PH4210 Statistical Mechanics

Problem Sheet 1 — Answers

1 Demonstrate that *entropy*, as given by the Boltzmann expression $S = k \ln \Omega$, is an *extensive* property. The best way to do this is to argue *clearly* that Ω is multiplicative.

We must prove that if one system has entropy S_1 and another has S_2 then when considered together they have entropy $S = S_1 + S_2$. Note that we are *not* considering bringing the two systems into contact, so the energy levels and their populations are not changed. We are considering a composite system of two separate parts.

A microstate of the composite system is specified when the microstate of each of the systems is specified. If the macrostate of system 1 has Ω_1 microstates and the macrostate of system 2 has Ω_2 microstates, then when system 1 is in one of its microstates then system 2 can be in any one of its Ω_2 microstates. For every microstate of system 1 there are Ω_2 microstates. But since system 1 can exist in any of its Ω_1 microstates it follows that there must be $\Omega_1\Omega_2$ microstates in the macrostate of the composite system:

$$\Omega = \Omega_1\Omega_2$$

so that the entropy of the composite system is

$$S = kT \ln \Omega$$
$$= kt \ln \Omega_1\Omega_2$$
$$= kT \ln \Omega_1 + kT \ln \Omega_2$$
$$= S_1 + S_2 \, .$$

We have shown that the entropy for two isolated systems is additive, which means that entropy is an extensive quantity.

2 Demonstrate that gravitational energy is not extensive: show that the gravitational energy of a sphere of radius r and uniform density varies with volume as V^n and find the exponent n.

We shall calculate the work done against the force of gravity in assembling a sphere of matter by bringing together the constituent parts from bolnfinity. When all the matter is off at infinity we take the gravitational energy to be zero. The gravitational energy of the body is the work done in bringing the matter together.

We consider an intermediate state of the system: we have a spherical mass M of radius R and we evaluate the work done in bringing up an extra mass dm from infinity to the surface.

The force between masses M and m separated by a distance r is given by Newton's law of gravitation

$$F = -G\frac{Mm}{r^2} \, .$$

Then the work done in moving a mass dM from infinity to distance R is

$$dE = -\int_{\infty}^{R} F dr,$$

where the minus sign means that we are doing work by applying a force against the force of gravitation. So integrating up the Newton expression we obtain

$$dE = -\frac{GM}{R} dM.$$

But in adding this extra mass the radius will have increased slightly. Since

$$M = \frac{4}{3}\pi R^3 \rho,$$

where ρ is the density, it follows that

$$dM = 4\pi R^2 \rho dR.$$

We substitute for M and dM in the work expression:

$$dE = -\frac{G}{R}\frac{4}{3}\pi R^3 \rho \, 4\pi R^2 \rho dR$$

$$= -G\frac{16}{3}\pi^2 \rho^2 R^4 dR.$$

The total gravitational energy is found by assembling the complete system, by building the radius up from zero to its final value. Upon integration we find

$$E = -G\frac{16}{15}\pi^2 \rho^2 R^5.$$

Finally we must express this energy in terms of the volume of the sphere

$$V = \frac{4}{3}\pi R^3,$$

so that

$$R = \left(\frac{3}{4\pi}V\right)^{1/3}.$$

Then we obtain

$$E = -G\frac{16}{15}\left(\frac{3}{4\pi}\right)^{5/3}\pi^2 \rho^2 V^{5/3}.$$

Thus the gravitational energy varies as the 5/3 power of volume; the exponent $n = 5/3$. This shows that gravitational energy is not extensive; extensivity requires energy to be proportional to volume; the exponent n would be unity.

3 In investigating the conditions for the establishment of equilibrium through the transfer of thermal energy the fundamental requirement is that the entropy of the equilibrium state should be a maximum. Equality of temperature was established from the vanishing of the first derivative of S. What follows from a consideration of the *second derivative*?

The total entropy of the composite system may be written $S(E) = S_1(E) + S_2(E_t - E)$. Setting the first derivative of this to zero leads to the equality of the temperatures of the two systems.

