

TSP-2022/23 — Thermal and Statistical Physics (Part II)

Problem sheet I: questions 1-12

1. Van der Waals gas

Show that, for a van der Waals gas, the specific heat at constant volume, C_V , obeys

$$\left(\frac{\partial C_V}{\partial V}\right)_T = 0.$$

Solution: The heat capacity at constant volume is given by

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

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

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial}{\partial V}\right)_T \left[T \left(\frac{\partial S}{\partial T}\right)_V \right] \quad (2)$$

$$= T \left(\frac{\partial}{\partial V}\right)_T \left(\frac{\partial S}{\partial T}\right)_V \quad (3)$$

$$= T \left(\frac{\partial}{\partial T}\right)_V \left(\frac{\partial S}{\partial V}\right)_T \quad \text{switch order} \quad (4)$$

$$= T \left(\frac{\partial}{\partial T}\right)_V \left(\frac{\partial p}{\partial T}\right)_V \quad \text{Maxwell relation} \quad (5)$$

$$= T \left(\frac{\partial^2 p}{\partial T^2}\right)_V \quad \text{we have } (p, V, T) : \text{ stop!} \quad (6)$$

The van der Waals equation of state:

$$p = \frac{Nk_B T}{V - Nb} - \frac{N^2 a}{V^2}. \quad (7)$$

Therefore

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

2. Entropy of the monatomic gas

The entropy of a monatomic ideal gas is given by the Sackur-Tetrode equation which can be written in the form:

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

where α is a constant to be derived later in the course.

Invert this expression to get $U(S, V, N)$. From this, obtain the equation of state expressing p as a function of V, N and T .

Solution: The given equation for S can be inverted, giving

$$U(S, V, N) = N \left(\frac{N}{\alpha V}\right)^{2/3} e^{2S/3Nk_B}. \quad (9)$$

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

$$p = - \left(\frac{\partial U}{\partial V} \right)_{S,N} = \frac{2}{3} \frac{U}{V} \quad (10)$$

$$T = \left(\frac{\partial U}{\partial S} \right)_{V,N} = \frac{2}{3Nk_B} U \quad (11)$$

$$\Rightarrow U = \frac{3}{2} Nk_B T, \quad pV = Nk_B T. \quad (12)$$

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

3. Analytic thermodynamics

Use a Maxwell relation and the chain rule to show that for any substance the rate of change of T with p in a reversible adiabatic compression is given by

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

Find an equivalent expression for the adiabatic rate of change of T with V , and check that both results are valid for an ideal monatomic gas.

Solution: 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)

$$\frac{\partial^2 H}{\partial S \partial p} = \left(\frac{\partial T}{\partial p} \right)_S = \left(\frac{\partial V}{\partial S} \right)_p. \quad (13)$$

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:

$$\left(\frac{\partial V}{\partial S} \right)_p = \left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial T}{\partial S} \right)_p. \quad (14)$$

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

$$\left(\frac{\partial T}{\partial p} \right)_S = \frac{T}{C_p} \left(\frac{\partial V}{\partial T} \right)_p. \quad (15)$$

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

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial p}{\partial S} \right)_V \quad (16)$$

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

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial p}{\partial S} \right)_V = - \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial T}{\partial S} \right)_V = - \frac{T}{C_V} \left(\frac{\partial p}{\partial T} \right)_V. \quad (17)$$

To show these relationships work for an ideal gas, the most direct route is to consider change in the enthalpy for the first expression and change in the internal energy for the second expression. These are always just given by heat capacity and temperature change for ideal gases:

For an adiabatic process in an ideal gas we have, because $dS = 0$:

$$dH = c_p dT = V dp \quad (18)$$

From this, it follows that $\left(\frac{\partial T}{\partial p}\right)_S = V/c_p = \left(\frac{\partial V}{\partial T}\right)_p T/c_p$, because in an ideal gas, $V \propto T$.

Similarly, we have, again for $dS = 0$:

$$dU = c_v dT = -p dV \quad (19)$$

From this, it follows that $\left(\frac{\partial T}{\partial V}\right)_S = -p/c_v = -\left(\frac{\partial p}{\partial T}\right)_V T/c_v$, because in an ideal gas, $p \propto T$.

