

1.8 Problems for Chapter 1

- 1.1 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 infinity. 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 dM separated by a distance r is given by Newton's law of gravitation

$$F = -G \frac{M dM}{r^2}.$$

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:

$$\begin{aligned} dE &= - \frac{G}{R} \frac{4}{3} \pi R^3 \rho \cdot 4\pi R^2 \rho dR \\ &= -G \frac{16}{3} \pi^2 \rho^2 R^4 dR. \end{aligned}$$

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.

- 1.2 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

$$\begin{aligned} S &= k \ln \Omega \\ &= k \ln \Omega_1 \Omega_2 \\ &= k \ln \Omega_1 + k \ln \Omega_2 \\ &= S_1 + S_2. \end{aligned}$$

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

- 1.3 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*? (Hint: consider the heat capacity.)

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.

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 be positive.

1.4 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

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

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 .

1.5 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 were neglected. Discuss the validity of this.

We derived that

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

where $E = E_T$. We expanded S as a Taylor series:

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

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 third term is then

$$\begin{aligned} \frac{\partial^2 S}{\partial E^2} &= \frac{\partial}{\partial E} \frac{1}{T} \\ &= -\frac{1}{T^2} \frac{\partial T}{\partial E}. \end{aligned}$$

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

$$S(E_T - E) = S(E_T) - \frac{E}{T} - \frac{E^2}{2T^2} \frac{1}{C} - \dots$$

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

The key point of the argument is that the heat 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 heat capacity is essentially infinite. Another way of looking at this is to say that since heat capacity is an extensive quantity then in the limit that the reservoir is large, its heat capacity will be large. Then the inverse of the heat capacity will be small and then the third term in the entropy expansion can be neglected. The higher-order terms involve derivatives of the heat capacity so that these also can be ignored.

- 1.6 The Boltzmann factor might 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

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

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

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

or

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

the higher-order terms don't vanish. 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.

1.7 Show that $\ln N! = \sum_{n=1}^N \ln n$. By approximating this sum by an integral obtain *Stirling's approximation*: $\ln N! \approx N \ln N - N = N \ln(N/e)$.

The factorial is given by

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

so that the logarithm is

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

as required.

Now we approximate the sum by an integral:

$$\sum_{n=1}^N \ln n \approx \int_0^N \ln n \, dn$$

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

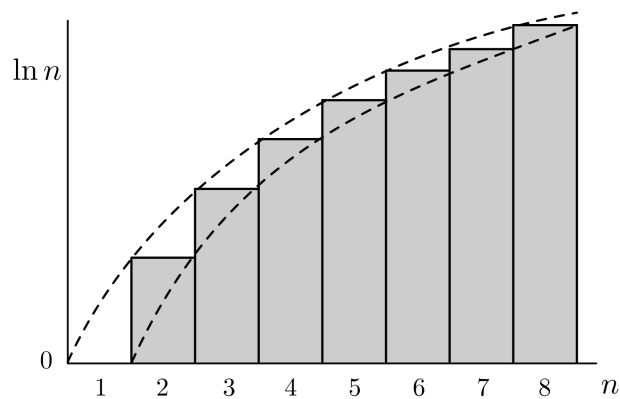


Figure 1.16: Approximating the factorial

Evaluation of the integral gives

$$\int_0^N \ln n \, dn = N \ln N - N$$

so that we obtain the approximation to the factorial:

$$\begin{aligned}\ln N! &= N \ln N - N \\ &= N \ln(N/e).\end{aligned}$$

This is known as Stirling's approximation.

- 1.8 Show that the Gibbs expression for entropy: $S = -k \sum_j P_j \ln P_j$, reduces to the Boltzmann expression $S = k \ln \Omega$ in the case of an isolated system.

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 generalized entropy expression is then

$$\begin{aligned}S &= -k \sum_j P_j \ln P_j \\ &= -k \sum_j \left(\frac{1}{\Omega}\right) \ln \left(\frac{1}{\Omega}\right) \\ &= k \sum_j \left(\frac{1}{\Omega}\right) \ln \Omega.\end{aligned}$$

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.

