Solutions to Examples

1. The heat capacity at constant volume is given by

$$C_V = T \left(\frac{\partial S}{\partial T} \right)_V \tag{1}$$

We need to show that $\left(\frac{\partial C_V}{\partial V} \right)_T$ is zero. There are several ways, as usual – for instance:

$$
\begin{aligned}
\left(\frac{\partial C_V}{\partial V} \right)_T &= \left. \frac{\partial}{\partial V} \right)_T \left[T \left(\frac{\partial S}{\partial T} \right)_V \right] && \tag{2} \\
&= T \left. \frac{\partial}{\partial V} \right)_T \left(\frac{\partial S}{\partial T} \right)_V && \tag{3} \\
&= T \left. \frac{\partial}{\partial T} \right)_V \left(\frac{\partial S}{\partial V} \right)_T && \text{switch order} \tag{4} \\
&= T \left. \frac{\partial}{\partial T} \right)_V \left(\frac{\partial p}{\partial T} \right)_V && \text{Maxwell relation} \tag{5} \\
&= T \left(\frac{\partial^2 p}{\partial T^2} \right)_V && \text{we have } (p, V, T): \text{ stop!} \tag{6}
\end{aligned}
$$

The van der Waals equation of state:

$$p = \frac{Nk_BT}{V - Nb} - \frac{N^2 a}{V^2}. \tag{7}$$

Therefore

$$\left(\frac{\partial^2 p}{\partial T^2} \right)_V = 0, \quad \text{hence} \quad \left(\frac{\partial C_V}{\partial V} \right)_T = 0. \tag{8}$$

2. The important point is that a thermodynamic potential (G) is given in terms of its natural variables $(dG = -SdT + V\,dp + \mu dN,)$. This allows us to evaluate complete thermodynamical information about the system.
(a) Equation of state is the (p, V, T) relationship, so we need V:

$$V = \left(\frac{\partial G}{\partial p} \right)_{T,N} = \frac{Nk_BT}{p} - NA, \tag{9}$$

which is the required equation of state.
(b) The entropy is the thermodynamic force conjugate to T, so:

$$S = - \left(\frac{\partial G}{\partial T} \right)_{p,N} = -Nk_B \ln \left(\frac{p}{p_0} \right) + N \left(\frac{\partial A}{\partial T} \right)_{p,N} p. \tag{10}$$

(c) Enthalpy is $H(S, p, N)$, so it is obtained by the (T, S) Legendre transformation (watch the sign):

$$H = G + TS, \quad \text{i.e.} \quad H = Np \left[\left(\frac{\partial A}{\partial T} \right)_{p,N} T - A \right]. \tag{11}$$

(d) Similarly

$$U = H - pV, \quad \text{substituting } H, V : \quad U = NT \left[\left(\frac{\partial A}{\partial T} \right)_{p,N} p - k_B \right]. \tag{12}$$

(e)

$$F = U - TS \ \text{ or } \ F = G - pV : \quad F = Nk_BT \left[\ln \left(\frac{p}{p_0} \right) - 1 \right]. \tag{13}$$

Please note, that although we have obtained H, U and F, the expressions above are **not** expressed in their individual natural variables, i.e. they still have (T, p, N) in them. So these expressions are not yet ready to evaluate the subsequent thermodynamic derivative, if you needed ones.

(i) $F(T, V, N)$. These are the natural variables of F so all equilibrium thermodynamic information can be obtained.
(ii) Cannot obtain all equilibrium thermodynamic information from the equation of state and $U(T, p, N)$. Two variables need to be changed (T to S and p to V) and the equation of state would only allow one such change to be made.

3. The given equation for S can be inverted, giving

$$U(S, V, N) = N \left(\frac{N}{\alpha V} \right)^{2/3} e^{2S/3Nk_B}. \tag{14}$$

This gives U in its natural variables, so we can find the "derived quantities" p and T:

$$p = -\left(\frac{\partial U}{\partial V} \right)_{S,N} = \frac{2}{3} \frac{U}{V} \tag{15}$$

$$T = \left(\frac{\partial U}{\partial S} \right)_{V,N} = \frac{2}{3Nk_B} U \tag{16}$$

$$\Rightarrow U = \frac{3}{2} Nk_BT, \qquad pV = Nk_BT. \tag{17}$$

We have obtained the ideal gas law and the equipartition of energy.

4. There is more than one way to do this question, depending on whether you apply the chain rule before or after using the Maxwell relation. The way given here follows the suggested logic: always use the Maxwell relation when you see one!

Here the Maxwell relation for $(\partial T / \partial p)_S$ arises from the differential of the thermodynamic potential with $T \, dS + V \, dp$ (which happens to be the enthalpy H)

$$\frac{\partial^2 H}{\partial S \partial p} = \left(\frac{\partial T}{\partial p} \right)_S = \left(\frac{\partial V}{\partial S} \right)_p. \tag{18}$$

We did get some benefit: the constant-S constraint is now replaced by a more convenient constant-p. However, we need temperature, so the chain rule seems an appropriate thing to do:

$$\left(\frac{\partial V}{\partial S} \right)_p = \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial T}{\partial S} \right)_p. \tag{19}$$

In the first fraction we have (p, V, T), so don't do anything else with it. The second fraction allows you to bring in the heat capacity, if you recall the definition $C_p = T \left(\frac{\partial S}{\partial T} \right)_p$. So we obtain

$$\left(\frac{\partial T}{\partial p} \right)_S = \frac{T}{C_p} \left(\frac{\partial V}{\partial T} \right)_p. \tag{20}$$

Similarly, for the derivative $(\partial T / \partial V)_S$ we need the Maxwell relation that arises from the thermodynamic potential with $T\, dS - p\, dV$ (which happens to be U), giving

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial p}{\partial S} \right)_V \tag{21}$$

Again, we need T in the final answer, so use the chain rule, and then follow the same logic as before:

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial p}{\partial S} \right)_V = - \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial T}{\partial S} \right)_V = - \frac{T}{C_V} \left(\frac{\partial p}{\partial T} \right)_V. \tag{22}$$

For an ideal gas we know $pV = Nk_BT$, and for an adiabatic process $pV^\gamma = (Nk_BT)^\gamma p^{1-\gamma} = const$. Thus in the left hand side, at constant S we can use the adiabatic relation (the efficient way to make use of the unknown *const* is to evaluate its differential)

$$d\left(pV^\gamma\right) = d\left[(Nk_BT)^\gamma p^{1-\gamma}\right] = 0\,, \quad p \text{ and } T \text{ variables here} \tag{23}$$
$$\gamma T^{\gamma-1}p^{1-\gamma}\, dT + (1-\gamma)T^\gamma p^{-\gamma}\, dp = 0\,, \quad \text{so the ratio of increments gives} \tag{24}$$
$$\left(\frac{\partial T}{\partial p} \right)_S = -\frac{1-\gamma}{\gamma}\frac{T}{p} = \frac{2}{5}\frac{T}{p} \tag{25}$$

where we used $\gamma = 5/3$ for a monatomic ideal gas. This left hand side is to be compared with the right hand side of Eq.(20):

$$\frac{T}{C_p} \left(\frac{\partial V}{\partial T} \right)_p = \frac{T}{\frac{5}{2}Nk_B}\frac{Nk_B}{p} = \frac{2}{5}\frac{T}{p}. \tag{26}$$

The second relation can be demonstrated similarly. An alternative is to use the expression for the entropy of an ideal gas:

$$S = S_o - Nk_B \ln Nk_B + C_V \ln T + Nk_B \ln V \tag{27}$$
$$dS = 0 = \frac{C_V}{T}\, dT + \frac{Nk_B}{V}\, dV \quad \Rightarrow \tag{28}$$
$$\left(\frac{\partial T}{\partial V} \right)_S = -\frac{Nk_B}{C_V}\frac{T}{V} = -\frac{p}{C_V} = -\frac{1}{C_V}T \left(\frac{\partial p}{\partial T} \right)_V. \tag{29}$$

5. Thermodynamic equilibrium is the state in which the thermodynamic variables are independent of time. The governing principle of thermodynamic equilibrium is that the entropy of the universe tends to a maximum. This is the entropy statement of the second law of thermodynamics. Thus the equilibrium condition is that the *total* entropy is maximised.

The maximum entropy condition can be applied straightforwardly to closed systems (that is, to systems which do not exchange energy or particles with the outside world). To do this, we put

internal constraints in place and then maximise the entropy with respect to those constraints. To apply this in the most general way to a system consisting of fluid of total energy U, total volume V, and total particle number N, we place an imaginary wall into the system which partitions it into two volumes V_1 and V_2, with energies U_1 and U_2 and particle numbers N_1 and N_2. Because the system is closed, $V_1 + V_2 = V$, $U_1 + U_2 = U$ and $N_1 + N_2 = N$. We now maximise the total entropy $S = S_1 + S_2$, setting $dS = 0$:

$$dS = 0 = dS_1 + dS_2 \tag{30}$$

$$= \left(\frac{\partial S_1}{\partial U_1}\right)_{V_1,N_1} dU_1 + \left(\frac{\partial S_2}{\partial U_2}\right)_{V_2,N_2} dU_2 + \left(\frac{\partial S_1}{\partial V_1}\right)_{U_1,N_1} dV_1 + \left(\frac{\partial S_2}{\partial V_2}\right)_{U_2,N_2} dV_2 \tag{31}$$

$$+ \left(\frac{\partial S_1}{\partial N_1}\right)_{V_1,U_1} dN_1 + \left(\frac{\partial S_2}{\partial N_2}\right)_{V_2,U_2} dN_2 \tag{32}$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right) dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) dN_1, \tag{33}$$

where we have used $T\,dS = dU + p\,dV - \mu\,dN$. The three separate terms mean that in equilibrium, the temperatures of the two parts are equal, the pressures are equal, and the chemical potentials are equal. Moreover, in the approach to equilibrium, heat will flow from the hot to the cold part, the high pressure part will expand and the low pressure part will contract and, finally, particles will flow from high to low chemical potential.

In order to apply the principle of maximum entropy to *open* systems, we consider the open system plus the reservoir as a closed system. This immediately tells us that when the system is in complete equilibrium with the reservoir, its temperature equals the reservoir temperature, its pressure equals the reservoir pressure, and its chemical potential equals that of the reservoir.