<center>Answers 1.2</center>

The second derivative of the total entropy is easily expressed in terms of the first derivatives of the temperatures of the two systems

$$\frac{d^2 S}{dE^2} = \frac{d}{dE}\left(\frac{1}{T_1}\right) + \frac{d}{dE}\left(\frac{1}{T_2}\right).$$

The requirement that in equilibrium the entropy be a *maximum* means that the second derivative must be *negative*. If we evaluate the derivative of the reciprocals we find

$$-\frac{1}{T_1^2}\frac{dT_1}{dE} - \frac{1}{T_2^2}\frac{dT_2}{dE} < 0$$

or

$$\frac{1}{C_1} + \frac{1}{C_2} > 0,$$

since the temperatures are equal in equilibrium. Here the C are the thermal capacities of the subsystems. The inequality must be satisfied for all allowed values of C_1 and C_2. In particular it must be satisfied when either system becomes vanishingly small so that its heat capacity approaches zero. Then the inequality requires that the thermal capacities must be positive.

4 Do particles flow from high μ to low μ or *vice versa*? Explain your reasoning.

The change in entropy, when particles flow is given by

$$\Delta S = \left(\frac{\partial S_1}{\partial N} - \frac{\partial S_2}{\partial N}\right)\Delta N_1,$$

which must be greater than or equal to zero by the Second Law. But since

$$\frac{\partial S}{\partial N} = -\frac{\mu}{T}$$

it follows that

$$\Delta S = \frac{1}{T}\left(\mu_2 - \mu_1\right)\Delta N_1 \geq 0$$

since temperature is the same in both systems.

We conclude that when $\mu_2 > \mu_1$ then ΔN_1 will be positive; N_1 will increase. In other words, particles will flow from high μ to low μ.

5 In the derivation of the Boltzmann factor the entropy of the bath was expanded in powers of the energy of the 'system of interest'. The higher order terms of the expansion are neglected. Discuss the validity of this.

We derived that

$$P(E) \propto e^{S(E_T - E)/k}$$

where $E \ll E_T$ so that we expand S as a Taylor series:

$$S(E_T - E) = S(E_T) - E\frac{\partial S}{\partial E} + \frac{E^2}{2}\frac{\partial^2 S}{\partial E^2} - \cdots$$

The derivative in the second term is immediately identified as the inverse temperature

$$\frac{\partial S}{\partial E} = \frac{1}{T}.$$

The derivative in the second term is then

$$\frac{\partial^2 S}{\partial E^2} = \frac{\partial}{\partial E}\frac{1}{T}$$

$$= -\frac{1}{T^2}\frac{\partial T}{\partial E}.$$

But here $\partial T / \partial E$ is the inverse of the thermal capacity C (of the reservoir). Then the entropy expansion becomes

$$S(E_\mathrm{T} - E) = S(E_\mathrm{T}) - \frac{E}{T} - \frac{E^2}{2T^2}\frac{1}{C} - \cdots$$

and the higher order terms involve derivatives of the thermal capacity.

The key point of the argument is that the thermal capacity of the reservoir is very large. The assumption is that while the reservoir determines the properties of our "system of interest", the system of interest can have no effect on the reservoir. This is what we mean by a reservoir, and it may be encapsulated by saying that its thermal capacity is essentially infinite. Another way of looking at this is to say that since thermal capacity is an extensive quantity then in the limit that the reservoir is large, its thermal capacity will be large. Then the inverse of the thermal capacity will be small and then the third term in the entropy expansion can be neglected. The higher-order terms involve derivatives of the thermal capacity so that these can also be ignored.

6 The Boltzmann factor could have been derived by expanding Ω rather than by expanding S. In that case, however, the expansion cannot be terminated. Why not?

If we expand Ω we get

$$\Omega(E_T - E) = \Omega(E_T) - E\frac{\partial \Omega}{\partial E} + \frac{E^2}{2}\frac{\partial^2 \Omega}{\partial E^2} - \cdots$$

Since $S = k \ln\Omega$, and $\partial S / \partial E = 1/T$, it follows that

$$\frac{\partial \Omega}{\partial E} = \frac{\Omega}{kT}, \quad \frac{\partial^2 \Omega}{\partial E^2} = \frac{\Omega}{(kT)^2}, \quad \text{etc.}$$

then

$$\Omega(E_T - E) = \Omega(E_T)\left\{1 - \frac{E}{kT} + \frac{1}{2}\left(\frac{E}{kT}\right)^2 - \cdots\right\}$$

or

$$P(E) \propto \left\{1 - \frac{E}{kT} + \frac{1}{2}\left(\frac{E}{kT}\right)^2 - \cdots\right\}.$$

So in this case you certainly can't terminate the expansion. But you can sum the infinite series (it is the exponential function) – and this gives the Boltzmann factor.