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

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

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

Show that

$$\sigma_n = (-1)^n \frac{1}{Z e^{\beta \varepsilon}} \frac{\partial^n \{Z e^{\beta \varepsilon}\}}{\partial \beta^n}$$

and use this to prove that the energy fluctuations in an ideal gas, in the thermodynamic limit, follow a *normal distribution*. It will prove to be convenient to take ε as the mean energy. (This is difficult. 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 $(E_j - \varepsilon)$ in the sum:

$$\frac{\partial^n}{\partial \beta^n} \{Z e^{\beta \varepsilon}\} = (-1)^n \sum_j (E_j - \varepsilon)^n e^{-\beta(E_j - \varepsilon)}.$$

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

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

whereupon we observe the right hand side to be $(-1)^n Z \sigma_n$. And thus we find

$$Z \sigma_n = (-1)^n e^{-\beta \varepsilon} \frac{\partial^n}{\partial \beta^n} \{Z e^{\beta \varepsilon}\}$$

or

$$\sigma_n = (-1)^n \frac{1}{Z e^{\beta \varepsilon}} \frac{\partial^n}{\partial \beta^n} \{Z e^{\beta \varepsilon}\}$$

as required.

The ideal gas the partition function Z is given by

$$\begin{aligned} Z &= \left\{ \frac{mkT}{2\pi\hbar^2} \right\}^{3N/2} \left\{ \frac{Ve}{N} \right\}^N \\ &= \left\{ \frac{m}{2\pi\hbar^2\beta} \right\}^{3N/2} \left\{ \frac{Ve}{N} \right\}^N \end{aligned}$$

and it is convenient to factorize out the β dependence thus:

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

Then the n^{th} moment is then

$$\sigma_n = (-1)^n \frac{\left\{ \frac{m}{2\pi\hbar^2} \right\}^{3N/2} \left\{ \frac{V\epsilon}{N} \right\}^N \times \frac{\partial^n}{\partial \beta^n} \beta^{-3N/2} e^{\beta\epsilon}}{\left\{ \frac{m}{2\pi\hbar^2} \right\}^{3N/2} \left\{ \frac{V\epsilon}{N} \right\}^N \times \beta^{-3N/2} e^{\beta\epsilon}}$$

so that all the stuff on the left cancels, giving

$$\sigma_n = (-1)^n \frac{\frac{\partial^n}{\partial \beta^n} \{ \beta^{-3N/2} e^{\beta\epsilon} \}}{\beta^{-3N/2} e^{\beta\epsilon}}.$$

The zeroth moment is, of course, 1. The first moment is evaluated as

$$\begin{aligned} \sigma_1 &= \frac{3N}{2\beta} - \epsilon \\ &= \frac{3}{2}NkT - \epsilon. \end{aligned}$$

Observe that $\frac{3}{2}NkT$ is the internal energy (the mean energy).

At the outset we said that ϵ was an, as yet, un-specified quantity. We now set

$$\epsilon = \frac{3}{2}NkT$$

so that $\sigma_1 = 0$. The resultant moments are referred to as the *central* moments.

The central moments are evaluated by successive differentiation:

$$\begin{aligned} \sigma_0 &= 1 \\ \sigma_1 &= 0 \\ \sigma_2 &= 3N/2\beta^2 \\ \sigma_3 &= 3N/\beta^3 \\ \sigma_4 &= 9N(4 + 3N/4\beta^2) \\ &\text{etc.} \end{aligned}$$

But since we are interested in the thermodynamic limit we need take

only the leading power of N thus

$$\begin{aligned}\sigma_0 &= 1 \\ \sigma_1 &= 0 \\ \sigma_2 &= 3N/2\beta^2 \\ \sigma_3 &= 3N/\beta^3 \\ \sigma_4 &= 27N^2/4\beta^4 \\ \sigma_5 &= 45N^2/\beta^5 \\ \sigma_6 &= 405N^3/8\beta^6 \\ &\text{etc.}\end{aligned}$$

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

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

We find

$$\begin{aligned}m_0 &= 1 \\ m_1 &= 0 \\ m_2 &= 1 \\ m_3 &= \frac{2\sqrt{2}}{3} \frac{1}{\sqrt{N}} \\ m_4 &= 3 \\ m_5 &= \frac{20\sqrt{2}}{3} \frac{1}{\sqrt{N}} \\ m_6 &= 15 \\ &\text{etc.}\end{aligned}$$

In the thermodynamic limit, $N \rightarrow \infty$, the odd reduced moments vanish while the even ones tend to the constant values

$$\begin{aligned}m_0 &= 1 \\ m_2 &= 1 \\ m_4 &= 3 \\ m_6 &= 15 \\ m_8 &= 105 \\ &\text{etc.}\end{aligned}$$

The even reduced moments of the normal distribution are given by

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

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 follow a normal distribution.