It is generally not convenient to have to consider the entropy of the reservoir explicitly, in maximising S. It turns out however that there is a property of the *system* whose minimisation produces the same result as maximising the total entropy. If we use the same labels as before (where 1 is the system and 2 is the reservoir) then the maximum entropy condition is:

$$dS = 0 = dS_1 + dS_2 = dS_1 + \frac{1}{T_2}\left(dU_2 + p_2\,dV_2 - \mu_2\,dN_2\right) \tag{34}$$

$$= \frac{1}{T_2}\left(T_2 dS_1 - dU_1 - p_2\,dV_1 + \mu_2\,dN_1\right) \tag{35}$$

$$\equiv -\frac{dA_1}{T} \tag{36}$$

which defines a new property of the system, the *availability*, as $A_1 = U_1 - T_2 S_1 + p_2 V_1 - \mu_2 N_1$. In obtaining the second line above we used conservation of energy, and assumed that the total volume and particle number were conserved. Moreover, we used the fact that because the reservoir is much larger than the system, for any change of the system the reservoir temperature, pressure and chemical potential don't change. Note that the availability mixes system variables (subscript 1) with reservoir variables (subscript 2).

From this we see that the condition of maximum entropy of the universe reduces to minimising the availability of the system. When the system is in complete thermal equilibrium with the reservoir, the availability is zero. To show this, we use $U_1 = T_1 S_1 - p_1 V_1 + \mu_1 N_1$, so that $A = (T_1 - T_2)S_1 - (p_1 - p_2)V_1 + (\mu_1 - \mu_2)N_1$.

For particular constraints, minimising the availability is equivalent to minimising a particular

thermodynamic potential. For example, at constant T and V, we have

$$(dA_1)_{T,V} = d(U_1 - T_1 S_1) = dF_1 \tag{37}$$

where we used the fact that $dT_1 = dT = 0$ for constant temperature. The quantity F is called the Helmholtz free energy. Similarly, for constant T and p we can minimise the Gibbs free energy $G = U - TS - pV$, for constant S and p we can minimise the enthalpy $H = U - pV$, and for constant T and μ we can minimise the grand potential $\Phi = F - \mu N$.

The Gibbs free energy is useful in considering phase equilibrium and chemical equilibrium. In this case, we hold the system at fixed temperature and pressure, and consider particle equilibrium between the two phases, or between the molecular species taking part in the chemical reaction. To illustrate the application to phase equilibrium, we write the total Gibbs free energy as the sum over the Gibbs free energies of (say) the liquid phase and the vapour phase: $G = G_l + G_v$. At fixed temperature and pressure $dG_l = \mu_l \, dN_l$, and $dG_v = \mu_v \, dN_v$, and using $dN_v = -dN_l$ we conclude that the equilibrium condition is $\mu_l = \mu_v$. The change in the Gibbs free energy along phase equilibrium lines can also be used to derive the *Clausius-Clapeyron* equation: $dp/dT = L_m/T\Delta V_m$, where L_m is the latent heat per mole, and ΔV_m is the change in the molar volume at the transition. We also used G to derive the equal area rule, which allows us to determine the vapour pressure along a van der Waals isotherm.

Could have used mixtures and chemical equilibria as other examples and could have contrasted thermal equilibrium with the equilibrium of dynamical systems, drawing a parallel between minimising thermodynamic potentials and minimising the potential energy, etc.

6. The Helmholtz free energy F is a minimum for a system at constant T, V, N. We imagine that the entire system of the bubble plus the surrounding liquid is in a container of fixed volume held at constant temperature. In this case we have to minimise the total Helmholtz free energy, which is the sum of terms from the liquid, air, and surface (perhaps better to say the interface region between the liquid and air),

$$dF = dF_l + dF_a + dF_s = 0. \tag{38}$$

For the two bulk systems (air and liquid): $dF = -SdT - pdV + \mu dN$, but for the interface the corresponding work function involves the surface tension term $\Gamma \, dA$ term. Using $dT = 0$, $dV_l = -dV_a$, and all components species keep their particle numbers, $dN_i = 0$, we have

$$dF_l = p_l \, dV_a \tag{39}$$
$$dF_a = -p_a \, dV_a \tag{40}$$
$$dF_s = \Gamma \, dA. \tag{41}$$

The surface area and volume of the bubble are $A = 4\pi r^2$ and $V_a = 4\pi r^3/3$, so that Eq. (38) gives

$$p_a = p_l + \frac{2\Gamma}{r}. \tag{42}$$

The pressure inside is higher than the pressure outside. The local pressure in the air inside the bubble is proportional to the local radius of curvature. If the bubble isn't spherical, there is a pressure gradient in the air inside the bubble, and this gradient will cause a flow of air inside the bubble which acts to restore the bubble to a spherical shape.

7. No one finds this question easy when they first encounter it. The correct numerical answer can be achieved using incorrect arguments, while a correct argument needs careful and consistent

thought to get the signs correct. Here are two contrasting approaches that give the correct result. The first is an example of pure thermodynamic reasoning. It gives the answer with little effort but provides no explanation of "why" it is necessary to do work to separate the gases. The second calculates the work explicitly so the "why" is clear; however, it takes a little more effort and more care is needed with signs. In both we start the argument by noting that the work done must be greater than that from a reversible change. So, we calculate the work done reversibly and get the minimum work done, as required by the question.

The sketch show the initial and final states as well as an intermediate state discussed later. The shaded area is the gas mixture (Nitrogen at $P_{N_2} = 4p_o/5$ and Oxygen at $p_{O_2} = p_o/5$). The small clear area represents oxygen after separation. Volumes and pressures at each stage are indicated on the sketch.
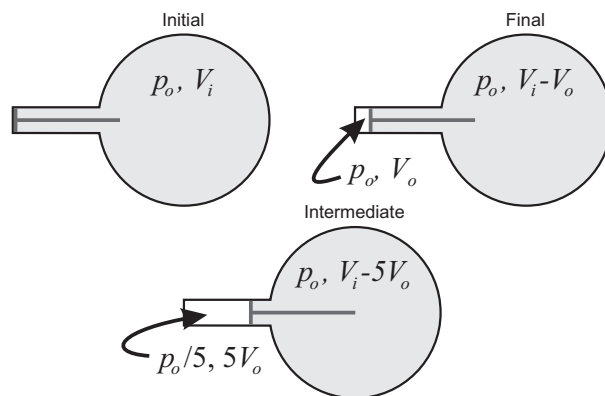
Starting with the pure thermodynamic argument, we note that the reverse process (from final to initial) mixes the gases and is a Joule expansion in which $dW = dQ = 0$ so that the internal energy of the initial and the final states are equal, $dU = 0$. Now consider the forward process (initial to final) done in some reversible way (i.e. such that $dQ = TdS$) and we can write

$$dU = 0 = T\Delta S + \Delta W, \tag{43}$$

where $\Delta S = S_{Final} - S_{Initial}$ is the change in entropy. Hence, the reversible work-done is $\Delta W = -T\Delta S$. Note that the entropy of the final state is less than that of the initial state so $\Delta S < 0$ and the work-done is positive. The simplest way to calculate the entropy change is to note that any change in the entropy of the mixed region can be ignored (it's volume and pressure change negligibly). Thus, ΔS is that for 1 mole of oxygen with initial pressure $p_i = p_o/5$ and final pressure $p_f = p_o$. The Sackur-Tetrode equation then gives $\Delta S = R\ln(1/p_f) - R\ln(1/p_i) = -R\ln 5$, which results in $\Delta W = +13.4T$ J.

Next we invent a process to separate the oxygen reversibly. It takes two steps and the first step uses piston through which oxygen, but not nitrogen, can pass freely. Moving the piston to the intermediate state separates 1 mole of oxygen at a pressure of $p_o/5$. We must do work on the system in this step since there is a net pressure of $p_{N_2} = 4p_o/5$ opposing the motion of the piston. The external work-done in this first step is $\Delta W_1 = +p_{N_2}5V_o = +4p_oV_o$, where V_o will be the volume occupied by 1 mole, in the final state, at p_o and T. Since $p_oV_o = RT$, we have $\Delta W_1 = 4RT$.

Now we make the piston impermeable and compress the oxygen to one atmosphere. All of this

work is done by the system so can be recovered. Compressing the oxygen requires

$$W_{O_2} = -\int_{5V_o}^{V_o} p \, dV = -RT \int_{5V_o}^{V_o} \frac{RT}{V} \, dV = +RT \ln 5. \tag{44}$$

At the same time the mixture volume increases by $4V_o$ and the work done on it is $W_{mixture} = -p_o 4V_o = -4RT$. In the second step the total work done on the whole system is, therefore, $W_2 = W_{O_2} + W_{mixture} = RT \ln 5 - 4RT$.

Combining W_1 and W_2 gives the total work-done on the system $\Delta W = W_1 + W_2 = RT \ln 5 = +13.4T$ J, as before.

8. First we find the entropy as a function of temperature by integrating $C = T(dS/dT)$, which gives

$$S_s = V\frac{\alpha T^3}{3} + \text{constant} \tag{45}$$

$$S_n = V\frac{\beta T^3}{3} + V\gamma T + \text{constant}. \tag{46}$$

The Third Law (at $T = 0$) tells us that the constants of integration are zero. The Latent heat at the transition is then given by

$$L = T_c \left[S_n(T_c) - S_s(T_c) \right] = 0. \tag{47}$$

Using the expressions for the entropies we have

$$T_c \left[V\frac{\alpha T_c^3}{3} - V\frac{\beta T_c^3}{3} - V\gamma T_c \right] = 0, \tag{48}$$

which gives the solution

$$T_c = \sqrt{\frac{3\gamma}{\alpha - \beta}}. \tag{49}$$

9. We are given the partition function $Z = \exp\left[aT^3 V\right]$. From that we should find the Helmholtz free energy, since Z is given as a function of T, V:

$$
\begin{aligned}
F &= -k_B T \ln Z = -ak_B T^4 V \\
p &= -\left(\frac{\partial F}{\partial V}\right)_{T,N} = ak_B T^4 \\
S &= -\left(\frac{\partial F}{\partial T}\right)_{V,N} = 4ak_B T^3 V \\
U &= F + TS = 3ak_B T^4 V \\
C_v &= \left(\frac{\partial U}{\partial T}\right)_{V,N} = 12ak_B T^3 V \\
\mu &= \left(\frac{\partial F}{\partial N}\right)_{T,V} = 0 \\
p &= \frac{1}{3}\frac{U}{V}.
\end{aligned}
$$

The system, obviously, corresponds to the black-body radiation.

