

## 24

# Quantum Canonical Ensemble

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*I do not like it, and I am sorry I ever had anything to do with it.*

Erwin Schrödinger, Austrian physicist (1887–1961), Nobel Prize 1933,  
speaking about quantum mechanics.

The quantum canonical ensemble, like its classical counterpart, which was discussed in Chapter 19, describes the behavior of a system in contact with a thermal reservoir. As in the classical case, the detailed nature of the reservoir is not important; it must only be big. This is partly to allow us to expand the entropy in powers of the ratio of the size of the system to that of the reservoir, and also to allow us to treat the eigenvalue spectrum of the reservoir as continuous.

We have already seen in Chapter 21 that the canonical entropy gives an improved expression for the entropy of a classical system. This is also true of the quantum canonical entropy, which has the advantage of being defined on a continuum of energy values, instead of just being defined on the eigenvalues of the Hamiltonian.

An important thing to notice about quantum statistical mechanics as you go through the following chapters is that the same ideas and equations keep showing up to solve different problems. In particular, the solution to the quantum simple harmonic oscillator (QSHO) turns out to be the key to understanding crystal vibrations, black-body radiation, and Bose–Einstein statistics. The basic calculation for the QSHO is discussed in Section 24.10; if you understand it completely, the topics in Chapters 25 through 28 will be much easier. The other kind of calculation that will appear repeatedly is one in which there are only a small number of quantum energy levels. Indeed, in the most important case there are only two energy levels. This might seem like a very limited example, but it provides the essential equations for Chapters 27, 29, and 31.

## 24.1 Derivation of the QM Canonical Ensemble

The derivation of the quantum canonical ensemble follows the same pattern as the derivation of the classical canonical ensemble in Section 19.3.

Let an eigenstate  $|n\rangle$  for the system of interest have energy  $E_n$  and the reservoir have energy  $E_R$ , so that the total energy is  $E_T = E_n + E_R$ . Let  $\Omega_R(E_R) = \Omega_R(E_T - E_n)$  be the degeneracy (number of eigenstates) of the energy level  $E_R$  in the reservoir. The ‘probability’  $P_n$  of an eigenstate with energy  $E_n$  in the system of interest is then given by:

$$P_n = \frac{\Omega_R(E_T - E_n)}{\Omega_T(E_T)}. \quad (24.1)$$

As we did in Section 19.3, take the logarithm of both sides and use the fact that  $E_T \gg E_n$  to expand  $\ln \Omega_R(E_T - E_n)$  in powers of  $E_n/E_T$ ,

$$\begin{aligned} \ln P_n &= \ln \Omega_R(E_T - E_n) - \ln \Omega_T(E_T) \\ &\approx \ln \Omega_R(E_T) - E_n \frac{\partial}{\partial E_T} \ln \Omega_R(E_T) - \ln \Omega_T(E_T). \end{aligned} \quad (24.2)$$

The approximation becomes exact in the limit of an infinite reservoir. In practice, the error due to using finite reservoirs is so small, that we will ignore the higher-order terms and use an equal sign for simplicity.

In analogy to the classical derivation in Section 19.3, we identify

$$\beta = \frac{1}{k_B T} = \frac{\partial}{\partial E_T} \ln \Omega_R(E_T), \quad (24.3)$$

so that we can write eq. (24.2) as

$$\ln P_n = -\ln Z - \beta E_n, \quad (24.4)$$

or

$$P_n = \frac{1}{Z} \exp(-\beta E_n), \quad (24.5)$$

where

$$-\ln Z = \ln \Omega_R(E_T) - \ln \Omega_T(E_T). \quad (24.6)$$

The normalization factor  $Z$  is known as the quantum mechanical partition function (in analogy to the classical partition function) and can be evaluated by summation over all eigenstates,

$$Z = \sum_n \exp(-\beta E_n). \quad (24.7)$$

Note that the quantum Boltzmann factor  $\exp(-\beta E_n)$  plays the same role as the classical Boltzmann factor in eq. (19.17). The quantum mechanical partition function plays the same role as the classical partition function.

Eq. (24.7) is often used as a starting point in textbooks on quantum statistical mechanics because of its simplicity. Unfortunately, its validity and significance are not completely obvious without an explanation. It is a good starting point for many calculations in quantum statistical mechanics. However, a problem arises if we consider a quantum theory of distinguishable particles. A common procedure is to ignore this possibility, but since a quantum theory of colloidal particles (which are distinguishable) should make sense, we will include this case in a later chapter. It should not come as a surprise that a factor of  $1/N!$  will play a role in the discussion, and eq. (24.7) will have to be modified to include the factor of  $1/N!$  explicitly.

It is often convenient to reexpress eq. (24.7) in terms of the energy levels. In that case, we must include the degeneracy  $\Omega(\ell)$  for each energy level  $\ell$ ,

$$Z = \sum_{\ell} \Omega(\ell) \exp(-\beta E_{\ell}). \quad (24.8)$$

It is essential to remember that in eq. (24.7) the index  $n$  runs over the quantum numbers for the eigenstates of the system—not the energy levels—and that you need to include the degeneracy as in eq. (24.8) if you are summing over energy levels.

## 24.2 Thermal Averages and the Average Energy

Combining eq. (24.7) with eq. (23.35), we find a very useful expression for the average of an operator  $\mathcal{A}$  in the canonical ensemble, that is, at a temperature  $T = 1/k_B\beta$ ,

$$\langle \mathcal{A} \rangle = \sum_n P_n \langle n | \mathcal{A} | n \rangle. \quad (24.9)$$

Inserting the expression for  $P_n$  from eq. (24.5), this becomes

$$\langle \mathcal{A} \rangle = \frac{1}{Z} \sum_n \langle n | \mathcal{A} | n \rangle \exp(-\beta E_n). \quad (24.10)$$

A particularly important case is the average energy

$$U = \langle H \rangle = \frac{1}{Z} \sum_n \langle n | H | n \rangle \exp(-\beta E_n) = \frac{1}{Z} \sum_n E_n \exp(-\beta E_n). \quad (24.11)$$

## 24.3 The Quantum Mechanical Partition Function

Although the partition function  $Z$  was introduced simply as a normalization factor in eq. (24.7), it turns out to be very useful in its own right in the same way that the classical

partition function was found to be useful in Chapter 19. As in the classical case, the partition function in eq. (24.7) depends on the temperature as  $\beta = 1/k_B T$ . If we take the derivative of the logarithm of the partition function, we find

$$\left(\frac{\partial}{\partial \beta} \ln Z\right)_{V,N} = \frac{1}{Z} \left(\frac{\partial}{\partial \beta} \sum_n \exp(-\beta E_n)\right)_{V,N} = \frac{1}{Z} \sum_n (-E_n) \exp(-\beta E_n) = -U. \quad (24.12)$$

If we compare this equation to the thermodynamic identity

$$\left(\frac{\partial(\beta F)}{\partial \beta}\right)_{V,N} = U, \quad (24.13)$$

we see that we can integrate it to obtain

$$\ln Z = -\beta F + f(V, N), \quad (24.14)$$

in which the function  $f(V, N)$  has not yet been determined.

