Solution

Problem 1

This problem is based on the following expression for entropy (the Shannon entropy),

$$S = -k_B \sum_r p_r \ln p_r. \quad (1)$$

(a) To maximize S subject to the constraint that $\sum_r p_r = 1$ we introduce a Lagrange multiplier λ and extremize the quantity $S' = S - \lambda(\sum_r p_r - 1)$, i.e.

$$S' = -k_B \sum_r p_r \ln p_r - \lambda(\sum_r p_r - 1) \quad (2)$$

Thus we require

$$\frac{\partial S'}{\partial p_r} = -k_B(\ln p_r + 1) - \lambda = 0 \quad (3)$$

from which we find

$$p_r = e^{-\lambda/k_B - 1} = \text{Const.} \quad (4)$$

This results shows that, in this case, the value of p_r is independent of r . As usual, the value of the Lagrange multiplier λ (which determines the value of p_r) is found by requiring the constraint be satisfied (in this case $\sum_r p_r = 1$). Here this implies that

$$p_r = \frac{1}{\Omega} \quad (5)$$

where Ω is the total number of microstates.

(b) Now we add the constraint that $\langle E \rangle = \sum_r E_r p_r = E$. To do this we must introduce a second Lagrange multiplier, γ , and extremize the following quantity

$$S' = -k_B \sum_r p_r \ln p_r - \lambda(\sum_r p_r - 1) - \gamma(\sum_r E_r p_r - E) \quad (6)$$

Thus we require

$$\frac{\partial S'}{\partial p_r} = -k_B(\ln p_r + 1) - \lambda - \gamma E_r = 0 \quad (7)$$

from which we find

$$p_r = e^{-\lambda/k_B - \gamma E_r/k_B} = C e^{-\beta E_r} \quad (8)$$

where $\beta = \gamma/k_B$.

(c) Finally we add a third constraint, that $N = \sum_r N_r p_r$. To do this we add a third Lagrange multiplier ρ , and extremize

$$S' = -k_B \sum_r p_r \ln p_r - \lambda(\sum_r p_r - 1) - \gamma(\sum_r E_r p_r - E) - \rho(\sum_r N_r p_r - N) \quad (9)$$

Thus we require

$$\frac{\partial S'}{\partial p_r} = -k_B(\ln p_r + 1) - \lambda - \gamma E_r - \rho N_r = 0 \quad (10)$$

from which we find

$$p_r = e^{-\lambda/k_B - \gamma E_r/k_B - \rho N_r/k_B} = C e^{-\beta(E_r - \mu N_r)} \quad (11)$$

where $\beta = \gamma/k_B$ and $\mu = -\rho/T$.

Problem 2

The specific heat at constant pressure is defined to be $C_p = T(\partial S/\partial T)_P$. If we are given S as a function of V and T , we can obtain S as a function of P and T by solving the equation of state relating P , V and T to find $V = V(P, T)$. We then have

$$S(T, P) = S(T, V(P, T)) \quad (12)$$

from which, using the chain rule, we find

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \quad (13)$$

Thus we have

$$C_p = T \left(\frac{\partial S}{\partial T}\right)_P = T \left(\left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \right) \quad (14)$$

which yields the following expression for $C_p - C_v$

$$C_p - C_v = T \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \quad (15)$$

Next, using the general result (valid for any three variables related by a single equation — in this case the equation of state $P = P(V, T)$)

$$\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T = -1 \quad (16)$$

we have

$$\left(\frac{\partial V}{\partial T}\right)_P = -\frac{\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial P}{\partial V}\right)_T} \quad (17)$$

which, when combined with the above expression for $C_p - C_v$ yields

$$C_p - C_v = -T \left(\frac{\partial S}{\partial V}\right)_T \frac{\left(\frac{\partial P}{\partial T}\right)_V}{\left(\frac{\partial P}{\partial V}\right)_T} \quad (18)$$

Finally, using the Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \quad (19)$$

we find

$$C_p - C_v = -T \frac{\left[\left(\frac{\partial P}{\partial T}\right)_V\right]^2}{\left(\frac{\partial P}{\partial V}\right)_T} \quad (20)$$

This expression is useful for finding $C_p - C_v$ if we are given P as a function of V and T , and this is precisely what we find using the canonical ensemble:

$$P = -\left(\frac{\partial A(V, T)}{\partial V}\right)_T = +k_B T \left(\frac{\partial \ln Q(V, T)}{\partial V}\right)_T \quad (21)$$

Plugging this expression for P into the above expression for $C_p - C_v$ yields the desired result. To prove that $C_p - C_v \geq 0$ we need only show that

$$\left(\frac{\partial P}{\partial V}\right)_T \leq 0 \quad (22)$$

This follows from the fact that for a system with fixed T and V the Helmholtz free energy $A = E - TS$ is minimized. To see this imagine we have a gas divided into two equal volumes V . The total free energy of the gas would then be $2A(T, V)$.