10. We have N atoms, N lattice sites, and N interstitial sites. Of the N lattice sites, $N - n$ are occupied by atoms, and n are empty. The corresponding number of configurations is $\Omega_l = N!/(N-n)!\,n!$. Of the N interstitial sites, n are occupied by atoms, and $N - n$ are empty, and the number of their possible configurations is $\Omega_v = N!/n!\,(N-n)!$. The configurations of the lattice and the vacancies are independent (once the number of vacancies is fixed), so the total number of configurations is just their product, and the resulting entropy is

$$S_{\mathrm{config}} = k_B \ln \Omega_l \Omega_v = k_B \ln \left(\frac{N!}{(N-n)!\,n!} \right)^2 = 2k_B \ln \frac{N!}{(N-n)!\,n!}. \tag{50}$$

(this explains the factor of 2 you might be wondering about). Moving an atom from a *particular* lattice site to a *particular* vacancy involves no change in the configurational part of the entropy, hence ε_c is the change in the non-configurational part of the free energy. Note that this is where the requirement of a small number of atoms on vacancy sites comes in: all vacancies can only have the same ε_c if the number of vacancies is so small that there is vanishing probability of finding two vacancies close enough together to interact. The free energy when there are n atoms on vacancy sites is

$$F(n) = F(n = 0) + n\varepsilon_c - T S_{\mathrm{config}} = F_0 + n\varepsilon_c - 2k_B T \ln \frac{N!}{(N-n)!\,n!}. \tag{51}$$

The terms in the free energy F that depend on n are, after the Stirling approximation,

$$\Delta F(n) = n\varepsilon_c + 2k_B T \left((N-n)\ln(N-n) + n \ln n \right). \tag{52}$$

At temperature T the free energy is minimised to determine the value of its variable (n in this case) at which it takes the equilibrium thermodynamic value. Setting $\partial F/\partial n = 0$ gives

$$\varepsilon_c = 2T k_B \left\{ \ln(N-n) - \ln n \right\} \quad \text{i.e.,} \quad \frac{n}{N} = \frac{1}{1 + e^{\varepsilon_c/2k_B T}}. \tag{53}$$

11. The partition function is given by the geometric series, since each microstate (with n links open) has only one conformation. You should know, or remember how to derive the sum:

$$Z = \sum_{n=0}^{N} \left(e^{-\beta \varepsilon} \right)^n = \frac{1 - e^{-(N+1)\beta \varepsilon}}{1 - e^{-\beta \varepsilon}}.$$

(b) If $\varepsilon \gg k_B T$ (which is the low-temperature limit) then $e^{-\beta \varepsilon} \ll 1$, and $e^{-(N+1)\beta \varepsilon} \ll e^{-\beta \varepsilon}$, so $Z \simeq 1 + e^{-\beta \varepsilon}$ (it is often useful to take the limit early, at the stage of partition function, rather than derive the full result and then simplify it). The average number of broken links can be evaluated directly from the statistical probability:

$$\langle n \rangle = \frac{1}{Z} \sum_{n=0}^{N} n \left(e^{-\beta \varepsilon} \right)^n \simeq e^{-\beta \varepsilon}. \tag{54}$$

The same result will follow if you realise that the mean energy $U = \langle n \rangle \varepsilon$ and find U from Z in the usual way.

12. (a) The classical partition function of a one-dimensional simple harmonic oscillator:

$$\begin{aligned}
Z_{cl} &= \int_{-\infty}^{\infty} e^{-p^2/2mk_B T} \frac{dp}{2\pi\hbar} \int_{-\infty}^{\infty} e^{-kx^2/2k_B T} \, dx \\
&= \frac{1}{2\pi\hbar} \sqrt{2\pi k_B T m} \sqrt{2\pi k_B T/k} \; = \; \frac{k_B T}{\hbar} \sqrt{\frac{m}{k}}.
\end{aligned}$$

Note that the ratio $k/m = \omega_0^2$, the natural frequency of the oscillator, so in fact $Z = k_B T/\hbar\omega_0$, which is the high-temperature limit of Z of the general quantum oscillator. Obviously, the low-temperature limit of the classical partition function is wrong, the full quantum-oscillator Z will have the limit $Z \to e^{-\frac{1}{2}\beta\hbar\omega}$.

This looks very easy, but one should think about the limits of integrals... We chose $\pm\infty$ for the $\int dx$, but is it correct? If this system did not have any potential energy, only kinetic, then this would be an example of 1-dimensional ideal gas – and there we certainly *do not* take infinite limits of x-integration (instead we take the interval of the length L for the resulting $Z = L/\lambda$). We are allowed to replace the "proper" limits ($\pm L/2$, say) with infinities only if the exponential integrand decays to zero before the end of the interval is reached, that is, when $kL^2 \gg k_B T$. When this relation is reversed (at a very high T) the limits of $\int dx$ should be taken finite, and then the ultimate high-T limit of ideal gas will be reached. Note that the momentum integral $\int dp$ does not have this problem, at least not immediately, because the momentum *can* go up to infinity (in the relativistic limit of a massive particle $p = mv/\sqrt{1 - v^2/c^2}$).

(b) The classical partition function of a particle moving in three dimensions in a uniform gravitational field:

$$
\begin{aligned}
Z_{cl} &= \int_0^\infty e^{-p^2/2mk_B T}\,\frac{4\pi p^2 dp}{(2\pi\hbar)^3} \int_0^\infty e^{-\beta mgz}\,dz\,dx dy \\
&= \frac{A\sqrt{m}}{(2\pi\hbar)^3 g}\,(2\pi)^{3/2}\,(k_B T)^{5/2}\ ,
\end{aligned}
$$

where A is the area perpendicular to z. As in the part (a), there is something to think about when deciding on the limits of $\int dz$ integral. Again, taking the upper limit to infinity is an approximation (when the exponential integrand decays to zero, at $mgL \gg k_B T$) while at a very high temperature (when this inequality is reversed) the integrand is ≈ 1 over the whole z-interval and the integral is equal to L, again recovering ideal gas with little "sedimentation". As for the lower limit taken as zero, this is arbitrary of course – but you should remember that the true gravitational potential is *not mgz* – it is the Newtonian $Gm_1 m_2/z$ and it only *looks* like mgz in a narrow interval. So it is important to have a lower limit finite, and zero (the height at the "floor level") is just a simplest value to take.

13. (a) For a single particle, the partition function is

$$
Z_1 = \int e^{-cp/k_B T}\frac{d^3 p\,d^3 x}{(2\pi\hbar)^3} = \frac{V(k_B T)^3}{\pi^2\hbar^3 c^3}
$$

To calculate this you need to convert $d^3 p$ into sphericals ($4\pi p^2 dp$) since now the factorisation of exponentials will not work (with $c|p|$ in the exponent).

For N identical non-interacting particles depends on T, V, N:

$$Z = \frac{1}{N!}Z_1^N = \frac{1}{N!}\left(\frac{V(k_BT)^3}{\pi^2\hbar^3c^3}\right)^N$$

$$\ln Z = N\left[\ln\left(\frac{V(k_BT)^3}{\pi^2\hbar^3c^3}\right) - \ln N + 1\right]$$

$$\text{soevaluate } F = -k_BT\ln Z = -Nk_BT\left[\ln\left(\frac{V(k_BT)^3}{\pi^2\hbar^3c^3N}\right) + 1\right]$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{Nk_BT}{V} \quad \text{still ideal gas!}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = Nk_B\left[4 + \ln\left(\frac{V(k_BT)^3}{\pi^2\hbar^3c^3N}\right)\right]$$

$$U = -\frac{\partial}{\partial\beta}\ln Z = 3Nk_BT$$

$$C = \left(\frac{\partial U}{\partial T}\right)_V = 3Nk_B.$$

It seems the equipartition does not work (i.e. it appears we have 6 degrees of freedom)? But of course equipartition only gives $k_BT/2$ when the energy depends on this degree of freedom quadratically, which is only the low-speed limit (the full $E = \sqrt{p^2c^2 + m^2c^4}$). In fact, the generalised equipartition theorem can be used to obtain exactly our result in relativistic case.

(b) The partition function for a two-level system with energy levels $+\Delta$ and $-\Delta$, with no extra degeneracy, is

$$Z_\Delta = e^{\beta\Delta} + e^{-\beta\Delta} = 2\cosh\frac{\Delta}{k_BT}.$$

The total partition function of the system is then

$$Z = \frac{1}{N!}\left(\frac{V(k_BT)^3}{\pi^2\hbar^3c^3}\right)^N\left(e^{\beta\Delta} + e^{-\beta\Delta}\right)^N.$$

The thermodynamic functions depend on $\ln Z$, and therefore to find their values for the ideal gas including the internal states of the particles (Z_Δ in this case) we just have to add N times the contribution from a single particle. These contributions are

$$Z_\Delta = e^{\beta\Delta} + e^{-\beta\Delta}$$

$$F_\Delta = -k_BT\ln Z_\Delta = -k_BT\ln\left(e^{\beta\Delta} + e^{-\beta\Delta}\right)$$

$$p_\Delta = -\left(\frac{\partial F_\Delta}{\partial V}\right)_T = 0, \quad \text{equation of state remains unchanged}$$

$$S_\Delta = -\left(\frac{\partial F_\Delta}{\partial T}\right)_V = k_B\ln\left(1 + e^{-2\beta\Delta}\right) + \frac{1}{T}\frac{2\Delta}{e^{2\beta\Delta} + 1}$$

$$U_\Delta = -\frac{\partial}{\partial\beta}\ln Z_\Delta = -\Delta\tanh(\beta\Delta)$$

$$C_\Delta = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\Delta^2}{k_BT^2\cosh^2(\beta\Delta)}.$$

14. Let us do this question in two ways. (a) Canonical ensemble. We have two sub-systems in contact: the 3D ideal gas of helium atoms in the vapour, and the 2-dimensional gas of adsorbed

particles. The equilibrium between these two sub-systems is when $\mu_{3D} = \mu_{2D}$ (of course, along with p and T equality as well). The chemical potential of an ordinary 3D ideal gas is derived in the lectures:

$$\mu_{3D} = k_B T \ln\left(\frac{N\lambda^3}{V}\right), \tag{55}$$

where the de Broglie wavelength $\lambda = \sqrt{2\pi\hbar^2/mk_B T}$.