To determine the function  $f(V, N)$ , first consider the derivative of

$$F = -k_B T [\ln Z - f(V, N)], \quad (24.15)$$

with respect to temperature,

$$\begin{aligned} \left(\frac{\partial F}{\partial T}\right)_{V,N} &= -k_B [\ln Z - f(V, N)] - k_B T \frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta} \ln Z \\ &= -k_B [-\beta F] - k_B T \left(\frac{-1}{k_B T^2}\right) (-U) \\ &= \frac{1}{T} (F - U) = \frac{1}{T} (U - TS - U) = -S. \end{aligned} \quad (24.16)$$

Clearly, the function  $f(V, N)$  has no effect on either the energy or the entropy.

Next consider the derivative of  $F$  with respect to volume,

$$\begin{aligned} \left(\frac{\partial F}{\partial V}\right)_{T,N} &= -k_B T \left[ \frac{\partial}{\partial V} \ln Z - \frac{\partial}{\partial V} f(V, N) \right] \\ &= -k_B T \frac{1}{Z} \sum_n \left( -\beta \frac{\partial E_n}{\partial V} \right) \exp(-\beta E_n) - k_B T \frac{\partial f}{\partial V} \\ &= \frac{1}{Z} \sum_n \left( \frac{\partial E_n}{\partial V} \right) \exp(-\beta E_n) - k_B T \frac{\partial f}{\partial V}. \end{aligned} \quad (24.17)$$

Now we need the relationship between the pressure the system would have in an eigenstate, and the partial derivative of the energy of that eigenstate with respect to the volume. To avoid confusion with  $P_n$  defined earlier in this section, we will denote the pressure of the system in an eigenstate by  $P(|n\rangle)$ ,

$$P(|n\rangle) = - \left( \frac{\partial E_n}{\partial V} \right)_{T,N}. \quad (24.18)$$

Combining eqs. (24.17) and (24.18), we find

$$\left( \frac{\partial F}{\partial V} \right)_{T,N} = - \frac{1}{Z} \sum_n P(|n\rangle) \exp(-\beta E_n) - k_B T \frac{\partial f}{\partial V} = -P, \quad (24.19)$$

where  $P$  is the average pressure. Since  $P$  must be given by the weighted average of the pressures in the eigenstates,

$$P = \frac{1}{Z} \sum_n P(|n\rangle) \exp(-\beta E_n), \quad (24.20)$$

the partial derivative of  $f(V, N)$  with respect to  $V$  must vanish;  $f$  can only be a function of  $N$ ,

$$f(V, N) = f(N). \quad (24.21)$$

At this point, we would need to examine the  $N$ -dependence of the energy eigenvalues, but this is best done later in the context of the discussion of the quantum ideal gas and the exchange of particles with a reservoir. For the time being we will tentatively assign the value zero to the function  $f(N)$ . This will turn out to be a valid choice for fermions or bosons, but not for distinguishable particles.

The (tentative) choice of  $f(N) = 0$  has the great advantage of simplifying eq. (24.14) and giving it the same form as in classical statistical mechanics:

$$\ln Z = -\beta F, \quad (24.22)$$

or

$$Z = \exp(-\beta F). \quad (24.23)$$

As noted in the first box in Section 24.1, the case of distinguishable particles has to be handled rather differently. We will see in Section 27.9 that the proper choice for a system of distinguishable particles is  $f(N) = -\ln(N!)$ .

## 24.4 The Quantum Mechanical Entropy

The expression for the entropy can also be written in another form, which is both useful and revealing.

As in eq. (24.16), take the derivative of the free energy with respect to temperature to find the (negative) entropy, but now set  $f(V, N) = 0$ ,

$$\begin{aligned} \left( \frac{\partial F}{\partial T} \right)_{V,N} &= -k_B \ln Z - k_B T \left( \frac{-1}{k_B T^2} \right) \frac{\partial}{\partial \beta} \ln Z \\ &= -k_B \ln Z + \frac{1}{TZ} \sum_n (-E_n) \exp(-\beta E_n). \end{aligned} \quad (24.24)$$

In the second line of this equation we have used eq. (24.7) to express the derivative of the partition function in terms of a sum. Now recall from eq. (24.5) that

$$P_n = \frac{1}{Z} \exp(-\beta E_n), \quad (24.25)$$

or

$$\ln P_n = -\ln Z - \beta E_n, \quad (24.26)$$

and, of course,

$$\sum_n P_n = \frac{1}{Z} \sum_n \exp(-\beta E_n) = 1. \quad (24.27)$$

Eq. (24.24) can now be written as

$$\begin{aligned} \left( \frac{\partial F}{\partial T} \right)_{V,N} &= -k_B \left[ \ln Z \sum_n P_n - \frac{\beta}{Z} \sum_n (-E_n) \exp(-\beta E_n) \right] \\ &= -k_B \sum_n [P_n \ln Z + \beta E_n P_n] \\ &= k_B \sum_n P_n \ln P_n = -S, \end{aligned} \quad (24.28)$$

which gives us an alternative expression for the entropy

$$S = -k_B \sum_n P_n \ln P_n. \quad (24.29)$$

Eq. (24.29) is often taken as a fundamental starting point in books on statistical mechanics. Its simplicity is certainly an advantage of this choice. Nevertheless, the validity of this equation is not really obvious without a derivation such as the one given above.

## 24.5 The Origin of the Third Law of Thermodynamics

An important consequence of eq. (24.29) is that since  $1 \geq P_n \geq 0$  and  $\ln P_n \leq 0$ , the entropy is always positive. This implies that the limit of the entropy as the temperature goes to zero is non-negative. Since the entropy at  $T = 0$  must be a constant, and not minus infinity as it is in classical statistical mechanics, this establishes the Nernst Postulate, or Third Law of Thermodynamics, as a general consequence of quantum mechanics.