Answers 1.4

The factorial is given by

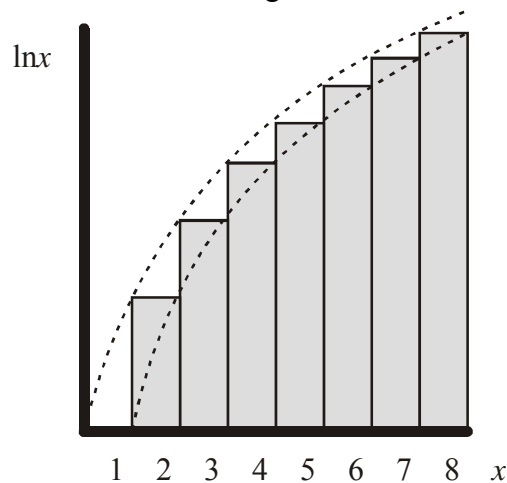$$N! = 1 \times 2 \times 3 \times \ \dots \ \times (N-1) \times N$$

so that the logarithm is

$$\ln N! = \ln \{1 \times 2 \times 3 \times \ \dots \ \times (N-1) \times N\}$$
$$= \ln 1 + \ln 2 + \ln 3 + \ \dots \ + \ln(N-1) + \ln N$$
$$= \sum_{n=1}^{N} \ln n \ ,$$

as required.

Now we approximate the sum by an integral:

$$\sum_{n=1}^{N} \ln n \approx \int_{0}^{N} \ln n \ \mathrm{d}n \ ;$$

this corresponds to the lower dotted line of the figure below.

Evaluation of the integral gives

$$\int_{0}^{N} \ln n \ \mathrm{d}n = N \ln N - N$$

so that we obtain Stirling's approximation as

$$\ln N! \approx N \ln N - N.$$

Answers 1.5

The fundamental postulate of statistical mechanics states that for an isolated system all microstates are equally likely. If this isolated system has Ω microstates then the probability of any one of these microstates is $1/\Omega$. Then generalised entropy expression is then

$$S = -k \sum_j P_j \ln P_j$$

$$= -k \sum_j \left(\frac{1}{\Omega}\right) \ln \left(\frac{1}{\Omega}\right)$$

$$= k \sum_j \left(\frac{1}{\Omega}\right) \ln \Omega.$$

Now each term in the sum is a constant, and there will be Ω such terms. Thus the expression for entropy becomes

$$S = k \ln \Omega$$

as required.

9 What is the condition that the geometric progression in deriving the Bose-Einstein distribution is convergent?

The geometric progression is

$$(pV)_k = kT \ln \sum_{n_k=0}^{\infty} \left\{ e^{-(\varepsilon_k - \mu)/kT} \right\}^{n_k}.$$

This will be convergent if

$$e^{-(\varepsilon_k - \mu)/kT} < 1.$$

In other words one requires

$$\varepsilon > \mu$$

for all single-particle energies ε. Now the ground state energy will be zero (or very close to it), so that the condition is on the chemical potential:

$$\mu < 0$$

the chemical potential must always be *negative*. Note that this requirement applies to Bose particles; it does not apply to Fermions.

10 Show that the trajectory of a 1d harmonic oscillator is an ellipse in phase space. What would the trajectory be if the oscillator were *weakly* damped.

The displacement of a simple harmonic oscillator evolves in time as

$$x(t) = A \sin(\omega t + \varphi).$$

The momentum is given by

$$p = m\dot{x} = Am\omega \cos(\omega t + \varphi).$$

The pair

$$x(t) = A \sin(\omega t + \varphi)$$
$$p(t) = B \cos(\omega t + \varphi)$$

Answers 1.6

are seen to specify an ellipse in x-p space (phase space), since $\left(x/A\right)^2 + \left(p/B\right)^2 = 1$.