The gas on the surface, with n_{ads} particles, has two things to consider. First of all, it has lower dimensionality, giving the basic contribution to the single-particle partition function A/λ^2. There is also the adsorption potential, i.e. the constant potential energy gain $-\Delta$ for each particle, resulting in the extra factor in the partition function:

$$Z_1(2D) = \frac{A}{\lambda^2}\, e^{\beta\Delta}.$$

Following the steps of derivation, the chemical potential of the 2D gas will be equal to

$$\mu_{2D} = k_B T \ln\left(\frac{n_{ads}\lambda^2}{A}\, e^{-\beta\Delta}\right).$$

Equating the two chemical potentials we obtain

$$\frac{n_{ads}}{A} = \frac{N}{V}\lambda e^{\beta\Delta} = \frac{p}{k_B T}\sqrt{\frac{2\pi\hbar^2}{mk_B T}}\, e^{\beta\Delta}.$$

(b) Grand canonical ensemble. The 3D gas of helium atoms in the vapour acts as a particle reservoir, setting the chemical potential for the helium atoms on the surface.

We need to calculate the grand potential of the 2D ideal gas on the surface, and find its chemical potential in that way. We can treat the helium atoms on the surface as a classical gas and, in the corresponding limit $\beta(\varepsilon_k - \mu) \gg 1$, retain only the first terms in the grand partition function of a microstate

$$\Xi_k = 1 + e^{-\beta(\varepsilon_k - \mu)} + ...$$

The grand potential for a microstate with the energy $\varepsilon_k = p^2/2m - \Delta$ is, therefore,

$$\Phi(\varepsilon_k) = -k_B T \ln \Xi_k \approx -k_B T e^{-\beta\mu} e^{\beta\Delta} e^{-p^2/2mk_B T}, \tag{56}$$

To obtain the full grand potential for the gas we need to integrate $\Phi(\varepsilon_k)$ over the corresponding phase space, which gives for the 2D gas (note, this is done in lectures for the 3D case):

$$\Phi = \int \Phi(\varepsilon_k)\frac{d^2x\, d^2p}{(2\pi\hbar)^2} = -k_B T \frac{A}{2\pi\hbar^2} e^{\beta\mu} e^{\beta\Delta} \int_0^\infty e^{-p^2/2mk_B T}\, p\, dp = -k_B^2 T^2 m \frac{A}{2\pi\hbar^2} e^{\beta\mu} e^{\beta\Delta}. \tag{57}$$

From this we get an expression for the density of adsorbed atoms,

$$n_{ads} = \frac{N_{ads}}{A} = -\frac{1}{A}\left(\frac{\partial\Phi}{\partial\mu}\right)_{T,V} = \frac{mk_B T}{2\pi\hbar^2} e^{\beta\mu} e^{\beta\Delta}. \tag{58}$$

We now substitute the chemical potential, which is equal to that of the 3D gas, Eq.(55), and this gives the desired result once again:

$$n_{ads} = \frac{p}{k_B T}\left(\frac{2\pi\hbar^2}{mk_B T}\right)^{1/2} e^{\Delta/k_B T}. \tag{59}$$

15. A table of states, occupancies, and energies may be constructed as follows.

i	N_i	E_i
1	0	0
2	1 ⇑	ϵ
3	1 ⇓	ϵ
4	2	$2\epsilon + U$

The grand partition function is

$$\Xi = \sum_i e^{-\beta(E_i - N_i \mu)} = 1 + 2e^{-\beta(\epsilon - \mu)} + e^{-\beta(2\epsilon + U - 2\mu)} ,$$

and the grand potential is $\Phi = -k_B T \ln \Xi$. The average electron occupancy of the defect is

$$N = -\frac{\partial \Phi}{\partial \mu} = k_B T \frac{1}{\Xi} \frac{\partial \Xi}{\partial \mu} .$$

$$\frac{\partial \Xi}{\partial \mu} = 2\beta e^{-\beta(\epsilon - \mu)} + 2\beta e^{-\beta(2\epsilon + U - 2\mu)} ,$$

and therefore

$$N = \frac{2e^{-\beta(\epsilon - \mu)} + 2e^{-\beta(2\epsilon + U - 2\mu)}}{1 + 2e^{-\beta(\epsilon - \mu)} + e^{-\beta(2\epsilon + U - 2\mu)}} .$$

Alternatively we can write the average directly from the discrete probability

$$N = \frac{\sum_i N_i e^{-\beta(E_i - N_i \mu)}}{\sum_i e^{-\beta(E_i - N_i \mu)}} = \frac{2e^{-\beta(\epsilon - \mu)} + 2e^{-\beta(2\epsilon + U - 2\mu)}}{1 + 2e^{-\beta(\epsilon - \mu)} + e^{-\beta(2\epsilon + U - 2\mu)}} .$$

Note that if we set $U = 0$, we obtain the familiar Fermi-Dirac distribution:

$$N = \frac{2}{e^{-\beta(\epsilon - \mu)} + 1} .$$

The sketch of N vs. $\mu - \epsilon$ should show two steps, one when the chemical potential exceeds ϵ, where the occupancy rises from 0 to 1, then a second one when the chemical potential exceeds $\epsilon + U$, where the occupancy rises to 2 (Fig.). This can be obtained by considering the limits of N for $U\beta \to \infty$ for various choices of $\mu - \epsilon$ such as $\mu - \epsilon < 0$, $\mu - \epsilon = 0$, $\mu - \epsilon > U$, and so on. Note that the wide plateau for which $N = 1$ would correspond physically to a magnetic moment bound to the defect.

16. For He $\rightleftharpoons$ He$^+$ + e$^-$ the equilibrium constant is $K_N = N_{\text{He}}/(N_{\text{He}^+} N_{\text{e}^-}) = Z_1^{\text{He}}/(Z_1^{\text{He}^+} Z_1^{\text{e}^-})$, where we have used results from the handout. Remembering that the He$^+$ and e$^-$ each have two spin states, the single-particle partition functions are

$$Z_1^{\text{He}} = (V/\lambda_{\text{He}}^3(T))\, e^{\beta e \phi}$$
$$Z_1^{\text{He}^+} = 2(V/\lambda_{\text{He}^+}^3(T))$$
$$Z_1^{\text{e}^-} = 2(V/\lambda_{\text{e}^-}^3(T))$$
$$\Rightarrow \quad \frac{N_{\text{He}}}{N_{\text{He}^+} N_{\text{e}^-}} = \frac{\lambda_{\text{He}^+}^3 \lambda_{\text{e}^-}^3}{\lambda_{\text{He}}^3} \frac{1}{4V} e^{e\phi/k_B T} .$$
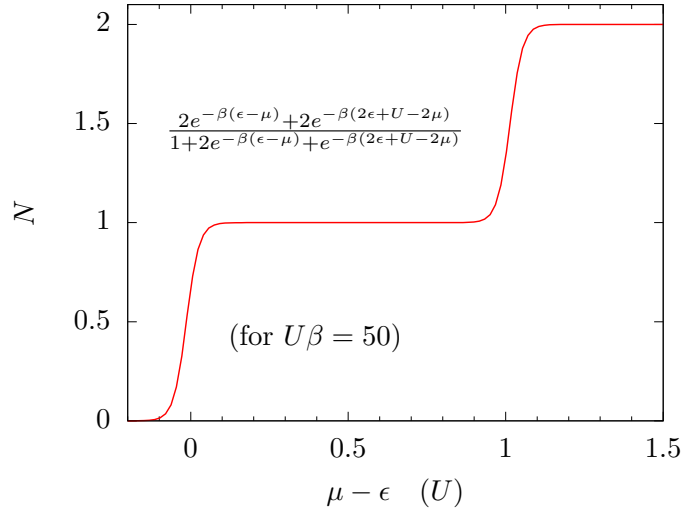
Figure 1: Use computers to help with tricky questions! Here, gnuplot: 'plot [-0.2:1.5] 2*(exp(beta*x)+exp(-beta*(-2*x+U)))/(1+2*exp(beta*x)+exp(-beta*(-2*x+U)))'

Ignoring the mass difference between He and He^+, so that $\lambda_{He^+} = \lambda_{He}$, we get

$$K_N = \frac{1}{4V} \left(\frac{2\pi\hbar^2}{m_e k_B T} \right)^{3/2} e^{e\phi/k_B T}. \tag{60}$$

Now $N_{He^+} = N_{e^-}$, so

$$N_{e^-}^2 = N_{He} 4V \left(\frac{m_e k_B T}{2\pi\hbar^2} \right)^{3/2} e^{-e\phi/k_B T}$$

$$n_{e^-}^2 = n_{He} 4(n_{He} + 2n_{e^-}) \frac{k_B T}{p} \left(\frac{m_e k_B T}{2\pi\hbar^2} \right)^{3/2} e^{-e\phi/k_B T}.$$

To get the last equation we have first used the ideal gas law in the form $V = (N_{He} + 2N_{e^-}) k_B T/p$, and then divided through by V^2. Next, dividing through by n_{He}^2 gives a quadratic equation for the ratio of the electron and Helium densities. Solving and substituting the numbers gives ratios of 7.4×10^{-5} at 1 atmosphere, and 0.33 at 10^{-2} Pa.

The ratio is pressure dependent because the probability of dissociation only depends on the temperature, while the probability of recombination also depends on the probability of two dissociation products running into each other, so it depends on p. At low pressure recombination becomes much less likely.

17. The question aims to focus candidates on the difference in general approach to quantum and classical systems. In the classical case a single-particle partition function Z_1 is obtained first. Then the N-particle partition function follows depending on whether the particles are distinguishable or indistinguishable. In the quantum case the system is considered as a whole (all the particles and all the states). For the Fermi case this system can only exist with a total energy ϵ, in the Bose case it can have all possible three values of energy:
(a) $Z = e^{-\beta\epsilon}$.
(b) $Z = 1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon}$.
(One might complain that in order for particles to be Fermi or Bose, they need to have spin – and in that case our counting of states would be different.)

(c) $Z = Z_1^2/2! = \left(1 + e^{-\beta\epsilon}\right)^2/2$.

(d) $Z = Z_1^2 = \left(1 + e^{-\beta\epsilon}\right)^2$.