To investigate the value of the entropy at  $T = 0$ , we note that

$$P_n = \frac{1}{Z} \exp(-\beta E_n) = \frac{\exp(-\beta E_n)}{\sum_n \exp(-\beta E_n)}. \quad (24.30)$$

If we express the partition function in terms of energy levels indexed by  $\ell$ , we can write

$$Z = \sum_{\ell} \Omega(\ell) \exp(-\beta E_{\ell}), \quad (24.31)$$

where  $\Omega(\ell)$  is the degeneracy of the  $\ell$ th level.

Let  $\ell = 0$  be the lowest energy level, so that  $\Omega(0)$  is the degeneracy of the ground state. Eq. (24.31) can then be written as

$$Z = \Omega(0) \exp(-\beta E_0) \left[ 1 + \sum_{\ell > 0} \left( \frac{\Omega(\ell)}{\Omega(0)} \right) \exp(-\beta(E_{\ell} - E_0)) \right]. \quad (24.32)$$

Since  $\ell = 0$  is the lowest energy level,  $E_{\ell} - E_0 > 0$ , for all  $\ell > 0$ . That implies that as  $T \rightarrow 0$ , the ground state probability,  $P_0$ , is given by

$$\begin{aligned} \lim_{T \rightarrow 0} P_0 &= \lim_{T \rightarrow 0} \left( \frac{\exp(-\beta E_0)}{\Omega(0) \exp(-\beta E_0) \left[ 1 + \sum_{\ell > 0} \left( \frac{\Omega(\ell)}{\Omega(0)} \right) \exp(-\beta(E_{\ell} - E_0)) \right]} \right) \\ &= \frac{1}{\Omega(0)} \lim_{T \rightarrow 0} \left[ 1 + \sum_{\ell > 0} \left( \frac{\Omega(\ell)}{\Omega(0)} \right) \exp(-\beta(E_{\ell} - E_0)) \right]^{-1} \\ &= \frac{1}{\Omega(0)}, \end{aligned} \quad (24.33)$$

and the probability of any higher level with  $E_\ell > E_0$  is

$$\begin{aligned}\lim_{T \rightarrow 0} P_\ell &= \lim_{T \rightarrow 0} \left( \frac{\exp(-\beta E_\ell)}{\Omega(0) \exp(-\beta E_0) \left[ 1 + \sum_{\ell' > 0} \left( \frac{\Omega(\ell')}{\Omega(0)} \right) \exp(-\beta(E_{\ell'} - E_0)) \right]} \right) \\ &= \frac{\exp(-\beta(E_\ell - E_0))}{\Omega(0)} \lim_{T \rightarrow 0} \left[ 1 + \sum_{\ell' > 0} \left( \frac{\Omega(\ell')}{\Omega(0)} \right) \exp(-\beta(E_{\ell'} - E_0)) \right]^{-1} \\ &= 0.\end{aligned}\quad (24.34)$$

Now return to eq. (24.29) for the entropy in terms of the set of ‘probabilities’  $\{P_n\}$ . Since it is well known that  $\lim_{x \rightarrow 0} (x \ln x) = 0$ , we can see that

$$\lim_{T \rightarrow 0} S(T) = -k_B \Omega(0) \frac{1}{\Omega(0)} \ln \frac{1}{\Omega(0)} = k_B \ln \Omega(0). \quad (24.35)$$

If the ground state is non-degenerate,  $\Omega(0) = 1$ , and  $S(T = 0) = 0$ . Otherwise, it is a positive number.

We are often interested in the entropy per particle, rather than the total entropy. At zero temperature,  $S(T = 0)/N$ , is given by

$$\frac{S(T = 0)}{N} = \frac{k_B \ln \Omega(0)}{N}. \quad (24.36)$$

If  $\Omega(0)$  does not depend on the size of the system, the entropy per particle vanishes as the system size diverges. For a finite but macroscopic system, the entropy per site at zero temperature is non-zero, but immeasurably small. This is the origin of the Planck formulation of the Nernst Postulate (or Third Law of Thermodynamics), which requires the entropy to be zero at  $T = 0$ .

However, there is another possibility. Suppose that the degeneracy of the ground state depends on the size of the system as,

$$\Omega(0) = a^N, \quad (24.37)$$

where  $a > 1$  is some positive constant. Then the zero-temperature entropy per particle is given by

$$\frac{S(T = 0)}{N} = \frac{k_B \ln a^N}{N} = k_B \ln a > 0. \quad (24.38)$$

This would violate the Planck formulation of the Nernst Postulate, but Nernst’s original formulation would still be valid.



The possibility suggested by eq. (24.38) actually occurs, both in model calculations and real experiments. The essential feature of a system that exhibits  $S(T=0)/N > 0$  is a disordered ground state. This is true of normal window glass, and has been confirmed by experiment. It is also true of an interesting class of materials called ‘spin glasses’, which are formed when a small fraction of a magnetic atom (such as iron) is dissolved in a non-magnetic material (such as copper). For reasons that go beyond the scope of this book, the ground state of this system is highly disordered, leading to a large number of very low-lying energy levels. Although the ground-state degeneracy for these materials does not strictly follow eq. (24.37), the predicted zero-temperature limit  $S(T=0)/N > 0$  is found experimentally. There are simple models of spin glasses for which the inequality in eq. (24.38) can be shown to be exactly correct.

## 24.6 Derivatives of Thermal Averages

Since the partition function depends on the temperature in a simple way, we can express derivatives of thermal averages with respect to  $T$  or  $\beta$  in terms of fluctuations. This extremely useful mathematical technique has already been discussed for the classical case in Section 19.8.

For simplicity, begin with derivatives with respect to  $\beta$ . Eq. (24.10) gives the formal expression for the thermal average  $\langle \mathcal{A} \rangle$ ,

$$\langle \mathcal{A} \rangle = \frac{1}{Z} \sum_n \langle n | \mathcal{A} | n \rangle \exp(-\beta E_n). \quad (24.39)$$

The partial derivative of  $\langle \mathcal{A} \rangle$  with respect to  $\beta$  gives the equation

$$\begin{aligned} \frac{\partial}{\partial \beta} \langle \mathcal{A} \rangle &= -\frac{1}{Z} \frac{\partial Z}{\partial \beta} \langle \mathcal{A} \rangle + \frac{1}{Z} \sum_n \langle n | \mathcal{A} | n \rangle (-E_n) \exp(-\beta E_n) \\ &= \langle \mathcal{A} \rangle \langle H \rangle - \langle \mathcal{A} H \rangle. \end{aligned} \quad (24.40)$$

This result is completely general.

Applying eq. (24.40) to the thermal average of the energy, we find

$$\frac{\partial}{\partial \beta} \langle H \rangle = \frac{\partial U}{\partial \beta} = -[\langle H^2 \rangle - \langle H \rangle^2].$$

The derivative of the energy with respect to  $\beta$  is given by the negative of the variance of the energy.