- 1.10 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 k th single-particle state.

One starts from the Gibbs factor

$$P_{N,j}(V, T, \mu) = \frac{1}{\Xi(V, T, \mu)} e^{-\{E_{N,j}(N,V) - \mu N\}/kT}.$$

The normalization constant Ξ is the grand partition function:

$$\Xi(V, T, \mu) = \sum_{N,j} e^{-\{E_{N,j}(N,V) - \mu N\}/kT}$$

where N, j specify the j^{th} 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 :

$$(n_1, n_2, n_3, \dots) \equiv \{n_k\}.$$

So in this case the grand partition function is expressed as

$$\begin{aligned} \Xi(V, T, \mu) &= \sum_{\{n_k\}} e^{-\sum_k (\varepsilon_k - \mu) n_k / kT} \\ &= \sum_{\{n_k\}} \prod_k e^{-(\varepsilon_k - \mu) n_k / kT}. \end{aligned}$$

Now the n_k are all *independent*, so that

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

Now we have the definition

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

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

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

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.

- 1.11 What is the condition for the geometric progression in the derivation of the Bose-Einstein distribution to be convergent?

The geometric progression is

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

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.

- 1.12 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 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 generalized 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.

- 1.13 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

$$\begin{aligned} x(t) &= A \sin(\omega t + \varphi) \\ p(t) &= B \cos(\omega t + \varphi) \end{aligned}$$

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

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.

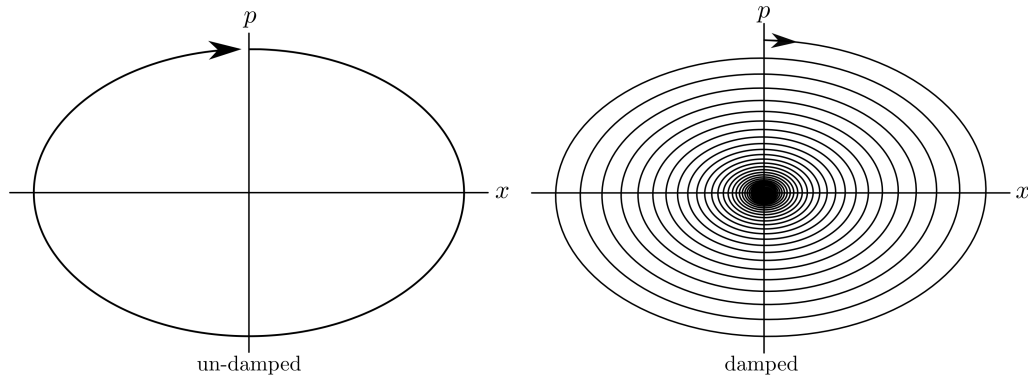


Figure 1.17: Phase trajectory of harmonic oscillator

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

- 1.14 The Fundamental Postulate of classical statistical mechanics states that for an isolated system all available regions of phase space on the constant energy hyper-surface are equally likely.

In terms of this discuss the properties of the phase space of a Boltzmann ensemble of simple harmonic oscillators of identical energy.

For a Boltzmann ensemble each particle is represented by a point in phase space. The phase trajectory of an SHO will be an ellipse. As each SHO has the same energy it will trace out the *same* ellipse. The Fundamental postulate implies that the points will be randomly distributed around the ellipse, with a uniform (mean) density.

- 1.15 A *quartic* oscillator has a potential energy that varies with its displacement as $V(x) = gx^4$. What would be the equipartition thermal energy corresponding to the displacement degree of freedom?

The thermal energy associated with an individual x_i degree of freedom is given from Eq. (1.6.8) as

$$\langle E_i \rangle = -\frac{\partial}{\partial \beta} \ln \int e^{-\beta E(x_i)} dx_i.$$

where $\beta = 1/kT$.