The partition functions for quantum cases (a) and (b) do not tend to the classical value at high temperatures because the level occupation probabilities never become small here to implement the proper classical limit (since there are only two energy levels). In this sense the system does not show classical behaviour at high temperatures. Note also that the Classical result can give a partition function less than one (which is a sure sign the classical approximation fails)

18. (a) The thermal wavelengths are, as usual

$$\lambda = \sqrt{\frac{2\pi\hbar^2}{mk_BT}}.$$

Therefore, substituting the values of all parameters,

$$\begin{aligned}
\lambda_e &= 1.86 \times 10^{-11} \text{ m} \\
\lambda_p &= 4.35 \times 10^{-13} \text{ m} \\
\lambda_\alpha &= \frac{1}{2}\lambda_p = 2.17 \times 10^{-13} \text{ m}.
\end{aligned}$$

(b) The number densities are $n = (N/V) = \rho/m$:

$$\begin{aligned}
n_p &= \frac{6 \times 10^4}{1.7 \times 10^{-27}} = 3.59 \times 10^{31} \text{ m}^{-3} \\
n_\alpha &= \frac{1 \times 10^5}{4 \times 1.7 \times 10^{-27}} = 1.50 \times 10^{31} \text{ m}^{-3} \\
n_e &= n_p + 2n_\alpha = 6.58 \times 10^{31} \text{ m}^{-3}.
\end{aligned}$$

The criterion for degeneracy, or for entering the quantum regime, is $(N/V)\lambda^3 > 1$, and

$$\begin{aligned}
n_p\lambda_p^3 &= 2.9 \times 10^{-6} \\
n_\alpha\lambda_\alpha^3 &= 1.5 \times 10^{-7} \\
n_e\lambda_e^3 &= 0.42,
\end{aligned}$$

so the protons and alpha particles are non-degenerate, i.e. fully in classical regime, while the electrons are weakly degenerate and so has to be considered as quantum particles (Fermions). I hope my use of calculator was OK here...

(c) Since the protons and alpha particles are classical and the electrons are only weakly quantum, it is reasonable to calculate their contribution to the pressure using the ideal gas law:

$$\begin{aligned}
p &= (n_p + n_\alpha + n_e)k_BT \\
&= 11.7 \times 10^{31} \times 1.38 \times 10^{-23} \times 1.6 \times 10^7 = 2.6 \times 10^{16} \text{ Nm}^{-2}.
\end{aligned}$$

The alternative (if you are reasonably unhappy interpreting nearly-overlapping electrons as ideal gas) is to treat is as Fermi gas and blatantly try the estimate of Fermi pressure (which we only know at $T \to 0$), $p_F = (\hbar^2/2m_e) * n_e^{5/3}$. The true answer will be somewhere in between, but clearly the ideal gas of protons and alpha particles will dominate.

The energy density of black body radiation is given by

$$u = \frac{\pi^2 k_B^4}{15\hbar^3 c^3} T^4, \quad \text{so radiation pressure } p = \frac{u}{3} = 1.6 \times 10^{13} \text{ Nm}^{-2}.$$

The particle pressure at the centre of the sun is much larger than the radiation pressure, and therefore the particle pressure prevents gravitational collapse.

19. For a degenerate Fermi gas the heat capacity for N particles in volume V is

$$C = \frac{\pi^2}{3} D(\varepsilon_F) k_B^2 T = \frac{\pi^2 N k_B^2}{2\,\varepsilon_F} T, \tag{61}$$

where $\varepsilon_F = \hbar^2 (3\pi^2 N/V)^{2/3}/2m^*$ is the Fermi energy, and m^* is the effective mass of the fermion "quasiparticles". If the density of the mixture is 140 kg m^{-3}, then the average atomic mass of the mixture is 0.05 times the ^{3}He mass plus 0.95 times the ^{4}He mass $= 6.61 \times 10^{-27}$ kg per atom. The total number density is then $n_{\text{Tot}} = 2.12 \times 10^{28}$ atoms m^{-3}, and the number density of ^{3}He atoms is $n_{3\text{He}} = 0.05 n_{\text{Tot}} = 1.06 \times 10^{27}$ atoms per m^{-3}.

Considering the ^{3}He atoms as a Fermi gas we obtain

$$\varepsilon_F = 4.60 \times 10^{-24} \text{ J }, \; T_F = \frac{\varepsilon_F}{k_B} = 0.33 \text{ K}. \tag{62}$$

The heat capacity is written as $C = \gamma T$, and from equations (61) and (62) we have

$$\frac{\gamma}{N} = 2.0 \times 10^{-22} \text{ J atom}^{-1} \text{K}^{-2}. \tag{63}$$

20. We can treat the elementary excitations as a Bose gas in which N in not conserved (i.e., like black-body radiation, $\mu = 0$), and which has a dispersion relation $\varepsilon_k = \hbar\omega = \Delta + \alpha k^2$, where Δ is the energy gap at the origin. The average energy is given by

$$U = V \int_0^\infty \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \frac{4\pi k^2 dk}{(2\pi)^3} = \frac{V}{2\pi^2} \int_0^\infty \frac{(\Delta + \alpha k^2)}{e^{\beta(\Delta + \alpha k^2)} - 1} k^2 dk. \tag{64}$$

In the low temperature limit $(k_B T \ll \Delta)$ we can approximate the integral as

$$
\begin{aligned}
U &\simeq \frac{V}{2\pi^2} \int_0^\infty e^{-\beta(\Delta + \alpha k^2)} (\Delta + \alpha k^2) k^2\, dk = \frac{V}{2\pi^2} e^{-\beta\Delta} \left\{ \Delta \int_0^\infty e^{-\beta\alpha k^2} k^2\, dk + \alpha \int_0^\infty e^{-\beta\alpha k^2} k^4\, dk \right\} \\
&= \frac{V}{2\pi^2} e^{-\beta\Delta} \left\{ \frac{\Delta}{(\beta\alpha)^{3/2}} \int_0^\infty e^{-y^2} y^2\, dy + \frac{\alpha}{(\beta\alpha)^{5/2}} \int_0^\infty e^{-y^2} y^4\, dy \right\} \\
&= \frac{V}{8} \left(\frac{k_B T}{\alpha\pi} \right)^{3/2} e^{-\beta\Delta} \left\{ \Delta + \frac{3 k_B T}{2} \right\}
\end{aligned}
$$

The important temperature dependence is contained in the $e^{-\beta\Delta}$ term, and this would certainly dominate experimental results for the heat capacity. This term is typical of a system with a gap between the ground state and first excited states (and you have seen it in the simple 2-level system already).

At temperatures where $k_B T \gg \Delta$, but still small compared with (say) the Curie temperature, the denominator in the integrand can be approximated as

$$\frac{1}{e^{\beta(\Delta + \alpha k^2)} - 1} \simeq \frac{1}{e^{\beta\alpha k^2}(1 + \beta\Delta) - 1} = \frac{1}{(e^{\beta\alpha k^2} - 1)\left(1 + \frac{\beta\Delta e^{\beta\alpha k^2}}{e^{\beta\alpha k^2} - 1}\right)} \simeq \frac{1}{e^{\beta\alpha k^2} - 1}\left(1 - \frac{e^{\beta\alpha k^2} \beta\Delta}{e^{\beta\alpha k^1} - 1}\right).$$

U can be rewritten as

$$U \simeq \frac{V}{2\pi^2} \int_0^\infty \frac{(\Delta + \alpha k^2)k^2}{e^{\beta \alpha k^2} - 1}\left(1 - \frac{e^{\beta \alpha k^2}\beta \Delta}{e^{\beta \alpha k^2} - 1}\right) dk.$$

$$= \frac{V}{2\pi^2}\int_0^\infty \frac{\alpha k^2 k^2}{e^{\beta \alpha k^2} - 1} dk + \frac{V}{2\pi^2}\int_0^\infty \frac{\Delta k^2}{e^{\beta \alpha k^2} - 1} dk + 0(\beta \Delta)$$

$$= \frac{\alpha V}{4\pi^2}\left(\frac{k_B T}{\alpha}\right)^{5/2}\int_0^\infty \frac{x^{3/2}}{e^x - 1} dx + \frac{V\Delta}{2\pi^2}\left(\frac{k_B T}{\alpha}\right)^{3/2}\int_0^\infty \frac{x^{1/2}}{e^x - 1} dx + 0(\beta \Delta).$$

The first term varies with temperature as $T^{5/2}$; it is the standard ferromagnetic spin wave energy that we would have if there were no gap. The second term, which varies as $T^{3/2}$, comes from the offset of each spin-wave energy by Δ (for example the $k = 0$ spin-wave has no energy if $\Delta = 0$, so it wouldn't contribute to the thermal energy, but when $\Delta > 0$ it does contribute). When $k_B T/\alpha$ is large compared to Δ, the $T^{5/2}$ term dominates. The next largest term has an integrand which vanishes as $\beta \Delta$ everywhere except near $k \to 0$, where it is finite, but this is a small region of phase space so I'm ignoring it.

To make the sketch, take the derivative of U with respect to T. At low temperature the specific heat rises exponentially (signalling that there is a gap in the energy spectrum), then when $k_B T/\alpha \sim \Delta$ it crosses over to $T^{3/2}$ behaviour characteristic of a quadratic dispersion relation.

21. The question deals with Black-body radiation and, more generally, the relationship between the spectrum of excitations and the dimensionality of the system. The "long air-filled coaxial cable" acts as an EM cavity, at temperature T, with a spectrum of black-body radiation.

At $\nu = 10^9$Hz, the wavelength, λ, is ≈ 0.3m, which is greater than the diameter of the cable. Thus the system is essentially one-dimensional. In 1-D, with 2 polarisations, the density of states is

$$g(\omega)d\omega = \frac{2L}{\pi c}d\omega \tag{65}$$

and the internal energy, U is

$$U = \int \frac{\hbar \omega}{e^{\hbar \omega/k_B T} - 1}\frac{2L}{\pi c}d\omega. \tag{66}$$

We can approximate the Bose factor, $1/(e^{\hbar \omega/k_B T} - 1) \approx k_B T/\hbar \omega$, since we are in the high-temperature limit at this frequency and $\hbar \omega/k_B T \ll 1$. Thus, the energy in the frequency range $d\omega$ is $2k_B T d\omega/\pi c$.