If we apply this equation to the calculation of the specific heat, we find

$$c_V = \frac{1}{N} \frac{\partial U}{\partial T} = \frac{1}{N} \frac{\partial \beta}{\partial T} \frac{\partial U}{\partial \beta} = \frac{1}{N k_B T^2} [\langle H^2 \rangle - \langle H \rangle^2]. \quad (24.41)$$

The proportionality between the specific heat and the variance of the energy is exactly the same in quantum and classical mechanics. (We derived the classical version in Section 19.9.)

The relationship between thermal fluctuations and thermodynamic derivatives is both deep and powerful. Using it can make seemingly difficult calculations become very easy. It is particularly useful in computer simulations.

## 24.7 Factorization of the Partition Function

The best trick in quantum statistical mechanics corresponds directly to the best trick in classical statistical mechanics, which was discussed in Section 19.12. In both cases, the form of the Hamiltonian allows us to factor the partition function, transforming a many-dimensional problem into many low-dimensional problems.

It is quite common to encounter problems in which the Hamiltonian can—at least approximately—be written as a sum of  $N$  terms

$$H = \sum_{j=1}^N H_j, \quad (24.42)$$

where the terms  $H_j$  all commute with one another. If this is true, the eigenvalue equation for  $H_j$  is

$$H_j |n_j\rangle = E_{n_j} |n_j\rangle, \quad (24.43)$$

and the eigenvector of the full system can be written as,

$$|n\rangle = \prod_{k=1}^N |n_k\rangle, \quad (24.44)$$

where we have used the index  $n$  to denote the full set of quantum numbers,

$$n \equiv \{n_j | j = 1, \dots, N\}. \quad (24.45)$$

Since the term  $H_j$  only acts on  $|n_j\rangle$ ,

$$H_j |n\rangle = E_{n_j} \prod_{k=1}^N |n_k\rangle = E_{n_j} |n\rangle. \quad (24.46)$$

The full eigenvalue equation becomes,

$$H |n\rangle = \sum_{j=1}^N H_j \prod_{k=1}^N |n_k\rangle = \sum_{j=1}^N E_{n_j} \prod_{k=1}^N |n_k\rangle = \sum_{j=1}^N E_{n_j} |n\rangle = E_n |n\rangle, \quad (24.47)$$

where

$$E_n = \sum_{j=1}^N E_{n_j}. \quad (24.48)$$

We can use eq. (24.48) to cast the partition function in a very convenient form:

$$\begin{aligned} Z &= \sum_{\{n_j\}} \exp \left( -\beta \sum_{j=1}^N E_{n_j} \right) \\ &= \sum_{\{n_j\}} \prod_{j=1}^N \exp(-\beta E_{n_j}) \\ &= \sum_{n_N} \exp(-\beta E_{n_N}) \cdots \sum_{n_2} \exp(-\beta E_{n_2}) \sum_{n_1} \exp(-\beta E_{n_1}) \\ &= \prod_{j=1}^N \left( \sum_{n_j} \exp(-\beta E_{n_j}) \right). \end{aligned} \quad (24.49)$$

Because this equation turns out to be extremely useful, we will repeat it without the intermediate steps,

$$Z = \sum_{\{n_j\}} \prod_{j=1}^N \exp(-\beta E_{n_j}) = \prod_{j=1}^N \left( \sum_{n_j} \exp(-\beta E_{n_j}) \right). \quad (24.50)$$

This form of the partition function allows us to factor it into a product of terms, each of which is much easier to evaluate than the original expression. Just as for the corresponding equation in classical mechanics (see Section 19.12), difficult problems can become very easy by using eq. (24.50).

Because of the importance of eq. (24.50) and the frequency with which it is used, we should call attention to a mental hazard associated with it that can catch the unwary. In eq. (24.50) we are exchanging a sum and a product,

$$\sum_{\{n_j\}} \prod_{j=1}^N \longleftrightarrow \prod_{j=1}^N \sum_{n_j}.$$

However, the sums on the right and left sides of the equation are *not* over the same quantum numbers. The sum on the right,  $\sum_{n_j}$ , is only over the quantum numbers associated with the term  $H_j$  in the Hamiltonian. The sum on the left,  $\sum_{\{n_j\}}$ , is over the set of all quantum numbers for the entire system. In the heat of battle

*continued*

(while taking a test), it is not unusual to forget to write the indices of sums and products explicitly. Omitting the indices is always a bad way to save time, but it can be especially dangerous when using eq. (24.50).

We are now in a position to see why eq. (24.50) is so valuable. From eq. (24.22), the free energy is given by the logarithm of the partition function. When the Hamiltonian has the form given in eq. (24.42), the free energy becomes particularly simple,

$$\begin{aligned}
 F &= -k_B T \ln Z = -k_B T \ln \sum_{\{n_j\}} \prod_{j=1}^N \exp(-\beta E_{n_j}) \\
 &= -k_B T \ln \prod_{j=1}^N \left( \sum_{n_j} \exp(-\beta E_{n_j}) \right) \\
 &= -k_B T \sum_{j=1}^N \ln \left( \sum_{n_j} \exp(-\beta E_{n_j}) \right). \tag{24.51}
 \end{aligned}$$

Since the sums in the last line of this equation are only over a single quantum number, rather than all combinations of  $N$  quantum numbers, they are much easier to carry out.

If the spectrum of eigenvalues is the same for every term  $H_j$ , eq. (24.50) simplifies further,

$$F = -k_B T N \ln \sum_{n_1} \exp(-\beta E_{n_1}). \tag{24.52}$$

The calculation of Helmholtz free energy of the  $N$ -body system is reduced to the calculation of the free energy of a one-body system, which is much easier.

## 24.8 Special Systems

In the following sections we will discuss the simplest examples of component systems that we might find *after* factorization. These examples are important because they occur repeatedly in quantum statistical mechanics. We will see applications of the same mathematical forms in the analysis of magnets, vibrations in crystals, black-body radiation, fermions, and bosons. Consequently, these examples are to be studied very carefully; if you know them well, most of the mathematics in the rest of the book will be easy.

There are a number of many-body systems for which the partition function can be easily found because they have a small number of energy levels. For such systems, it is an easy matter to sum up a small number of terms to obtain the partition function.

There are two classes of systems that are so important in the development of statistical mechanics that we will devote the remaining sections in this chapter to their analysis. These systems are simple harmonic oscillators and any system with only two energy eigenstates.

