

## Chapter 4

# The Partition Function

The partition function of a particle, as described in Equation 3.16 is a sum of the Boltzmann factors corresponding to the accessible energy states of that particle. We can write this summation either with respect to the states themselves or the energies of those states. In the latter case, the degeneracy of each energy state must be included.

$$Z = \sum_{\substack{n \\ \text{states}}} e^{-\beta\epsilon_n} \quad Z = \sum_{\substack{i \\ \text{energies}}} g_i e^{-\beta\epsilon_i}$$

We discuss in this and in subsequent chapters that calculating the partition function for a system is the usual starting point for developing a thermodynamic description of a system.

### Mean Energy

The mean energy of a particle can be determined using Equation 2.1 and Equation 3.15.

$$\begin{aligned} \bar{\epsilon} &= \frac{\sum_i p_i \epsilon_i}{\sum_i p_i} \rightarrow \bar{\epsilon} = \frac{\sum_i \frac{g_i \epsilon_i e^{-\beta\epsilon_i}}{\sum_i g_i e^{-\beta\epsilon_i}}}{\sum_i \frac{g_i e^{-\beta\epsilon_i}}{\sum_i g_i e^{-\beta\epsilon_i}}} \rightarrow \bar{\epsilon} = \frac{\sum_i \frac{g_i \epsilon_i e^{-\beta\epsilon_i}}{Z}}{\sum_i \frac{g_i e^{-\beta\epsilon_i}}{Z}} \\ \bar{\epsilon} &= \frac{\frac{1}{Z} \sum_i g_i \epsilon_i e^{-\beta\epsilon_i}}{\frac{1}{Z} \sum_i g_i e^{-\beta\epsilon_i}} \rightarrow \bar{\epsilon} = \frac{\sum_i g_i e^{-\beta\epsilon_i} \epsilon_i}{\sum_i g_i e^{-\beta\epsilon_i}} \end{aligned}$$

We can rewrite the numerator in this expression using a partial derivative.

$$\epsilon_i e^{-\beta\epsilon_i} = -\frac{\partial}{\partial\beta} e^{-\beta\epsilon_i} \rightarrow \bar{\epsilon} = -\frac{1}{Z} \sum_i g_i \frac{\partial}{\partial\beta} e^{-\beta\epsilon_i}$$

The partial derivative can now be taken outside of the summation.

$$\bar{\epsilon} = -\frac{1}{Z} \frac{\partial}{\partial \beta} \sum_i g_i e^{-\beta \epsilon_i} \rightarrow \bar{\epsilon} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$$

This expression is frequently written in terms of the natural log of the partition function.

$$\bar{\epsilon} = -\frac{\partial}{\partial \beta} \ln(Z) \quad (4.1)$$

Let's consider a system consisting of a single particle that has two accessible energy states with energies  $\epsilon$  and  $2\epsilon$ . Both of these energy states have a degeneracy of 1. The partition function for this particle is

$$Z = e^{-\beta \epsilon} + e^{-2\beta \epsilon} \rightarrow Z = e^{-\beta \epsilon} (1 + e^{-\beta \epsilon})$$

$$\ln(Z) = -\beta \epsilon + \ln(1 + e^{-\beta \epsilon})$$

Therefore,

$$\bar{\epsilon} = -\frac{\partial}{\partial \beta} [-\beta \epsilon + \ln(1 + e^{-\beta \epsilon})]$$

$$\bar{\epsilon} = \epsilon + \frac{\epsilon e^{-\beta \epsilon}}{1 + e^{-\beta \epsilon}} \rightarrow \bar{E} = \epsilon \left( 1 + \frac{e^{-\beta \epsilon}}{1 + e^{-\beta \epsilon}} \right)$$

$$\bar{\epsilon} = \epsilon \left( \frac{1 + e^{-\beta \epsilon}}{1 + e^{-\beta \epsilon}} + \frac{e^{-\beta \epsilon}}{1 + e^{-\beta \epsilon}} \right) \rightarrow \bar{\epsilon} = \epsilon \left[ \frac{1 + 2e^{-\beta \epsilon}}{1 + e^{-\beta \epsilon}} \right]$$