In the case of damping there will be an exponential decay superimposed on the sine and cosine. So the phase point will approach the point $x = 0$, $p = 0$. In the case of *weak* damping the phase point will trace out many cycles of the ellipse before the "radius" changes appreciably. The effect of weak damping is thus to cause the phase point to gradually spiral into the origin.

The point about *weak* damping is that any single cycle is still observed to be essentially elliptical.

11 Why can't the evolutionary curve in phase space intersect? You need to demonstrate that the evolution from a point is unique.

Newton's equations of motion are second order differential equations – there are up to second derivatives of the spatial coordinates. A complete solution to the equations thus involves two constants of integration for each degree of freedom. And these constants could be the position coordinate and the momentum component at a given instant in time. (Hamilton's formulation of dynamics then extends the idea to a generalised view of coordinates and momenta.) Such a complete solution of the equations of motion gives a unique solution; the evolution in time is completely determined. Now a 'point' in phase space represents a given value of position and momentum. So the future (and past) evolution of the system, and thus the phase space trajectory, is completely determined from this point. It then follows that the evolutionary path through a point in phase space is unique. Then two paths cannot pass through the same phase point and so the evolutionary curve in phase space cannot intersect itself.

12 Starting from the expression for the Gibbs factor for a many-particle system, write down the grand partition function Ξ and show how it may be expressed as the product of Ξ_k, the grand partition function for the subsystem comprising particles in the kth single-particle state.

One starts from the Gibbs factor
$$P_{N,j}\left(V,T,\mu\right) = \frac{1}{\Xi\left(V,T,\mu\right)} e^{-\left\{E_{N,j}(N,V)-\mu N\right\}/kT}.$$
The normalization constant Ξ is the grand partition function:
$$\Xi\left(V,T,\mu\right) = \sum_{N,j} e^{-\left\{E_{N,j}(N,V)-\mu N\right\}/kT}$$
where N, j specify the jth quantum state of the system when it contains N particles.

Now for a system of identical particles
$$N = \sum_k n_k$$
$$E = \sum_k n_k \varepsilon$$
and a given state of the system is specified by the occupation of the single-particle states k:

Answers 1.7

$$\left(n_1, n_2, n_3, \ \ldots\right) \equiv \left\{n_k\right\}.$$

So in this case the grand partition function is expressed as

$$\Xi\left(V,T,\mu\right) = \sum_{\{n_k\}} e^{-\sum_k (\varepsilon_k - \mu)n_k / kT}$$

$$= \sum_{\{n_k\}} \prod_k e^{-(\varepsilon_k - \mu)n_k / kT}.$$

Now the n_k are all *independent*, so that

$$\Xi\left(V,T,\mu\right) = \prod_k \sum_{n_k} e^{-(\varepsilon_k - \mu)n_k / kT}.$$

Now we have the definition

$$\Xi_k\left(V,T,\mu\right) = \sum_{n_k} e^{-(\varepsilon_k - \mu)n_k / kT},$$

so that the grand partition function may be expressed as the product

$$\Xi\left(V,T,\mu\right) = \prod_k \Xi_k\left(V,T,\mu\right)$$

as required.

It is important to note the *logic* of this answer. It is not good enough to start from Ξ_k and then to argue that it must be multiplicative since the $(pV)_k$ contributions must be additive; this is *not* what is asked for. — That was the way things were argued in the text.

13 This problem considers the probability distribution for the energy fluctuations in the canonical ensemble. The *moments* of the energy fluctuations are defined by

$$\sigma_n = \frac{1}{Z} \sum_j \left(E_j - \varepsilon\right)^n e^{\beta E_j}$$

where $\beta = -1/kT$ and ε is an arbitrary (at this stage) energy.
Show that

$$Z\sigma_n = e^{\beta\varepsilon} \frac{\partial^n}{\partial\beta^n}\left\{Z\, e^{-\beta\varepsilon}\right\}$$

and use this to prove that the fluctuations in an ideal gas obey a *normal distribution* around ε. (You really need to use a computer algebra system to do this problem.)