## 24.9 Two-Level Systems

The simplest imaginable quantum system would have only one state—but it would not be very interesting.

The next simplest system has two quantum eigenstates for each element making up the system. There are two forms in which we will encounter a two-level system. The mathematics is essentially the same in both cases, but since the usual ways of expressing the results differ, they are both worth studying.

Because two-level systems can support negative temperatures, it is appropriate to use Massieu functions in their analysis.

### 24.9.1 Energies 0 and $\epsilon$

The first form for a two-level system assigns the energies 0 and  $\epsilon$  to the levels. Letting the quantum number  $n$  take on the values of 0 and 1, the Hamiltonian is simply

$$H = \epsilon n. \quad (24.53)$$

The partition function contains just two terms,

$$Z = \sum_{n=0}^1 \exp(-\beta \epsilon n) = 1 + \exp(-\beta \epsilon). \quad (24.54)$$

The Massieu function,  $\tilde{S}[\beta]$ , and the energy are easily found,

$$\tilde{S}[\beta] = \ln Z = \ln(1 + \exp(-\beta \epsilon)) \quad (24.55)$$

$$U = -\frac{\partial \tilde{S}[\beta]}{\partial \beta} = \frac{\epsilon \exp(-\beta \epsilon)}{1 + \exp(-\beta \epsilon)} = \frac{\epsilon}{\exp(\beta \epsilon) + 1}. \quad (24.56)$$

Note that the average value of the quantum number  $n$  (average number of excitations in the system) is given by

$$\langle n \rangle = \sum_{n=0}^1 n \frac{1}{Z} \exp(-\beta \epsilon n) = \frac{0 + \exp(-\beta \epsilon)}{1 + \exp(-\beta \epsilon)} = \frac{1}{\exp(\beta \epsilon) + 1}, \quad (24.57)$$

which is consistent with the average value of the energy

$$U = \langle H \rangle = \sum_{n=0}^1 H \frac{1}{Z} \exp(-\beta \epsilon n) = \sum_{n=0}^1 \epsilon n \frac{1}{Z} \exp(-\beta \epsilon n) = \epsilon \langle n \rangle. \quad (24.58)$$

It will be very important to remember the expression for  $\langle n \rangle$  given in eq. (24.57), and *especially the positive sign of the exponent in the denominator*. Because the usual Boltzmann factor  $\exp(-\beta H)$  contains a negative sign, confusing the sign is a well-known mental hazard.

To express the Planck entropy for the full  $N$ -body system, first note that the energy of the  $\ell$ -th level is  $\epsilon \ell$ . The Planck entropy of the two-level of the  $N$  two-level objects is then

$$S_{P,2\text{-level}} = k_B \ln \left( \frac{N!}{\ell!(N-\ell)!} \right). \quad (24.59)$$

This expression is not exactly extensive, even though it should be since the system is composed of  $N$  independent objects. It is also defined only for energies that are integer multiples of  $\epsilon$ . In the limit of infinite  $N$ , it agrees with the canonical entropy, which is given next.

The canonical entropy for the full  $N$ -body is

$$S_{C,2\text{-level}} = -Nk_B [y \ln y + (1-y) \ln(1-y)], \quad (24.60)$$

where,

$$y = \frac{U_{2\text{-level}}}{N\epsilon}. \quad (24.61)$$

It is obviously exactly extensive and a continuous function of energy. The derivation of this expression is the subject of Problem 24.4.

### 24.9.2 Spin-One-Half

The second form in which we encounter two-level systems is related to magnetism. If the operator  $\sigma$  takes on the values  $+1$  and  $-1$  (ignoring factors of Planck's constant), the Hamiltonian,

$$H = -b\sigma, \quad (24.62)$$

corresponds to a spin-one-half magnetic moment in a magnetic field  $b$ . In this equation  $b$  has units of energy, which makes life easier.

The partition function again contains just two terms:

$$Z = \sum_{\sigma=\pm 1} \exp(-\beta(-b\sigma)) = \exp(\beta b) + \exp(-\beta b). \quad (24.63)$$

The free energy and the energy are again easily found,

$$\tilde{S}[\beta] = \ln Z = \ln [\exp(\beta b) + \exp(-\beta b)] \quad (24.64)$$

$$U = -\frac{\partial(\tilde{S}[\beta])}{\partial \beta} = -b \left( \frac{\exp(\beta b) - \exp(-\beta b)}{\exp(\beta b) + \exp(-\beta b)} \right) = -b \tanh(\beta b). \quad (24.65)$$

Note that the average value of  $\sigma$  (average magnetization) is given by

$$\langle \sigma \rangle = \sum_{\sigma=\pm 1} \sigma \frac{1}{Z} \exp(\beta b \sigma) = \frac{\exp(\beta b) - \exp(-\beta b)}{\exp(\beta b) + \exp(-\beta b)} = \tanh(\beta b), \quad (24.66)$$

which is consistent with the average value of the energy.

It is traditional to use the hyperbolic tangent in magnetic problems and the exponential sums for other two-level systems. The two forms are, of course, equivalent. The mathematical expressions

$$\tanh x = \frac{e^x - e^{-x}}{e^x + e^{-x}} = \frac{1 - e^{-2x}}{1 + e^{-2x}}, \quad (24.67)$$

are good choices for memorization.

The Planck entropy can be easily obtained from eq. (24.59), and the canonical entropy from eq. (24.60).

## 24.10 Simple Harmonic Oscillator

The Hamiltonian of a simple harmonic oscillator (SHO) in one dimension is given by

$$H = \frac{1}{2} K x^2 + \frac{p^2}{2m} = \frac{1}{2} K x^2 - \frac{\hbar^2}{2m} \frac{d^2}{dx^2}, \quad (24.68)$$

where  $m$  is the mass of the particle and  $K$  is the spring constant.

The energy spectrum for a simple harmonic oscillator (SHO) has an infinite number of states, labeled by a quantum number that takes on non-negative integer values,  $n = 0, 1, \dots, \infty$ ,

$$E_n = \hbar \omega \left( n + \frac{1}{2} \right). \quad (24.69)$$

The angular frequency,  $\omega$ , in eq. (24.69) is identical to the classical value,

$$\omega = \sqrt{\frac{K}{m}}. \quad (24.70)$$

Even though there is an infinite number of states, the uniform spacing makes the evaluation of the partition function only slightly more difficult than for a two-level system,

$$\begin{aligned} Z &= \sum_{n=0}^{\infty} \exp(-\beta \hbar \omega (n + 1/2)) \\ &= \frac{\exp(-\beta \hbar \omega / 2)}{1 - \exp(-\beta \hbar \omega)}. \end{aligned} \quad (24.71)$$

Sums of the form

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$$

for  $|x| < 1$ , occur frequently in quantum statistical mechanics. The savvy student should expect it to appear on tests—and not only know it, but know how to derive it.