Alternatively, you can work with the adiabatic equation of state: for an ideal gas we know $pV = Nk_B T$, and for an adiabatic process $pV^\gamma = (Nk_B T)^\gamma p^{1-\gamma} = \text{const}$. 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)

$$d(pV^\gamma) = d[(Nk_B T)^\gamma p^{1-\gamma}] = 0, \quad p \text{ and } T \text{ variables here} \quad (20)$$

$$\gamma T^{\gamma-1} p^{1-\gamma} dT + (1-\gamma) T^\gamma p^{-\gamma} dp = 0, \quad \text{so the ratio of increments gives} \quad (21)$$

$$\left(\frac{\partial T}{\partial p}\right)_S = -\frac{1-\gamma}{\gamma} \frac{T}{p} = \frac{2}{5} \frac{T}{p} \quad (22)$$

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.(??):

$$\frac{T}{C_p} \left(\frac{\partial V}{\partial T}\right)_p = \frac{T}{\frac{5}{2} Nk_B} \frac{Nk_B}{p} = \frac{2}{5} \frac{T}{p}. \quad (23)$$

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

$$S = S_o - Nk_B \ln Nk_B + C_V \ln T + Nk_B \ln V \quad (24)$$

$$dS = 0 = \frac{C_V}{T} dT + \frac{Nk_B}{V} dV \Rightarrow \quad (25)$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{Nk_B}{C_V} \frac{T}{V} = -\frac{p}{C_V} = -\frac{1}{C_V} T \left(\frac{\partial p}{\partial T}\right)_V. \quad (26)$$

4. Brief Notes

Write brief notes on thermodynamic equilibrium in closed and open systems.

Solution: 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 $dS = 0$:

$$dS = 0 = dS_1 + dS_2 \quad (27)$$

$$= \left(\frac{\partial S_1}{\partial U_1} \right)_{V_1, N_1} dU_1 + \left(\frac{\partial S_2}{\partial U_2} \right)_{V_2, N_2} dU_2 + \left(\frac{\partial S_1}{\partial V_1} \right)_{U_1, N_1} dV_1 + \left(\frac{\partial S_2}{\partial V_2} \right)_{U_2, N_2} dV_2 \quad (28)$$

$$+ \left(\frac{\partial S_1}{\partial N_1} \right)_{V_1, U_1} dN_1 + \left(\frac{\partial S_2}{\partial N_2} \right)_{V_2, U_2} dN_2 \quad (29)$$

$$= \left(\frac{1}{T_1} - \frac{1}{T_2} \right) dU_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2} \right) dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) dN_1, \quad (30)$$

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:

$$dS = 0 = dS_1 + dS_2 = dS_1 + \frac{1}{T_2} (dU_2 + p_2 dV_2 - \mu_2 dN_2) \quad (31)$$

$$= \frac{1}{T_2} (T_2 dS_1 - dU_1 - p_2 dV_1 + \mu_2 dN_1) \quad (32)$$

$$\equiv -\frac{dA_1}{T} \quad (33)$$

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

$$(dA_1)_{T,V} = d(U_1 - T_1 S_1) = dF_1 \quad (34)$$

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.

5. Bubble

Under what conditions is the Helmholtz free energy F a minimum for a system in equilibrium? The work corresponding to an increase in the surface area of a liquid is $dW = \Gamma dA$, where Γ is the surface tension, and A is the area of the surface.

Consider a bubble of air in a large container of liquid in equilibrium. Write the total Helmholtz free energy of the system as the sum of contributions from the air in the bubble, F_a , the surface of the bubble, F_s , and the surrounding liquid, F_l . Show that the pressure of the air inside the bubble is equal to $p_l + 2\Gamma/r$, where p_l is the pressure of the liquid.

Solution: 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),

$$dF = dF_l + dF_a + dF_s = 0. \quad (35)$$

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 ΓdA term. Using $dT = 0$, $dV_l = -dV_a$, and all components species keep their particle numbers, $dN_i = 0$, we have

$$dF_l = p_l dV_a \quad (36)$$

$$dF_a = -p_a dV_a \quad (37)$$

$$dF_s = \Gamma dA. \quad (38)$$

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. (??) gives

$$p_a = p_l + \frac{2\Gamma}{r}. \quad (39)$$

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.

So far for the simplest and most straightforward answer. The following complication may be considered: are the numbers N_i strictly speaking constant? After all, as the surface area changes, molecules are converted from liquid to surface. The consequence would be that the work term for the surface (or interface) is $\Gamma dA + \mu_s dN_s$, whereas the work term for the liquid becomes $p_l dV_a - \mu_l dN_s$. The total free energy acquires an extra term $(\mu_s - \mu_l) dN_s$. However, the number of molecules on the interface is proportional to its area, so this term actually can be reexpressed in terms of dA , like the surface tension term. It can therefore simply be absorbed into the surface tension term, making $\Gamma \rightarrow \Gamma'$. In fact, this is probably exactly the origin of the surface tension in the first place.

6. Superconductor

The heat capacities of the superconducting and normal phases of a metal at low temperatures are given approximately by

$$\begin{aligned} C_s(T) &= V\alpha T^3 && \text{superconducting phase} \\ C_n(T) &= V\beta T^3 + V\gamma T && \text{normal phase,} \end{aligned}$$

where V is the volume and α , β , and γ are constants. Above a temperature T_c , the normal phase is stable. At low temperatures the superconducting phase is stable, but it can be suppressed in high magnetic fields, which enabled the experimental determination of $C_n(T)$ given above.