At a frequency of $\nu = 10^{12}$Hz, the wavelength $\lambda = 0.3$mm, which is significantly smaller than the 4mm radial gap in the cable. It follows that the cable can support radial modes at this frequency alongside the longitudinal ones. Thus the system is approximately three-dimensional. The density of states is

$$g(\omega)d\omega = \frac{V\omega^2}{\pi^2 c^3}d\omega \tag{67}$$

and, as we are still in the high-temperature limit, the Bose factor is still $k_B T/\hbar \omega$. The energy in the frequency range $d\omega$ is, therefore, $k_B T V \omega^2 d\omega/\pi^2 c^3$.

22. The chemical potential μ appears as the conjugate variable of N in the thermodynamic potentials U, F, H, G, Φ, etc. From the thermodynamic potentials (e.g., from $dU = T\,dS -$

$p\,dV + \mu\,dN$) we find a number of expressions for μ, such as $\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$, but these are difficult to interpret intuitively except in special cases. For example, in general we don't know how to change the energy at constant entropy, but for the special case of the Fermi gas, the Gibbs entropy expression for the entropy per energy level,

$$S_k = -k_B\left(n_k \ln n_k + (1 - n_k)\ln(1 - n_k)\right) \tag{68}$$

shows us that $\left(\frac{\partial S}{\partial N}\right)$ is zero at $n_k = 1 - n_k$, i.e., at $n_k = 1/2$, so if we add a particle at the energy level where $n_k = 1/2$, then we are adding energy at constant entropy, and so this energy level must be located at the chemical potential. But this is only possible below the degeneracy temperature, since at high temperatures the chemical potential of a Fermi gas is negative (i.e., there are no states for which $n_k = 1/2$ for a Fermi gas at high temperature). In the limit as $T \to 0$, $n_k = 1/2$ is located at the Fermi energy, so the Fermi energy and the chemical potential coincide at low temperature.

A more intuitive way of writing μ is as follows. The changes leading to equilibrium must be allowed by the Second Law of thermodynamics. Using $dU = T\,dS - p\,dV + \mu\,dN$ we get $\mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V}$, that is, the chemical potential is related to the change in entropy of a system when a particle is added at constant energy and volume. To illustrate the appeal of this expression, say we have two systems 1 and 2 in contact so that they can exchange particles, energy and volume.

$$
\begin{aligned}
dS = dS_1 + dS_2 \quad &= \quad \left(\frac{\partial S_1}{\partial U_1}\right)_{N_1,V_1} dU_1 + \left(\frac{\partial S_1}{\partial V_1}\right)_{N_1,U_1} dV_1 + \left(\frac{\partial S_1}{\partial N_1}\right)_{U_1,V_1} dN_1 + \\
&\qquad \left(\frac{\partial S_2}{\partial U_2}\right)_{N_2,V_2} dU_2 + \left(\frac{\partial S_2}{\partial V_2}\right)_{N_2,U_2} dV_2 + \left(\frac{\partial S_2}{\partial N_2}\right)_{U_2,V_2} dN_2 \\
&= \quad \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right) dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) dN_1.
\end{aligned}
$$

We have used $dN_1 = -dN_2$, $dV_1 = -dV_2$ and $dU_1 = -dU_2$. The Law of Increase of entropy says that dS must be positive, so the first term tells us that energy flows from hot to cold, and the second term tells us that (for systems at equal temperature) the volume of the high pressure system will increase at the expense of the low pressure system. The last term is the one of interest here. To get it we used the expression for μ in terms of change of entropy with particle number. It tells us that particles flow from high to low chemical potential (for systems at equal temperature), i.e., dN_1 is negative is $\mu_1 > \mu_2$. The chemical potential controls particle flow just as the temperature controls energy flow.

Another useful way of writing the chemical potential for a pure phase is as the Gibbs free energy per particle, $\mu = G/N$. This is useful for describing phase equilibrium, because it can be shown (using the availability or otherwise) that the equilibrium of a system at constant temperature and pressure is determined by minimising the Gibbs free energy, and thus (again) that equilibrium involves equality of the chemical potentials of the phases involved. Among other things, we used this equality of chemical potentials at phase equilibrium to derive the Clausius-Clapeyron equation, from the fact that $d\mu = v\,dp - s\,dT$ for each phase as we move along the phase boundary, where v is the volume per molecule, and s is the entropy per molecule, in a given phase. Equating the changes in $d\mu$ produces the equation $dT/dp = \Delta v/\Delta s$, where Δv and Δs are the changes in the specific volume and entropy at the phase boundary. The chemical potential plays a similar role in the equilibrium properties of mixtures, where for example the change in chemical potential due to the addition of a solute to a solvent on one side of a semi-permeable membrane produces an osmotic pressure. Moreover, it is also central to chemical

equilibrium, where the condition $\sum_i \nu_i \mu_i = 0$ can be derived from the minimum Gibbs free energy condition. The ν_i are the number of molecules of species i involved in a unit reaction.

The chemical potential is important in statistical mechanics whenever particles can move between subsystems. In an ideal gas the single-particle energy levels can be treated as separate thermodynamic systems, which are in mutual equilibrium and have a common chemical potential. The statistical distribution of the energy eigenstates is then described by the Gibbs distribution: the probability of finding n particles in state i is

$$P(n_i) = \frac{\left(e^{-(\varepsilon_i - \mu)/k_B T}\right)^n}{\Xi}, \tag{69}$$

where $\Xi = \sum_n \left(e^{-(\varepsilon_i - \mu)/k_B T}\right)^n$ is the partition function for the state. The chemical potential therefore plays a central role in the occupation number distribution function. It can be set in two ways, either by equilibrium of the gas with a reservoir of particles which sets the chemical potential (this is the case for example in question 2, where the chemical potential of the two-dimensional gas adsorbed on the surface is set by the chemical potential of the three-dimensional gas, and it is also the case for a photon gas, where the absorption and emission of photons by the cavity walls sets the chemical potential to zero) or it may be set by the requirement that the total number of particles in the gas is N (for closed systems). The latter situation is encountered in standard treatments of Fermi and Bose gases, and of classical gases.

It should be noted that as well as containing terms that are related to the entropy, the chemical potential also contains terms that look like genuine potential energies, and in general particle equilibrium involves both kinds of terms. So for a classical ideal gas the chemical potential is

$$\mu = k_B T \left(\ln \left(\frac{N \lambda^3}{\sigma V} \right) - \ln Z_{\text{int}} \right) + \phi. \tag{70}$$

The first two terms, which come from the translational degrees of freedom of a classical gas and the internal degrees of freedom of the molecules, respectively, have to do with entropy, whereas the latter term is a potential energy per molecule, ϕ, which could for example be an electric potential if the molecules are charged, or a gravitational potential. General equilibrium involves particles flowing from high to low chemical potential. If the potential term is due to gravity, then this term tends to 'want' all the molecules to collect at the bottom of the system. However the entropic terms 'want' the molecules to spread out as much as possible. The final equilibrium represents a compromise between these two tendencies.
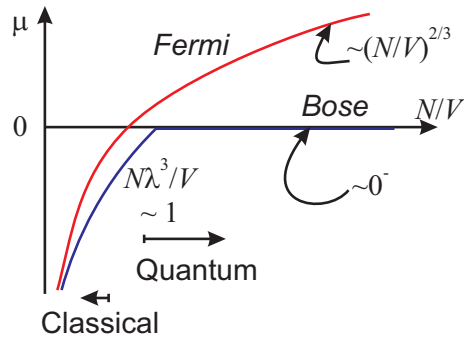
The sketch of μ plotted against N/V has the classical regime at small $(N\lambda^3/V) \ll 1$ where $\mu = k_B T \ln\left(N\lambda^3/\sigma V\right)$, hence for low values of N/V, μ is negative and diverges as $(N/V) \to 0$. When $N\lambda^3/V \sim 1$, quantum effects become important. There is, of course, a difficult crossover

region – and then in the deep quantum regime at $N\lambda^3/V \gg 1$ we have: the Bose-Einstein condensation in Bose-particles case, which results in $\mu \simeq 0^-$; it stays there as the density increases further. In the Fermi case we get a degenerate Fermi gas, for which $\mu \approx \varepsilon_F$, the Fermi energy, which is positive and grows with density as $(N/V)^{2/3}$ in 3D.

23. The partition function is given in T, V, N variables:

$$Z = \frac{A^N}{N!} T^{3N/2} V^N \exp\left[-\frac{B(T)N^2}{V}\right]$$

$$
\begin{aligned}
F &= -k_B T \ln Z \\
&= -Nk_B T \ln A + Nk_B T(\ln N - 1) - \frac{3}{2}Nk_B T \ln T - Nk_B T \ln V + \frac{k_B T N^2 B}{V} \\
p &= -\left(\frac{\partial F}{\partial V}\right)_{T,N} = \frac{Nk_B T}{V} + \frac{N^2}{V^2}k_B T B \quad \text{so it is the virial expansion!} \\
S &= -\left(\frac{\partial F}{\partial T}\right)_{V,N} = Nk_B \ln A - Nk_B(\ln N - 1) + \frac{3}{2}Nk_B + \frac{3}{2}Nk_B \ln T + Nk_B \ln V \\
&\qquad\qquad -\frac{k_B N^2 B}{V} - \frac{\partial B}{\partial T}\frac{k_B T N^2}{V} \\
\mu &= \left(\frac{\partial F}{\partial N}\right)_{T,V} = k_B T \ln \frac{N}{AVT^{3/2}} + 2\frac{N}{V}k_B T B \\
U &= F + TS = \frac{3}{2}Nk_B T - \frac{\partial B}{\partial T}\frac{k_B T^2 N^2}{V} \quad \text{expressed in variables } (T, V, N) \\
C_v &= \left(\frac{\partial U}{\partial T}\right)_{V,N} = \frac{3}{2}Nk_B - \frac{\partial^2 B}{\partial T^2}\frac{k_B T^2 N^2}{V} - \frac{\partial B}{\partial T}\frac{2k_B T N^2}{V}.
\end{aligned}
$$

The system is an imperfect monatomic gas with a pair inter-molecular interaction described by $B(T)$, which corresponds to the second virial coefficient.