The partition function is given by

$$Z = \sum_j e^{\beta E_j}$$

so that

$$Z e^{-\beta\varepsilon} = \sum_j e^{\beta(E_j - \varepsilon)}.$$

If we differentiate this n times with respect to β then this brings down n factors $(E_j - \varepsilon)$ on the right hand side:

$$\frac{\partial^n}{\partial \beta^n}\left\{Ze^{-\beta\varepsilon}\right\} = \sum_j \left(E_j - \varepsilon\right)^n e^{\beta\left(E_j - \varepsilon\right)}.$$

Multiply this by $e^{\beta\varepsilon}$, to obtain

$$e^{\beta\varepsilon}\frac{\partial^n}{\partial \beta^n}\left\{Ze^{-\beta\varepsilon}\right\} = \sum_j \left(E_j - \varepsilon\right)^n e^{\beta E_j}$$

whereupon we observe the right hand side to be $Z\sigma_n$. And thus we find

$$Z\sigma_n = e^{\beta\varepsilon}\frac{\partial^n}{\partial \beta^n}\left\{Z e^{-\beta\varepsilon}\right\}$$

as required.

The nth moment of the energy fluctuation distribution is then given by

$$\sigma_n = \frac{\dfrac{\partial^n}{\partial \beta^n}\left\{Z e^{-\beta\varepsilon}\right\}}{Z e^{-\beta\varepsilon}}$$

and for the ideal gas the partition function Z is given by

$$Z = \left\{\frac{mkT}{2\pi\hbar^2}\right\}^{3N/2}\left\{\frac{Ve}{N}\right\}^N$$

$$= \left\{\frac{-m}{2\pi\hbar^2\beta}\right\}^{3N/2}\left\{\frac{Ve}{N}\right\}^N.$$

Then the nth moment may be written as

$$\sigma_n = \frac{\dfrac{\partial^n}{\partial \beta^n}\left\{\left(-1/\beta\right)^{3N/2} e^{-\beta\varepsilon}\right\}}{\left(-1/\beta\right)^{3N/2} e^{-\beta\varepsilon}}$$

and, in particular, we find for the first moment

$$\sigma_1 = -\left(\varepsilon + \frac{3N}{2\beta}\right)$$

$$= \frac{3}{2}NkT - \varepsilon.$$

If we now choose the energy ε, about which the moments are evaluated, to be the mean energy $3NkT/2$ then the first moment will vanish. Thus we adopt this value for ε. The moments may then be evaluated as

$$\sigma_0 = 1$$
$$\sigma_1 = 0$$
$$\sigma_2 = 3N/2\beta^2$$
$$\sigma_3 = -3N/\beta^3$$
$$\sigma_4 = \left(27N^2 + 36N\right)/4\beta^2$$

etc.

Answers 1.9

The higher-order moments may be calculated in a straightforward, if tedious, manner.

The normal distribution (with zero mean) is characterised by the numerical value of the dimensionless 'reduced' moments

$$m_n = \sigma_n / \sigma_2^{n/2} \ .$$

In general these moments will be functions of the number of particles N. We find

$$m_0 = 1$$
$$m_1 = 0$$
$$m_2 = 1$$
$$m_3 = -\frac{2\sqrt{2}}{\sqrt{3N}}$$
$$m_4 = 3 + \frac{4}{N}$$
$$m_5 = -4\sqrt{\frac{2}{3}}\left(\frac{4}{N^{3/2}} + \frac{5}{N^{1/2}}\right)$$
$$m_6 = 15 + \frac{260}{3N} + \frac{160}{3N^2}$$

etc.

Then in the thermodynamic limit, $N \to \infty$, we see that the odd reduced moments vanish while the even ones tend to the values

$$m_0 = 1$$
$$m_2 = 1$$
$$m_4 = 3$$
$$m_6 = 15$$
$$m_8 = 105$$

etc.

The even reduced moments of the normal distribution are given by

$$m_{2n} = 1 \times 3 \times 5 \times \ldots \times (2n-1).$$

We see that these evaluate to the numbers calculated above. And thus we conclude that *in the thermodynamic limit* the energy fluctuations of an ideal gas obey a normal distribution.

14 For a single-component system with a variable number of particles, the Gibbs free energy is a function of temperature, pressure and number of particles: $G = G(T, p, N)$. Since N is the only extensive variable upon which G depends, show that the chemical potential for this system is equal to the Gibbs free energy per particle: $G = N\mu$.