[Hint:  $y = \sum_{n=0}^{\infty} x^n$ ,  $xy = y - 1$ ]

For high temperatures (small  $\beta$ ), we expect the partition function to go to the classical value,  $Z_{\text{class}} = 1/(\hbar\beta\omega)$ , as found in Section 19.13,

$$\begin{aligned} Z &= \frac{\exp(-\beta \hbar \omega / 2)}{1 - \exp(-\beta \hbar \omega)} \\ &\rightarrow (1 - \beta \hbar \omega / 2 + \cdots) \left[ 1 - \left( 1 - \beta \hbar \omega + \frac{1}{2}(\beta \hbar \omega)^2 + \cdots \right) \right]^{-1} \\ &\rightarrow \frac{1}{\beta \hbar \omega} \left( \frac{1 - \beta \hbar \omega / 2 + \cdots}{1 - \beta \hbar \omega / 2 + \cdots} \right) \\ &\rightarrow \frac{1}{\beta \hbar \omega}. \end{aligned} \quad (24.72)$$

This agreement between the classical and quantum results for an SHO is the basic justification for the inclusion of the factors involving  $1/h$  (where  $h$  is Planck's constant) in the classical definitions of the entropy in eqs. (7.3) and (7.30), and the partition function in eq. (19.27).



Returning to the full quantum partition function given in eq. (24.71), we can easily obtain the free energy and the energy,

$$\begin{aligned} F &= -k_B T \ln Z \\ &= -k_B T \ln \exp(-\beta \hbar \omega / 2) + k_B T \ln(1 - \exp(-\beta \hbar \omega)) \\ &= \frac{1}{2} \hbar \omega + k_B T \ln(1 - \exp(-\beta \hbar \omega)) \end{aligned} \quad (24.73)$$

$$\begin{aligned} U &= \frac{\partial(\beta F)}{\partial \beta} \\ &= \frac{1}{2} \hbar \omega + \frac{\hbar \omega \exp(-\beta \hbar \omega)}{1 - \exp(-\beta \hbar \omega)} \\ &= \frac{1}{2} \hbar \omega + \frac{\hbar \omega}{\exp(\beta \hbar \omega) - 1}. \end{aligned} \quad (24.74)$$

The form of the energy in eq. (24.74) can be compared with the formal expression for the average of the energy

$$\langle E_n \rangle = \frac{1}{2} \hbar \omega + \hbar \omega \langle n \rangle. \quad (24.75)$$

Either from this comparison or from a direct calculation, we can see that the average number of excitations of the SHO is given by the expression

$$\langle n \rangle = \frac{1}{\exp(\beta \hbar \omega) - 1}. \quad (24.76)$$

As it was for the average number of excitations in a two-level system in eq. (24.57), it will be very important to remember the expression for  $\langle n \rangle$  in eq. (24.76) for a quantum SHO. Here again, the positive sign of the exponent in the denominator can be easily forgotten.

The canonical entropy of a collection of  $N$  simple harmonic oscillators can be found from the equations for  $F$  and  $U$ .

## 24.11 Einstein Model of a Crystal

Our first application of the quantum simple harmonic oscillator is Einstein's model of the vibrations of a crystal. Einstein made the approximation that all atoms except one were fixed at their average locations. He then approximated the potential seen by the chosen atom as being parabolic, so that he could treat the motion of the remaining atom as a three-dimensional SHO.

Assuming for simplicity that the quadratic terms are isotropic, the Hamiltonian for the one moving particle is

$$H_1 = \frac{1}{2}K|\vec{r}_1|^2 + \frac{|\vec{p}_1|^2}{2m}, \quad (24.77)$$

where the subscript 1 indicates that this Hamiltonian only applies to the one special particle.

The partition function for this system factorizes into three identical terms, each given by the partition function of the one-dimensional SHO from eq. (24.72),

$$Z_1 = \left( \frac{\exp(-\beta\hbar\omega/2)}{1 - \exp(-\beta\hbar\omega)} \right)^3. \quad (24.78)$$

The energy is just three times the energy of a single one-dimensional SHO,

$$U_1 = \frac{3}{2}\hbar\omega + \frac{3\hbar\omega}{\exp(\beta\hbar\omega) - 1}. \quad (24.79)$$

For  $N$  atoms in the crystal, the total energy is just  $N$  times the energy of a single atom,

$$U_N = \frac{3}{2}N\hbar\omega + \frac{3N\hbar\omega}{\exp(\beta\hbar\omega) - 1}. \quad (24.80)$$

The specific heat at constant volume is given by the usual derivative with respect to temperature,

$$\begin{aligned} c_V(T) &= \frac{1}{N} \left( \frac{\partial U_N}{\partial T} \right)_{V,N} \\ &= \frac{1}{N} \frac{\partial \beta}{\partial T} \frac{\partial}{\partial \beta} \left( \frac{3}{2}N\hbar\omega + \frac{3N\hbar\omega}{\exp(\beta\hbar\omega) - 1} \right) \\ &= -\frac{3\hbar\omega}{k_B T^2} \frac{\partial}{\partial \beta} \left( \frac{1}{\exp(\beta\hbar\omega) - 1} \right) \\ &= -\frac{3\hbar\omega}{k_B T^2} \frac{-\hbar\omega \exp(\beta\hbar\omega)}{(\exp(\beta\hbar\omega) - 1)^2} \\ &= 3k_B \left( \frac{\hbar\omega}{k_B T} \right)^2 \frac{\exp(\beta\hbar\omega)}{(\exp(\beta\hbar\omega) - 1)^2}. \end{aligned} \quad (24.81)$$

The final expression for  $c_V(T)$  in eq. (24.81) has interesting properties at high and low temperatures.

At high temperatures (small  $\beta$ ), the factor of  $\exp(\beta\hbar\omega)$  in the numerator goes to one, while the expression in the denominator can be expanded,

$$(\exp(\beta\hbar\omega) - 1)^2 = (1 + \beta\hbar\omega + \cdots - 1)^2 \rightarrow (\beta\hbar\omega)^2. \quad (24.82)$$

Using this to find the high-temperature limit of  $c_V(T)$  gives

$$c_V(T) \rightarrow 3k_B \left( \frac{\hbar\omega}{k_B T} \right)^2 \frac{1}{(\beta\hbar\omega)^2} = 3k_B. \quad (24.83)$$

This constant value of the specific heat at high temperatures is just the well-known law of Dulong and Petit (Pierre Louis Dulong, French physicist and chemist, 1785–1837, and Alexis Thérèse Petit, French physicist, 1791–1820). It is identical to the specific heat of the corresponding classical model.