24. The virial expansion is:

$$
\begin{aligned}
g(r) &= g_0(r) + g_1(r)\,n + g_2(r)\,n^2 + \cdots \\
\frac{p}{k_B T} &= n + B_2(T)\,n^2 + B_3(T)\,n^3 + \cdots. \\
B_2(T) &= \int_0^\infty 2\pi r^2 \left(1 - e^{-\phi/k_B T}\right) dr.
\end{aligned}
$$

(a)

$$g_0(r) = e^{-\beta\phi(r)}.$$

(b)

$$
\begin{aligned}
B_2(T) &= \int_0^a 2\pi r^2 dr + \int_a^{2a} 2\pi r^2 \left(1 - e^{\beta\epsilon}\right) dr \\
&= \frac{2\pi}{3}a^3 + \frac{2\pi}{3}(8a^3 - a^3)\left(1 - e^{\beta\epsilon}\right) \\
&= \frac{16\pi}{3}a^3 - \frac{14\pi}{3}a^3 e^{\beta\epsilon}.
\end{aligned}
$$

T_B is where $B_2(T) = 0$, i.e.

$$T_B = \frac{\epsilon}{k_B \ln(8/7)}.$$

(c) We have

$$\frac{B_2}{a^3} = \frac{16\pi}{3} - \frac{14\pi}{3} e^{\beta\epsilon}.$$

Therefore

$$\frac{B_2(T^*)}{v_0^*} = 4 - \frac{7}{2} e^{1/T^*},$$

where $v_0^* = 4/3\,\pi a^3$ and $T^* = k_B T/\epsilon$.

25. (a) The free energy expansion suggests the 1st order transition since the cubic term is present: $F(Q,T) = a(T - T_c)Q^2 - bQ^3 + cQ^4$. The first step is to identify free energy minima:

$$\begin{aligned} \frac{\partial F}{\partial Q} &= 2a(T - T_c)Q - 3bQ^2 + 4cQ^3 \\ &= \left[2a(T - T_c) - 3bQ + 4cQ^2\right]Q = 0 \end{aligned}$$

The disordered phase corresponds to $Q = 0$, $F = 0$. The condition that the free energies of the ordered and disordered phases are equal at the transition point $T = T^*$ leads to

$$a(T^* - T_c) - bQ^* + cQ^{*2} = 0.$$

The condition that the free energy is stationary (i.e. has a minimum at Q^*) leads to

$$2a(T^* - T_c) - 3bQ^* + 4cQ^{*2} = 0.$$

Solving these equations for Q^* and T^* leads to

$$\begin{aligned} Q^* &= \frac{b}{2c} \quad \text{(the jump of order parameter)} \\ T^* &= T_c + \frac{b^2}{4ac} \quad \text{(point of equilibrium transition)} \end{aligned}$$

(b) The entropy is

$$S = -\left(\frac{\partial F}{\partial T}\right)_Q = -aQ^2.$$

You might be concerned that $Q = Q(T)$ itself, so why is there only the partial derivative here? The full expression is, of course, $S = (\partial F/\partial T)_{V,N} = (\partial F/\partial T)_Q + (\partial F/\partial Q)(\partial Q/\partial T)$. But the derivative $(\partial F/\partial Q) = 0$ in equilibrium, so the second (unpleasant) term drops out always.

For the disordered phase $S = 0$, while for the ordered phase $S = -ab^2/4c^2$, and therefore the latent heat of this phase transition is

$$L = T^*\Delta S = -\left(T_c + \frac{b^2}{4ac}\right)\frac{ab^2}{4c^2}.$$

The entropy of the ordered state is negative, but this should not worry us as there will be other contributions to the entropy which will ensure that the total entropy is positive. The fact that the jump in entropy is negative on entering the more ordered phase is, on the other hand, a natural expectation: the extra heat is released from the system (in contrast to requiring the heat, and thus cooling the vicinity environment, on entering the high-temperature disordered phase).

26. It looks like the free energy expansion in powers of P is in even powers only, i.e. there is no cubic term and thus one expects the second-order transition. However, this depends on the sign of the coefficient b. If $b > 0$ then, in fact, we don't need the 6th-order term at all because at small $P \ll 1$ (which is the basis for the Landau series expansion) $bP^4 > cP^6$ and they both have the similar qualitative effect of increasing F at higher P.

When b is negative, the situation may change depending on the relative magnitude of parameters. The plot (made at $b = -3$, $c = 3$, $a = 1$) illustrates the point: the solution is symmetric for $\pm P$ (as expected for even-power series), but has all the features of the ordinary 1st order transition.
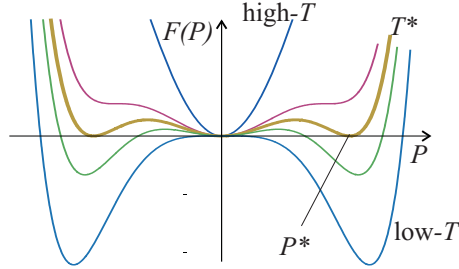
The analysis follows the standard steps: first identify free energy minima:

$$\frac{\partial F}{\partial P} = 2a(T - T_c)P - 4bP^3 + 6cP^5$$
$$= \left[2a(T - T_c) - 4bP^2 + 6cP^4\right] P = 0$$

(taking b to be explicitly negative). The disordered phase corresponds to $P = 0$, $F = 0$, as always. Solving the bi-quadratic equation gives

$$P^2 = \frac{b \pm \sqrt{b^2 - 3ac(T - T_c)}}{3c}$$

so the beginning of hysteresis region is when $b^2 - 3ac(T - T_c) = 0$ or at $T_B = T_c + b^2/3ac$.

At the thermodynamic equilibrium transition point $T = T^*$ the free energies of the ordered and disordered phases are equal, so

$$a(T^* - T_c) - bP^{*2} + cP^{*4} = 0.$$

Solving this, together with the $\partial F/\partial P = 0$ equation, for Q^* and T^* leads to

$$P^* = \pm\sqrt{\frac{b}{2c}} \quad \text{(the jump of order parameter)}$$
$$T^* = T_c + \frac{b^2}{4ac} \quad \text{(equilibrium transition point)}$$

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The entropy is, as in the previous question, $S = -aP^2$. For the disordered phase $S = 0$, while for the ordered phase $S = -ab/2c$ and therefore the latent heat of this transition is

$$L = T^*\Delta S = -\left(T_c + \frac{b^2}{4ac}\right)\frac{ab}{2c}.$$

27. We want to calculate

$$\langle \Delta N^2 \rangle = \langle N^2 \rangle - \langle N \rangle^2.$$

Using the grand partition function we have

$$\langle N \rangle = \frac{\sum_i N_i\, e^{-(E_i - \mu N_i)/k_B T}}{\sum_i e^{-(E_i - \mu N_i)/k_B T}} = \frac{k_B T}{\Xi}\left(\frac{\partial \Xi}{\partial \mu}\right)_{T,V},$$

$$\langle N^2 \rangle = \frac{\sum_i N_i^2 e^{-(E_i - \mu N_i)/k_B T}}{\sum_i e^{-(E_i - \mu N_i)/k_B T}} = \frac{(k_B T)^2}{\Xi}\left(\frac{\partial^2 \Xi}{\partial \mu^2}\right)_{T,V}.$$

(Note that I am now using the single index i to denote the microstates.) From the expression for $\langle N \rangle$ we have

$$\left(\frac{\partial \langle N \rangle}{\partial \mu}\right)_{T,V} = -\frac{k_B T}{\Xi^2}\left(\frac{\partial \Xi}{\partial \mu}\right)_{T,V}^2 + \frac{k_B T}{\Xi}\left(\frac{\partial^2 \Xi}{\partial \mu^2}\right)_{T,V} \tag{71}$$

$$= -\frac{\langle N \rangle^2}{k_B T} + \frac{\langle N^2 \rangle}{k_B T} \tag{72}$$

$$= \frac{\langle \Delta N^2 \rangle}{k_B T}, \tag{73}$$

so that

$$\langle \Delta N^2 \rangle = k_B T \left(\frac{\partial N}{\partial \mu}\right)_{T,V}.$$

Of course, this expression is an example of fluctuation-dissipation relation that one can derive directly from the general probability of fluctuation, see handout Eq.(10.21).

28. This is only one of several possible ways to derive the result... The statistical weight is

$$\Omega(U) \propto \exp(NU/\epsilon_0)^{1/2}, \quad \text{so that} \quad S = k_B \ln \Omega,$$

and we effectively have $U = U(S, N)$, i.e. in correct variables. In this case we can evaluate the usual thermodynamic derivative

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{\partial}{\partial U} k_B \ln \Omega = \frac{k_B}{2}\left(\frac{N}{\epsilon_0}\right)^{1/2} U^{-1/2},$$

and therefore

$$T = \frac{2}{k_B}\left(\frac{\epsilon_0 U}{N}\right)^{1/2},$$

where U in this expression is the average internal energy, which we will denote by $\langle U \rangle$. The specific heat capacity C (per particle) is given by

$$C = \frac{\partial}{\partial T}\frac{\langle U \rangle}{N} = \frac{\partial}{\partial T}\frac{T^2 k_B^2}{4\epsilon_0} = \frac{k_B^2 T}{2\epsilon_0}$$

$$= 2.8 \times 10^{-25}\ \text{JK}^{-1}.$$

The probability distribution of the internal energy is given by the Boltzmann distribution,

$$P(U) = \frac{\Omega(U)\,e^{-U/k_B T}}{Z}.$$

It is often easier to work with $\ln P$,

$$\ln P(U) = -\frac{U}{k_B T} + \ln \Omega(U) + \text{constant}.$$

The maximum in $\ln P(U)$ occurs at the same value of U as the maximum in $P(U)$. Expand $\ln P(U)$ about its maximum value which occurs at $\langle U \rangle$, defining $\Delta U = U - \langle U \rangle$:

$$\ln P(U) = \ln P|_{\langle U \rangle} + \frac{\Delta U^2}{2} \left.\frac{\partial^2}{\partial U^2} \ln P\right|_{\langle U \rangle} + \dots,$$

because the term linear in ΔU must vanish. Hence at constant T,

$$\left.\frac{\partial \ln P}{\partial U}\right|_{\langle U \rangle} = -\frac{1}{k_B T} + \left.\frac{\partial \ln \Omega}{\partial U}\right|_{\langle U \rangle} = 0.$$

Therefore

$$\left.\frac{\partial \ln \Omega}{\partial U}\right|_{\langle U \rangle} = \frac{1}{k_B T}$$

(in a sense, we have just re-defined the entropy). Note that $\Omega(U)$ is not a function of T, but $\langle U \rangle$ is. Solving for $\langle U \rangle$ we obtain

$$\langle U \rangle = \frac{k_B^2 T^2 N}{4\epsilon_0}.$$

The width of the distribution, $\langle \Delta U^2 \rangle$, can be obtained from

$$\left.\frac{\partial^2 \ln P}{\partial U^2}\right|_{\langle U \rangle} = \left.\frac{\partial^2 \ln \Omega}{\partial U^2}\right|_{\langle U \rangle} = \left.\frac{\partial^2}{\partial U^2} \left(\frac{NU}{\epsilon_0}\right)^{1/2}\right|_{\langle U \rangle}$$

$$= -\frac{1}{4}\left(\frac{N}{\epsilon_0}\right)^{1/2} \langle U \rangle^{-3/2},$$

and

$$\langle \Delta U^2 \rangle = -\frac{1}{\left.\frac{\partial^2 \ln P}{\partial U^2}\right|_{\langle U \rangle}} = \frac{k_B^3 T^3 N}{2\epsilon_0}.$$

Therefore

$$\frac{\langle \Delta U^2 \rangle}{\langle U \rangle^2} = \frac{8\epsilon_0}{k_B T N} = 4.5 \times 10^{-11} \quad \text{at } T = 290 \text{ K}.$$

The probability distribution of the energy of the system is therefore approximately a Gaussian of width $\langle \Delta U^2 \rangle$ and mean $\langle U \rangle$. This long-winded derivation is given to illustrate several points made in the lectures (see the end of handout section 11.2). If you want a simple shortcut, then see how Eq.(11.11) is derived in the handout.