If the system is increased by a factor x then the extensive variables G and N will be increased by this factor:

$$xG(T, p, N) = G(T, p, xN).$$

And in particular if $x = 1/N$ then

$$G(T,p,N) = NG(T,p,1);$$

the Gibbs free energy for a system of N particles is N times the Gibbs free energy per particle. But the gibbs free energy *per particle* may be expresses as

$$G(T,p,1) = \frac{\partial}{\partial N} G(T,p,N).$$

However we identify the derivative of the Gibbs free energy as the chemical potential. Thus we obtain the required result

$$G = N\mu.$$

15 Use the definition of the Gibbs free energy together with the result of the previous question to obtain the Euler relation of Appendix 1.

G is defined as

$$G = E - TS + pV.$$

But the previous Problem gives $G = N\mu$. Thus we have

$$E - TS + pV = \mu N$$

and the Euler relation

$$E = TS - pV + \mu N$$

then follows immediately.

16 The energy of a harmonic oscillator may be written as $m\omega^2 x^2/2 + p^2/2m$ so it is quadratic in both position and momentum – thus, classically, equipartition should apply. The energy levels of the quantum harmonic oscillator are given by $\varepsilon_n = \left(\frac{1}{2}+n\right)\hbar\omega$. Show that the partition function of this system is given by

$$Z = \frac{1}{2}\operatorname{cosech}\frac{\hbar\omega}{2kT}$$

and that the internal energy is given by

$$E = \frac{1}{2}\hbar\omega\coth\frac{\hbar\omega}{2kT} = \frac{\hbar\omega}{e^{\hbar\omega/kT}-1} + \frac{\hbar\omega}{2}.$$

Show that at high temperatures E may be expanded as

$$E = kT + \frac{\hbar^2\omega^2}{12kT} + \cdots$$

Identify the terms in this expansion.

The partition function is defined by

$$Z = \sum_{n=0}^{\infty} e^{-\varepsilon_n/kT}.$$

Upon substitution for ε_n we then have

Answers 1.11

$$Z = \sum_{n=0}^{\infty} e^{-\left(\frac{1}{2}+n\right)\hbar\omega/kT}$$

$$= e^{-\hbar\omega/2kT} \sum_{n=0}^{\infty} \left(e^{-\hbar\omega/kT}\right)^n .$$

We observe the second sum here to be a geometric progression, which is easily summed:

$$\sum_{n=0}^{\infty} \left(e^{-\hbar\omega/kT}\right)^n = \frac{1}{1-e^{-\hbar\omega/kT}} .$$

Thus Z is given by

$$Z = \frac{e^{-\hbar\omega/2kT}}{1-e^{-\hbar\omega/kT}}$$

$$= \frac{1}{e^{\hbar\omega/2kT} - e^{-\hbar\omega/2kT}}$$

which we identify to be

$$Z = \frac{1}{2} \operatorname{cosech} \frac{\hbar\omega}{2kT} ,$$

as required.

The internal energy is found from the partition function as

$$E = kT^2 \frac{\partial \ln Z}{\partial T} .$$

Upon differentiation we find

$$\frac{\partial \ln Z}{\partial T} = \frac{\hbar\omega}{2kT^2} \coth \frac{\hbar\omega}{2kT}$$

so that

$$E = \frac{1}{2} \hbar\omega \coth \frac{\hbar\omega}{2kT} = \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} + \frac{\hbar\omega}{2} .$$

The high temperature expansion of this expression may be found using the expansion of the hyperbolic cotangent:

$$\coth x = \frac{1}{x} + \frac{x}{3} - \frac{x^3}{45} + \frac{2x^5}{945} + \dots ,$$

giving

$$E = kT + \hbar\omega \left\{ \frac{1}{12} \frac{\hbar\omega}{kT} - \frac{1}{720} \left(\frac{\hbar\omega}{kT}\right)^3 + \frac{1}{30240} \left(\frac{\hbar\omega}{kT}\right)^5 + \dots \right\} .$$

The first term, kT, is the high-temperature equipartition contribution to the internal energy. There follows a series in inverse powers of T. These give the corrections as the temperature gets lower.