The latent heat for the transition is zero. What does this imply for the entropy of the normal and of the superconducting phase at T_c ? Find an expression for T_c .

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

$$S_s = V \frac{\alpha T^3}{3} + \text{constant} \quad (40)$$

$$S_n = V \frac{\beta T^3}{3} + V\gamma T + \text{constant}. \quad (41)$$

The Third Law (at $T = 0$) tells us that the constants of integration are zero. There is no problem applying this to the ‘s’ phase, which should last till $T = 0$, but the ‘n’ phase does not? It’s empirically observed, and the little comment in the question suggests why, that even though this phase only lasts until T_c , we nevertheless can assume that S_n ‘aims’ at zero at $T = 0$. Then both constants are zero. The Latent heat at the transition is then given by

$$L = T_c [S_n(T_c) - S_s(T_c)] = 0. \quad (42)$$

Using the expressions for the entropies we have

$$T_c \left[V \frac{\alpha T_c^3}{3} - V \frac{\beta T_c^3}{3} - V\gamma T_c \right] = 0, \quad (43)$$

which gives the solution

$$T_c = \sqrt{\frac{3\gamma}{\alpha - \beta}}. \quad (44)$$

7. Partition Function

The partition function of a system is

$$Z = \exp [aT^3V],$$

where a is a positive constant. Obtain expressions for the Helmholtz free energy, the equation of state, the internal energy, the heat capacity at constant volume, the pressure, and the chemical potential.

Can you identify the physical system that corresponds to such a partition function?

Solution: We are given the partition function $Z = \exp[aT^3V]$. 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 corresponds to black-body radiation.

8. Vacancies

A crystalline solid contains N identical atoms on N lattice sites, and N interstitial sites to which atoms may be transferred at the energy cost ε_c . If n atoms are on interstitial sites, show that the configurational entropy is $2k_B \ln(N!/n!(N-n)!)$.

Show that the equilibrium proportion of atoms on interstitial sites n/N is

$$\left\langle \frac{n}{N} \right\rangle = \frac{1}{1 + \exp(\varepsilon_c/2k_B T)}.$$

Solution: 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

$$S_{\text{config}} = k_B \ln \Omega_l \Omega_v = k_B \ln \left(\frac{N!}{(N-n)!n!} \right)^2 = 2k_B \ln \frac{N!}{(N-n)!n!}. \quad (45)$$

(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

$$F(n) = F(n=0) + n\varepsilon_c - TS_{\text{config}} = F_0 + n\varepsilon_c - 2k_B T \ln \frac{N!}{(N-n)!n!}. \quad (46)$$

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

$$\Delta F(n) = n\varepsilon_c + 2k_B T ((N - n) \ln(N - n) + n \ln n). \quad (47)$$

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

$$\varepsilon_c = 2T k_B \{\ln(N - n) - \ln n\} \quad \text{i.e.,} \quad \frac{n}{N} = \frac{1}{1 + e^{\varepsilon_c / 2k_B T}}. \quad (48)$$

The low-T limit, as always in systems with an energy gap, has $n = N e^{\varepsilon_c / 2k_B T}$, and the high-T limit is $n = N/2$.

9. Zipper

A zipper has N links; each link has a state in which it is closed with energy 0 and open with energy ε . We require, however, that the zipper can only unzip from the left end, and that the link number s can only open if all links to the left ($1, 2, \dots, s-1$) are already open. Find the partition function and the average number of open links in the low-T limit.

Solution: 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:

$$\langle n \rangle = \frac{1}{Z} \sum_{n=0}^N n \left(e^{-\beta \varepsilon} \right)^n \simeq e^{-\beta \varepsilon}. \quad (49)$$

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.

10. Some partition functions

Calculate the classical partition functions, and discuss the high- and low-temperature limits of:

(a) a one-dimensional simple harmonic oscillator, for which

$$E(p, x) = \frac{p^2}{2m} + \frac{1}{2} k x^2;$$

(b) a particle moving in three dimensions in a uniform gravitational field, for which

$$E(p, z) = \frac{p^2}{2m} + mgz.$$

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

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

Note that the ratio $k/m = \omega_0^2$, the natural frequency of the oscillator, so in fact $Z = k_BT/\hbar\omega_0$, 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 $Z \rightarrow e^{-\frac{1}{2}\beta\hbar\omega}$.

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 $kL^2 \gg k_BT$. 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:

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

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 $mgL \gg k_BT$) 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_1m_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.

11. Relativistic gas

Consider an ideal classical gas of volume V and temperature T , consisting of N indistinguishable particles in the extreme relativistic limit where the energy ϵ and momentum p of a particle are related by $\epsilon = cp$, where c is the speed of light.