29. This is a simplest form of Landau model of 2nd order transition. Evaluating the derivative of free free energy, we find the solution for the equilibrium magnetisation $M^*(T)$

$$\frac{\partial F}{\partial M} = 2M\left[a(T - T_c) + 2bM^2\right] = 0 \quad \text{gives} \quad M^* = \pm\sqrt{\frac{a(T_c - t)}{2b}}$$

The non-zero solution only exists below the critical point $T = T_c$.

Now, speaking about fluctuations, we have the generic expression valid on both sides of the transition,

$$\langle(\Delta M)^2\rangle = \frac{k_B T}{\left|\frac{\partial^2 F}{\partial M^2}\right|}\Bigg|_{M=M_{\text{eq.}}}$$

This gives different results above and below the phase transition:

$$T > T_c : \quad \langle(\Delta M)^2\rangle = \frac{k_B T}{2a(T - T_c)}$$

$$T < T_c : \quad \langle(\Delta M)^2\rangle = \frac{k_B T}{2a(T - T_c) + 12bM^{*2}} = \frac{k_B T}{4a(T_c - T)}$$

This is an important result showing that the m.s. amplitude of the order parameter fluctuations (magnetisation in this case) diverges on approaching the critical point. However, there is a constant factor between the two expressions, making the fluctuations in the disordered phase always bigger than in the ordered phase. If you plot both curves against T, the result will look like the Greek letter λ, hence the name for this effect: "lambda-point".

30. The first part of the question is straight bookwork, with details in the Handout Chapter 11, up to eq.(11.8)-(11.9). This requires knowledge of the Stokes' drag coefficient for a sphere, $\gamma = 6\pi\eta R$.

The second part of the question is calculation. In microscopic observations you only see a **plane** projection of a general 3D motion, so $\langle x^2 \rangle = 4Dt$ should be used. With the given $\langle x^2 \rangle = 3.3 \times 10^{-12}\text{m}^2$ and $t = 10\text{s}$, I obtain $D = 0.83 \times 10^{-13}\text{m}^2/\text{s}$, which then leads to the estimate of k_B which is smaller than the actual k_B, which is probably because the effective hydrodynamic radius R of the small Brownian particle is bigger than its physical size.

31. The classical fluctuation dissipation theorem gives $\langle|q(\omega)|^2\rangle = \frac{2k_B T}{\omega}\alpha''(\omega)$, with the response function $\alpha(\omega) = (1/C - i\omega R)^{-1}$. Taking the imaginary part of α, $\alpha'' = \frac{\omega C\tau}{1+\omega^2\tau^2}$ with $\tau = RC$, then gives the quoted result for the charge spectrum.

From this, we obtain $v(\omega)$ by dividing by α:

$$\langle|v(\omega)|^2\rangle = \langle|q(\omega)|^2\rangle/|\alpha(\omega)|^2 = 2k_B T\frac{\tau C}{1+\omega^2\tau^2}\frac{1+\omega^2\tau^2}{C^2} = 2k_B TR$$

Johnson noise in a frequency interval df is $4k_B TRdf$, which is consistent with our result, because the voltage noise we have found above has equal strength at $+\omega$ and $-\omega$, and both add to give the observed voltage noise in an interval $df = d\omega/(2\pi)$.

$v_C(\omega) = q(\omega)/C$, and so $\langle|v_C(\omega)|^2\rangle = 2k_B TR\frac{1}{1+\omega^2\tau^2}$. The integral $\int_{-\infty}^{\infty}\frac{1}{1+\omega^2\tau^2}\frac{d\omega}{2\pi} = 1/(2\tau)$, giving $\frac{1}{2}C\langle v_C^2\rangle = \frac{1}{2}k_B T$, as expected from the equipartition theorem,

Power supplied by $v(t)$ is $p(t) = v^*(t)\dot{q}$ (using $v^*(t) = v(t)$, as $v(t)$ is real-valued). We examine the frequency spectrum of p, and use the fact that for a real variable $x(t)$, $x_\omega^* = x_{-\omega}$. Hence, $\Re p_\omega = \Re p_{-\omega}$, whereas the imaginary parts have opposite sign: $\Im p_\omega = -\Im p_{-\omega}$ and cancel when integrating over frequency. The averaged frequency spectrum of supplied power is therefore given only by the real part:

$$\Re\langle v^*(\omega)(-i\omega)q(\omega)\rangle = \Re(-i\omega\alpha(\omega)\langle|v(\omega)|^2\rangle)$$
$$= 2k_BTR\Im(\omega\alpha(\omega)) = 2k_BT\frac{\omega^2\tau^2}{1+\omega^2\tau^2}$$

On the other hand, the power dissipated in R is I^2R, leading to

$$\omega^2\langle|q(\omega)|^2\rangle R = 2k_BTR\frac{\omega^2\tau C}{1+\omega^2\tau^2} = 2k_BT\frac{\omega^2\tau^2}{1+\omega^2\tau^2}$$

The dissipated power in the resistor therefore equals the supplied power provided by the noise voltage, demonstrating that the two mechanisms – dissipation and Langevin force – are connected.

The noise spectrum will be flat at low frequencies and roll off at a frequency $\omega_0 = 1/(RC)$. If C is known, we can find R from this characteristic frequency. Moreover, the temperature can be obtained from the noise intensity at low frequencies, which is proportional to T, or by the overall integrated noise, which as shown above is also proportional to T and given by the equipartition theorem applied to the capacitor.

32. The Feynman analysis of Brownian ratchet. In order to make a forward step of the ratchet, we need to lift the pawl and also do the work on lifting the weight, which requires the total energy $\varepsilon + L\theta$. The probability of this energy to be delivered from the vanes at $T = T_1$ is $\exp[-\frac{\varepsilon+L\theta}{k_BT_1}]$. Note that the useful work as a result of this step is just $L\theta$, so the extra energy has to go into heating the pawl.

Now look at the opposite, backward step. That can only happen if the pawl accidentally lifts high enough to let the ratchet slip back. The energy of this is ε and the probability for this to occur spontaneously is $\exp[-\frac{\varepsilon}{k_BT_2}]$, at $T = T_2$. When this happens, the work $L\theta$ is released. The system is reversible is both probabilities are the same, that is

$$e^{-\frac{\varepsilon+L\theta}{k_BT_1}} = e^{-\frac{\varepsilon}{k_BT_2}}, \quad \text{or} \quad \frac{\varepsilon+L\theta}{T_1} = \frac{\varepsilon}{T_2}$$

Suppose that for a particular weight the probabilities (or, equivalently, the rates of forward and backward motion) are the same. Then if we add a bit of weight, it will slowly go down and work will be done on the machine: energy will be taken from the wheel and given to the vanes. If instead we reduce the weight a bit, the imbalance will turn the other way: the weight is lifted and heat is taken from the vanes and put into the wheel.

Let us say the machine is slowly lifting the weight. The heat energy Q_1 is taken from the vanes and energy Q_2 is delivered to the ratchet, which are in proportion $(\varepsilon+L\theta)/\varepsilon$, so $Q_1/Q_2 = T_1/T_2$. Note that the useful work you can extract from the machine is $W = L\theta$, so the ratio of it to the heat taken from the vanes is

$$\frac{W}{Q_1} = \frac{L\theta}{\varepsilon+L\theta} = \frac{T_1-T_2}{T_1};$$

we cannot extract more work than that while operating reversibly.

32. This requires solving the free diffusion equation for $P(x,t)$ with the boundary conditions $P(x=L)=0$ and $dP/dx(x=0)=0$. Separating variables, we have:

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial^2 P}{\partial x^2} \quad \text{taking} \ \ P = T(t)X(x)$$
$$\dot{T} = -\lambda T \quad \text{and} \ \ X'' + (\lambda/D)X = 0$$

The time dependence gives a simple exponential, $T(t) = e^{-\lambda t}$. The x-dependence is best described by the harmonic functions (since we see the oscillator equation), $X = A\sin\sqrt{\lambda/D}x + B\cos\sqrt{\lambda/D}x$. The reflecting wall at $x=0$ means that $X'(0) = \sqrt{\lambda/D}\cdot A\cos 0 = 0$, that is, the constant $A=0$. The particle "sink" at the end of our range demands: $X(L) = B\cos\sqrt{\lambda/D}L = 0$. This gives the discrete values ("quantisation") of the parameter λ:

$$\sqrt{\frac{\lambda}{D}}L = \pi(n+1/2) \quad \text{so that} \ \ P(x,t) = \sum_n B_n e^{-\frac{\pi^2 D}{L^2}(n+1/2)^2 t} \cos\frac{\pi x}{L}(n+1/2)$$

One could analyse this solution, and the evolution of particle distribution in this system, in much greater detail (especially if an initial condition $P(t=0)$ would be given, of which B_n are the Fourier coefficients). To answer the question quickly, it is clear that the relevant time scale of particles escaping is $\tau = 4L^2/\pi^2 D$, which is the life time of the longest-surviving mode.