At low temperatures (large  $\beta$ ), the factor of  $\exp(\beta\hbar\omega)$  becomes extremely large, and the ‘ $-1$ ’ in the denominator can be neglected,

$$c_V(T) \rightarrow 3k_B (\beta\hbar\omega)^2 \exp(-\beta\hbar\omega). \quad (24.84)$$

Even though the factor of  $\beta^2$  diverges at low temperature, the factor of  $\exp(-\beta\hbar\omega)$  goes to zero much faster. The result is that the specific heat in the Einstein model goes to zero rapidly as the temperature goes to zero, as it must according to the Third Law of Thermodynamics.

The Einstein model was a great success in explaining the qualitative features of the specific heat of crystals at low temperatures and the quantitative behavior at high temperatures. Nevertheless, the specific heat of real crystals does not go to zero as rapidly as predicted by eq. (24.84). Instead, a  $T^3$  behavior is seen in insulators, while the specific heat of metals is linear in  $T$  at low temperatures. The explanations of these observations will be given in Chapters 26 and 29.

The next chapter discusses black-body radiation, which might seem to be a bit of a detour. However, it turns out that the mathematical form of the equations we will find is very similar to, but simpler than, the equations needed to explain the low-temperature behavior of the specific heat of crystals, which will follow in Chapter 26.

## 24.12 Problems

### PROBLEM 24.1

#### Quantum statistical mechanics: A spin in a magnetic field

Consider a magnetic moment with spin-one-half in a magnetic field. Being a lazy theorist, I prefer not to write  $\hbar/2$  repeatedly, so I will use units in which the spin  $\sigma = \pm 1$ . I will also choose the units of the magnetic field such that the energy of the system is just

$$E = -b\sigma.$$

The system is in contact with a heat reservoir at temperature  $T$ .

1. Calculate the probability of the spin having the value  $+1$ .
2. Calculate the average magnetization  $m = \langle \sigma \rangle$ . Express your answer in terms of hyperbolic functions.
3. Calculate the two leading terms in a high-temperature expansion of the magnetization in powers of  $\beta = 1/k_B T$ .
4. Calculate the leading (non-constant) term in a low-temperature power series expansion of the magnetization in some variable at low temperatures. (Hint: it will be in the form of an exponential.)
5. Calculate the average energy. Plot it as a function of temperature.
6. Calculate the specific heat. Plot it as a function of temperature
7. Calculate the magnetic susceptibility,

$$\chi = \frac{dm}{db}.$$

#### PROBLEM 24.2

##### **A computer simulation of a two-level system Quantum statistical mechanics: A spin in a magnetic field**

Consider the same magnetic moment with spin-one-half in a magnetic field that we looked at in an earlier problem. The units of the magnetic field are again chosen such that the energy of the system is just

$$E = -b\sigma.$$

The system is in contact with a heat reservoir at temperature  $T$ .

For this problem, instead of doing an analytic calculation, we will carry out a computer simulation using the Monte Carlo method. Although this might seem to be the hard way to do it, we will see later that the method can be generalized to solve problems that do not have analytic solutions.

1. Write a computer program to simulate this two-level system. The program should calculate the thermal probability of being in each state, as well as the average magnetization and the magnetic susceptibility. Have the program print out of the theoretical values for comparison.
2. Use your program to calculate the magnetization and magnetic susceptibility for a set of 'interesting' values of the magnetic field and temperature.

#### PROBLEM 24.3

##### **Quantum statistical mechanics: Another two-level system**

Although a two-level system might seem very simple, it is very important and occurs frequently in various guises. Here is another form that we will see often.

A system only has two states, which are both non-degenerate. The energies of these two states are  $E = 0$  and  $E = \epsilon > 0$ .

The system is in contact with a heat reservoir at temperature  $T$ .

1. Calculate the probability of being in the excited state.
2. Calculate the average energy. Sketch it as a function of temperature.
3. Calculate the average specific heat. Sketch it as a function of temperature.
4. Calculate the two leading terms in a high-temperature expansion of the energy in powers of  $\beta = 1/k_B T$ .
5. Calculate the leading (non-constant) term in a low-temperature power series expansion of the energy in some variable at low temperatures. (Hint: the variable will be in the form of an exponential.)

#### PROBLEM 24.4

##### Derivation of $S_C$ for $N$ two-level systems

Consider a collection of  $N$  two-level quantum objects. The Hamiltonian is

$$H_{2\text{-level}} = \epsilon \sum_{k=1}^N n_k,$$

$n_k = 0$  or  $1$ , and  $\epsilon$  is the energy difference between the two levels in each object.

The entropy is denoted as  $S = S(U, V, N)$ , and the dimensionless entropy is  $\tilde{S} = S/k_B$ .

1. Find the partition function for this Hamiltonian in closed form.
2. Find the Massieu function  $\tilde{S}[\beta]$
3. Find the energy  $U = U(\beta)$  from  $\tilde{S}_{2\text{-level}}[\beta]$ .
4. Simplify the notation by defining a dimensionless energy

$$y = \frac{U_{2\text{-level}}}{N\epsilon}.$$

Find  $\beta$  as a function of  $y$ .

5. Plot  $\beta$  as a function of  $y = U/N\epsilon$ .
6. Find  $\tilde{S}_{2\text{-level}}$  as a function of  $y = U/N\epsilon$ .
7. Plot  $S_{2\text{-level}}$  as a function of  $y = U/N\epsilon$ .

#### PROBLEM 24.5

##### Quantum statistical mechanics: Return of the simple harmonic oscillator

The energy levels of a quantum SHO are given by

$$E_n = \hbar\omega \left( n + \frac{1}{2} \right)$$

where  $n = 0, 1, 2, \dots$ ,

$$\hbar = \frac{h}{2\pi}$$

and

$$\omega = \sqrt{\frac{K}{m}}.$$

1. Calculate the QM partition function.
2. Calculate the probability that a measurement of the energy will find the QM SHO in the  $n$ -th eigenstate.
3. Calculate the average energy.
4. Calculate the specific heat.
5. Calculate the high-temperature limit of the specific heat.
6. Calculate the leading term in a low-temperature expansion of the specific heat. (You should be able to figure out what a good quantity to expand in would be.)