For generality, at this stage, we shall take $E(x_i) = gx_i^n$. We can drop the i subscript and note that x ranges from $-\infty$ to ∞ , so

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln \int_{-\infty}^{\infty} e^{-\beta gx^n} dx.$$

This is one of those cases where a change of variables brings the physics out of the integral. Change the variable of integration to y where

$$y^n = \beta x^n.$$

Here $dx = \beta^{-1/n} dy$ and then the integral becomes

$$\beta^{-1/n} \int_{-\infty}^{\infty} e^{-gy^n} dy$$

so that

$$\begin{aligned} \langle E \rangle &= -\frac{\partial}{\partial \beta} \ln \left(\beta^{-1/n} \int_{-\infty}^{\infty} e^{-gy^n} dy \right) \\ &= -\frac{\partial}{\partial \beta} \left\{ -\frac{1}{n} \ln \beta + \ln \int_{-\infty}^{\infty} e^{-gy^n} dy \right\}. \end{aligned}$$

The second term is independent of β so upon differentiation it vanishes. Now differentiating we obtain

$$\langle E \rangle = \frac{1}{n\beta}$$

or, in terms of T :

$$\langle E \rangle = \frac{1}{n} kT.$$

This problem asks for the thermal energy corresponding to a *quartic* degree of freedom, $n = 4$, so we have, finally

$$\langle E \rangle = \frac{1}{4} kT.$$

- 1.16 Consider a particle subject to a hypothetical confining potential $V(x) = gx^n$ (where n is even and positive).

- (a) Calculate the heat capacity of a collection of such particles as a function of n .
- (b) Show that in the limit $n \rightarrow \infty$ the heat capacity tends to that for a free particle.
- (c) Comment on this limit – in the context of a gas of free particles.

(a) The solution to the previous question gives the contribution to the equipartition energy from a degree of freedom varying with x as gx^n as

$$\frac{1}{n}kT. \quad (1.8.1)$$

The particles will have the conventional kinetic energy (quadratic in p) also. So the internal energy of N such particles will be, in total

$$E = \frac{1}{2}NkT + \frac{1}{n}NkT; \quad (1.8.2)$$

the first term being the kinetic energy contribution and the second term the potential energy contribution.

The heat capacity is the temperature derivative of this:

$$C = \frac{1}{2}Nk + \frac{1}{n}Nk.$$

- (b) As $n \rightarrow \infty$ the potential energy term vanishes so we have contribution only from the kinetic energy – just as for free particles.
- (c) The point is that as n gets larger (even n) the confining potential becomes steeper and squarer: more like a rigid wall box potential.

1.17 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 expressed 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

$$G = N\mu.$$

- 1.18 Use the definition of the Gibbs free energy together with the result of the previous question, Problem 1.17, to obtain the Euler relation of Appendix A.2:

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

The Gibbs free energy 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.

- 1.19 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 equipartition will give a classical internal energy of kT .

The energy levels of the quantum harmonic oscillator are given by $\varepsilon_n = (\frac{1}{2} + n)\hbar\omega$.

(a) Show that the partition function of this system is given by

$$Z = \frac{1}{2} \operatorname{cosech} \frac{\hbar\omega}{2kT} \quad (1.8.3)$$

and that the internal energy is given by

$$E = \frac{1}{2} \hbar\omega \coth \frac{\hbar\omega}{2kT} = \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} + \frac{\hbar\omega}{2}. \quad (1.8.4)$$

(b) Show that at high temperatures E may be expanded as

$$E = kT + \frac{\hbar^2\omega^2}{12kT} + \dots \quad (1.8.5)$$

(c) Identify the terms in this expansion.

(a) The partition function is defined by

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

Upon substitution for ε_n we then have

$$\begin{aligned} Z &= \sum_{n=0}^{\infty} e^{-(\frac{1}{2}+n)\hbar\omega/kT} \\ &= e^{-\hbar\omega/2kT} \sum_{n=0}^{\infty} (e^{-\hbar\omega/kT})^n. \end{aligned}$$

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

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

Thus Z is given by

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

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

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

(b) 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

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

(c) 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.