Now, if one half of the gas were spontaneously to contract by an amount ΔV while the other half expanded by ΔV so that the total volume remained fixed then the free energy would be $A(T, V + \Delta V) + A(T, V - \Delta V)$. If the gas is in equilibrium (which we are assuming to be the case) it must be stable against the formation of such an inhomogeneous state. Thus it must be the case that

$$A(T, V + \Delta V) + A(T, V - \Delta V) \geq 2A(T, V) \quad (23)$$

which implies that

$$\left(\frac{\partial^2 A}{\partial V^2}\right)_T \geq 0 \quad (24)$$

and using the fact that $\left(\frac{\partial A}{\partial V}\right)_T = -P$ this implies that

$$\left(\frac{\partial P}{\partial V}\right)_T \leq 0 \quad (25)$$

Finally, for an ideal gas

$$Q_N(V, T) = \frac{1}{N!} V^N \left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} \quad (26)$$

and

$$P = -\left(\frac{\partial A}{\partial V}\right)_T \quad (27)$$

$$= k_B T \left(\frac{\partial \ln Q_N}{\partial V}\right)_T \quad (28)$$

$$= \frac{N k_B T}{V} \quad (29)$$

(i.e. just the ideal gas law). We then have

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{N k_B}{V} \quad (30)$$

and

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{N k_B T}{V^2} \quad (31)$$

Plugging this into our expression for $C_p - C_v$ we find

$$C_p - C_v = -T \frac{\left(\frac{N k_B}{V}\right)^2}{-\frac{N k_B T}{V^2}} = N k_B \quad (32)$$

which is, of course, the correct result.

Problem 3

The partition function for a classical massless relativistic particle with $E = pc$, where p is the momentum, confined to a volume V is

$$Q_1 = \int \frac{d^3 r d^3 p}{h^3} e^{-\beta pc} \quad (33)$$

$$= \frac{V}{h^3} 4\pi \int_0^\infty p^2 dp e^{-\beta pc} \quad (34)$$

$$= \frac{V}{h^3} 4\pi 2(\beta c)^{-3} \quad (35)$$

$$= 8\pi V \left(\frac{k_B T}{hc}\right)^3 \quad (36)$$

The partition function for N such (indistinguishable & noninteracting) particles is then

$$Q_N(V, T) = \frac{1}{N!} Q_1(V, T)^N = \frac{1}{N!} \left(8\pi V \left(\frac{k_B T}{hc} \right)^3 \right)^N \quad (37)$$

The Helmholtz Free energy is easily found to be

$$A = -k_B T \ln Q_N(V, T) \quad (38)$$

$$= N k_B T \ln \left(\frac{1}{8\pi} \frac{1}{V} \left(\frac{hc}{k_B T} \right)^3 \right) + k_B T \ln N! \quad (39)$$

Using Stirling's approximation $\ln N! \simeq N \ln N - N$ we then find

$$A = N k_B T \left(\ln \left(\frac{1}{8\pi} \frac{N}{V} \left(\frac{hc}{k_B T} \right)^3 \right) - 1 \right) \quad (40)$$

Given the Helmholtz free energy we can find the pressure

$$P = - \left(\frac{\partial A}{\partial V} \right)_{N, T} = \frac{N k_B T}{V} \quad (41)$$

and so we see this gas obeys the ideal gas law

$$PV = N k_B T \quad (42)$$

Likewise we can find the entropy

$$S = - \left(\frac{\partial A}{\partial T} \right)_{V, T} \quad (43)$$

$$= N k_B \left(\ln \left(8\pi \frac{V}{N} \left(\frac{k_B T}{hc} \right)^3 \right) + 4 \right) \quad (44)$$

and the internal energy

$$E = - \frac{\partial}{\partial \beta} \ln Q_N = 3 N k_B T \quad (45)$$

Note: we can also find E using the above expressions for A and S and the fact that $E = A + TS$,

$$E = A + TS = 3 N k_B T \quad (46)$$

Combining this with the ideal gas law we find that for this gas

$$E = 3PV \quad (47)$$

Finally the specific heat at constant volume is

$$C_v = T \left(\frac{\partial S}{\partial T} \right)_{N, V} = \left(\frac{\partial E}{\partial T} \right)_{N, V} = 3 N k_B \quad (48)$$

and the specific heat at constant pressure is

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_{N, P} = \left(\frac{\partial E + PV}{\partial T} \right)_{N, P} = 4 N k_B \quad (49)$$

Thus the ratio C_p to C_v is

$$\gamma = C_p / C_v = 4/3. \quad (50)$$