Let's examine two limits of this expression

$$\lim_{\beta \rightarrow 0} \bar{\epsilon} = \epsilon \left( \frac{1 + 2}{1 + 1} \right) = \frac{3}{2} \epsilon$$

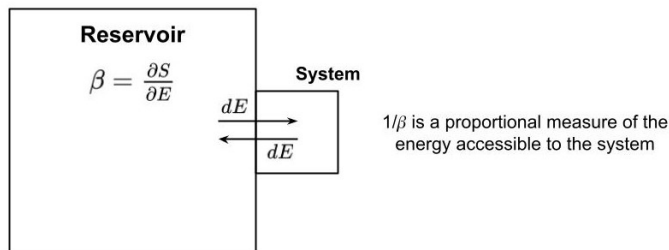
$$\lim_{\beta \rightarrow \infty} \bar{\epsilon} = \frac{\epsilon + 0}{1 + 0} = \epsilon$$

Thus, when  $\beta$  is small, the average energy of the particle is the arithmetic average of the energies of the energy states accessible to the particle. This follows, of course, from the fact that the Boltzmann factor for any energy states has a limit of one as  $\beta$  approaches zero. In contrast, the Boltzmann factor has a limit of zero as  $\beta$  approaches infinity. Thus, when  $\beta$  is large, only the lowest energy states have a non-zero probability of being occupied. In other words, as shown in Figure 4.1

When  $\beta$  is small, all energy states are equally probable.

When  $\beta$  is large, the only probable energy state is the energy state with the lowest energy.

When  $\beta$  is small, exchanging  $dE$  will cause a small change in the entropy of the reservoir  
 Thus, when  $\beta$  is small, the energy accessible to the system from the reservoir is large



When  $\beta$  is large, exchanging  $dE$  will cause a large change in the entropy of the reservoir  
 Thus, when  $\beta$  is large, the energy accessible to the system from the reservoir is small

Figure 4.1: Interpreting  $\beta$  in the context of a system interacting with an energy reservoir.

But what does this mean? Well, as shown in Equation 3.19,  $\beta$  is a measure of how the entropy of a system changes when the energy of that system changes. So, with respect to our thinking about the canonical distribution and Boltzmann factors, a small value of  $\beta$  means the entropy of the energy reservoir is a weak function of energy and a large value of  $\beta$  means the entropy of the energy reservoir is a strong function of energy. If entropy of the energy reservoir is a weak function of energy, the energy reservoir is capable of exchanging a lot of energy with its associated system without affecting its own entropy, which, by extension, means without affecting the entropy of the combination of the energy reservoir and the associated system<sup>1</sup>. This freedom to exchange energy means that there is significant energy available to the system to allow the system to populate any of its accessible energy states. In contrast, if  $\beta$  is large, the energy reservoir cannot exchange much energy without affecting its own entropy. We can therefore think of  $\frac{1}{\beta}$  as being proportional to (or a measure of) the energy accessible to the system from the energy reservoir at equilibrium. It therefore seems that we are drawing a connection between the mean energy of the molecules of gas in our system (the origin of  $\beta$  in Equation 3.28) and the mean energy of the energy reservoir (the origin of  $\beta$  in Equation 3.16 and Equation 3.21), which is not surprising as energy can be exchanged between the gas the reservoir. Indeed, we would expect that the mean energies of both the gas and the reservoir should be related when the entire system is in equilibrium.

### Dispersion of Energy States

We can use a process similar to that applied above to calculate  $\overline{\epsilon^2}$ .