#### PROBLEM 24.6

##### **A Monte Carlo computer simulation of a quantum SHO**

As we've seen before, the energy levels of a quantum SHO are given by

$$E_n = \hbar\omega \left( n + \frac{1}{2} \right)$$

where  $n = 0, 1, 2, \dots$ ,

$$\hbar = \frac{h}{2\pi}$$

and

$$\omega = \sqrt{\frac{K}{m}}.$$

This time we shall carry out a Monte Carlo simulation of this system. There are, of course, an infinite number of possible states. However, the probability of high-energy states is very small, making the simulation feasible.

1. Write a program to do a Monte Carlo simulation of a single quantum SHO. Label the state of the system with the quantum number  $n$ , as in the equations above. Let one MC step consist of an attempted move to increase or decrease  $n$  by  $\pm 1$ . Remember to reject any attempted move that would make  $n$  negative.
2. Compute the energy and specific heat (the latter from fluctuations) for a range of interesting temperature. For convenience, you may take  $\hbar\omega = 1.0$ . Have the program print out the exact values for comparison.

#### PROBLEM 24.7

##### **Quantum statistical mechanics: A many-spin system**

Consider a macroscopic crystal with a spin-one quantum mechanical magnetic moment located on each of  $N$  atoms. Assume that we can represent the energy eigenvalues of the system with a Hamiltonian of the form

$$H = D \sum_{n=1}^N \sigma_n^2$$

where each  $\sigma_n$  takes on the values  $-1, 0$ , or  $+1$ , and  $D$  is a constant representing a ‘crystal field’. The entire system is in contact with a thermal reservoir at temperature  $T$ .

1. Calculate the partition function for this system.
2. Calculate the free energy of this system.
3. Calculate the quantity

$$Q = \frac{1}{N} \left\langle \sum_{n=1}^N \sigma_n^2 \right\rangle.$$

4. Calculate the entropy per spin of this system.
5. Determine whether this system satisfies the Nernst Postulate for all values of the parameter  $D$ .

#### PROBLEM 24.8

**Quantum statistical mechanics: A many-spin system** (This is a slightly more difficult version of the previous problem).

Consider a macroscopic crystal with a spin-one quantum mechanical magnetic moment located on each of  $N$  atoms. Assume that we can represent the energy eigenvalues of the system with a Hamiltonian of the form

$$H = B \sum_{n=1}^N \sigma_n + D \sum_{n=1}^N \sigma_n^2$$

where each  $\sigma_n$  takes on the values  $-1, 0$ , or  $+1$ , and  $B$  and  $D$  are constants representing an external magnetic field and a ‘crystal field’, respectively. The entire system is in contact with a thermal reservoir at temperature  $T$ .

1. Calculate the partition function for this system.
2. Calculate the free energy of this system.
3. Calculate the magnetization per spin

$$m = \frac{1}{N} \left\langle \sum_{n=1}^N \sigma_n \right\rangle.$$

4. Calculate the entropy per spin of this system.
5. Determine whether this system satisfies the Nernst Postulate for all values of the parameters.

#### PROBLEM 24.9

**A diatomic ideal gas Quantum statistical mechanics—but only when needed**

Consider a dilute gas with  $N$  diatomic molecules that you can treat as ideal in the sense of neglecting interactions between the molecules. We shall assume that the molecules

consist of two-point masses with a fixed distance between them. They can rotate freely, but they cannot vibrate.

The center of mass motion (translational degrees of freedom) can be treated classically. However, the rotational degrees of freedom must be treated quantum mechanically.

The quantum mechanical energy levels take the form  $\epsilon(j) = j(j+1)\epsilon_0$ , where  $j = 0, 1, 2, \dots$  and the degeneracy of the  $j$ -th level is given by  $g(j) = 2j+1$ . (You can peek at a QM text to find the value of  $\epsilon_0$ , but you do not need it for this assignment.)

Although you do not need it for this assignment, the parameter  $\epsilon_0$  is given by

$$\epsilon_0 = \frac{\hbar^2}{2I}$$

where  $I$  is the moment of inertia of a molecule.

The whole system is in equilibrium with a thermal reservoir at temperature  $T$ .

1. Write down the canonical partition function, treating the translational degrees of freedom classically and the rotational degrees of freedom quantum mechanically.
2. Evaluate the energy and the specific heat for both high and low temperatures.
3. Sketch the energy and the specific heat as functions of temperature, indicating both the high- and low-temperature behavior.

#### PROBLEM 24.10

##### Another diatomic ideal gas—entirely classical this time, but in two dimensions

Consider a classical, dilute, diatomic gas with  $N$  molecules in two dimensions. The gas is again ideal in the sense of neglecting interactions between the molecules. Each molecule consist of two-point masses. Although there are no interactions between different molecules, there is an interaction between the atoms in the same molecule of the form

$$V(r) = \begin{cases} \mathcal{J} \ln(r) & r > a \\ \infty & r \leq a. \end{cases}$$

The gas is contained in a two-dimensional ‘box’ of area  $A = L^2$ . The whole system is in equilibrium with a thermal reservoir at temperature  $T$ .

1. What is the classical Hamiltonian for this system?
2. Write the canonical partition function as an integral over phase space.
3. Calculate the partition function in closed form, under the assumption that the molecule is much smaller than the box it is in. That is, let the limits on the integral over the separation between the atoms in a molecule extend to  $\infty$ .
4. This model is only valid for low temperatures. At what temperature do you expect it to break down?
5. Now calculate the average square separation  $\langle r^2 \rangle$  between the atoms in a molecule.

#### PROBLEM 24.11

##### Two-level quantum systems

1. Consider a simple set of  $N$  two-level subsystems. The subsystems are all independent, and each has two allowed states with energies 0 (ground state) and  $\epsilon$  (excited state) so that the full Hamiltonian can be written as



$$H = \sum_{n=1}^N E(n)$$

where  $E(n) = 0$  or  $E(n) = \epsilon$ . The entire system is in thermal equilibrium at temperature  $T$ .

1. At what temperature is the average total energy equal to  $\frac{1}{3}N\epsilon$ ?
2. At what temperature is the average total energy equal to  $\frac{2}{3}N\epsilon$ ?
2. Suppose the subsystems in the part 1 of the problem had the same ground state with energy 0, but different values of the energy in the excited states. Assume that the energy of the excited state of the  $n$ -th subsystem is  $n\epsilon$ .
  1. What is the average energy of the total system?
  2. Suppose we are in the low-temperature regime, for which  $k_B T \ll E_{max}$ . Calculate the average energy. You may leave your answer in terms of a dimensionless integral, but you should obtain the temperature dependence.
  3. What is the heat capacity of the total system?

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