(a) Calculate the partition function of the system Z , the equation of state, the entropy S , internal energy U , and the heat capacity C_V .

(b) Suppose that, in addition to its translational motion, each of the particles can exist in one of two states of energy Δ and $-\Delta$. Calculate Z , the equation of state, S , U , and C_V .

Solution: (a) For a single particle, the partition function is

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

To calculate this you need to convert d^3p 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 :

$$\begin{aligned}
 Z &= \frac{1}{N!} Z_1^N = \frac{1}{N!} \left(\frac{V(k_B T)^3}{\pi^2 \hbar^3 c^3} \right)^N \\
 \ln Z &= N \left[\ln \left(\frac{V(k_B T)^3}{\pi^2 \hbar^3 c^3} \right) - \ln N + 1 \right] \\
 \text{so evaluate } F &= -k_B T \ln Z = -N k_B T \left[\ln \left(\frac{V(k_B T)^3}{\pi^2 \hbar^3 c^3 N} \right) + 1 \right] \\
 p &= - \left(\frac{\partial F}{\partial V} \right)_T = \frac{N k_B T}{V} \quad \text{still ideal gas!} \\
 S &= - \left(\frac{\partial F}{\partial T} \right)_V = N k_B \left[4 + \ln \left(\frac{V(k_B T)^3}{\pi^2 \hbar^3 c^3 N} \right) \right] \\
 U &= - \frac{\partial}{\partial \beta} \ln Z = 3 N k_B T \\
 C &= \left(\frac{\partial U}{\partial T} \right)_V = 3 N k_B.
 \end{aligned}$$

It seems the equipartition does not work (i.e. it appears we have 6 degrees of freedom)? But of course equipartition only gives $k_B T/2$ when the energy depends on this degree of freedom quadratically, which is only the low-speed limit (the full $E = \sqrt{p^2 c^2 + m^2 c^4}$). 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

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

The total partition function of the system is then

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

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

$$\begin{aligned}
 Z_\Delta &= e^{\beta\Delta} + e^{-\beta\Delta} \\
 F_\Delta &= -k_B T \ln Z_\Delta = -k_B T \ln \left(e^{\beta\Delta} + e^{-\beta\Delta} \right) \\
 p_\Delta &= - \left(\frac{\partial F_\Delta}{\partial V} \right)_T = 0, \quad \text{equation of state remains unchanged} \\
 S_\Delta &= - \left(\frac{\partial F_\Delta}{\partial T} \right)_V = k_B \ln \left(1 + e^{-2\beta\Delta} \right) + \frac{1}{T} \frac{2\Delta}{e^{2\beta\Delta} + 1} \\
 U_\Delta &= - \frac{\partial}{\partial \beta} \ln Z_\Delta = -\Delta \tanh(\beta\Delta) \\
 C_\Delta &= \left(\frac{\partial U}{\partial T} \right)_V = \frac{\Delta^2}{k_B T^2 \cosh^2(\beta\Delta)}.
 \end{aligned}$$

12. Adsorption

Helium atoms of mass m may be adsorbed from the vapour phase at pressure p onto a solid surface where they can move freely without interaction, behaving as a two-dimensional perfect gas. If the adsorption energy is Δ , then by treating the vapour as a particle reservoir for the helium atoms on the solid surface, and treating both sets of atoms as ideal classical gases, show that the number density per unit area of helium atoms on the surface is

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

Solution: 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:

$$\mu_{3D} = k_B T \ln \left(\frac{N\lambda^3}{V} \right), \quad (50)$$

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

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

Equating the two chemical potentials we obtain

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

(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

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

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

$$\Phi(\varepsilon_k) = -k_B T \ln \Xi_k \approx -k_B T e^{-\beta\mu} e^{\beta\Delta} e^{-p^2/2mk_B T}, \quad (51)$$

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):

$$\Phi = \int \Phi(\varepsilon_k) \frac{d^2x d^2p}{(2\pi\hbar)^2} = -k_B T \frac{A}{2\pi\hbar^2} e^{\beta\mu} e^{\beta\Delta} \int_0^\infty e^{-p^2/2mk_B T} p dp = -k_B^2 T^2 m \frac{A}{2\pi\hbar^2} e^{\beta\mu} e^{\beta\Delta}. \quad (52)$$

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

$$n_{\text{ads}} = \frac{N_{\text{ads}}}{A} = -\frac{1}{A} \left(\frac{\partial \Phi}{\partial \mu} \right)_{T,V} = \frac{mk_B T}{2\pi\hbar^2} e^{\beta\mu} e^{\beta\Delta}. \quad (53)$$

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

$$n_{\text{ads}} = \frac{p}{k_B T} \left(\frac{2\pi\hbar^2}{mk_B T} \right)^{1/2} e^{\Delta/k_B T}. \quad (54)$$