<sup>1</sup>Recall that since the energy reservoir is so large the entropy of the total system is approximately equal to the entropy of the energy reservoir.

$$\begin{aligned}\bar{\epsilon^2} &= \frac{\sum_i \epsilon_i^2 g_i e^{-\beta \epsilon_i}}{\sum_i g_i e^{-\beta \epsilon_i}} \rightarrow \bar{\epsilon^2} = \frac{-\frac{\partial}{\partial \beta} \left( \sum_i \epsilon_i g_i e^{-\beta \epsilon_i} \right)}{\sum_i g_i e^{-\beta \epsilon_i}} \\ \bar{\epsilon^2} &= \frac{\left( -\frac{\partial}{\partial \beta} \right)^2 \left( \sum_i g_i e^{-\beta \epsilon_i} \right)}{\sum_i g_i e^{-\beta \epsilon_i}} \rightarrow \bar{\epsilon^2} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}\end{aligned}$$

Once again we invoke some mathematics that we probably wouldn't have thought to use unless we knew where we were going.

$$\begin{aligned}\frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} &= \frac{\partial}{\partial \beta} \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) + \frac{1}{Z^2} \left( \frac{\partial Z}{\partial \beta} \right)^2 \\ \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} &= \frac{\partial}{\partial \beta} \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) + \left( \frac{1}{Z} \frac{\partial Z}{\partial \beta} \right)^2\end{aligned}$$

We recognize the second term from Equation 4.1

$$\frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} = -\frac{\partial \bar{\epsilon}}{\partial \beta} + \bar{\epsilon}^2 \rightarrow \bar{\epsilon^2} = -\frac{\partial \bar{\epsilon}}{\partial \beta} + \bar{\epsilon}^2$$

Substitution into Equation 2.3 then yields

$$\begin{aligned}\overline{(\Delta \epsilon)^2} &= \bar{\epsilon^2} - \bar{\epsilon}^2 \rightarrow \overline{(\Delta \epsilon)^2} = -\frac{\partial \bar{\epsilon}}{\partial \beta} + \bar{\epsilon}^2 - \bar{\epsilon}^2 \\ \overline{(\Delta \epsilon)^2} &= -\frac{\partial \bar{\epsilon}}{\partial \beta}\end{aligned}\tag{4.2}$$

Since  $\overline{(\Delta \epsilon)^2} \geq 0$ , we see that  $\frac{\partial \bar{\epsilon}}{\partial \beta} \leq 0$ . We will return to this later.

### Relationship to entropy

Let's start with Equation 3.20 to describe canonical distribution for a single particle with accessible energy states denoted by  $\epsilon_n$ . In other words, we are summing over the states themselves rather than the energies of those states.

$$\begin{aligned}p_n &= \frac{e^{-\beta \epsilon_n}}{Z} \rightarrow p_n Z = e^{-\beta \epsilon_n} \rightarrow \ln(p_n Z) = -\beta \epsilon_n \\ \epsilon_n &= -\frac{1}{\beta} (\ln(Z) + \ln(p_n)) \rightarrow \beta \epsilon_n = -\ln(Z) - \ln(p_n)\end{aligned}$$

Let's multiply both sides by  $p_n$  and then sum over all possible states.

$$\sum_n p_n \beta \epsilon_n = -\sum_n p_n \ln(Z) - \sum_n p_n \ln(p_n)$$

$\ln(Z)$  is a constant and can be taken outside the summation.

$$\beta \sum_n p_n \epsilon_n = -\ln(Z) \sum_n p_n - \sum_n p_n \ln(p_n)$$

The first summation in this expression is the mean energy of the distribution and we recognize from Equation 3.24 that the final summation is the entropy.

$$\beta \bar{\epsilon} = -\ln(Z) \sum_n p_n + \mathcal{S}$$

The remaining summation is 1 if the probability distribution is normalized. This leaves us with

$$\mathcal{S} = \ln(Z) + \beta \bar{\epsilon} \quad (4.3)$$

If we substitute Equation 4.1 into Equation 4.3 we have

$$\mathcal{S} = \ln(Z) - \beta \left( \frac{\partial \ln(Z)}{\partial \beta} \right) \quad (4.4)$$

We see from Equation 4.3 or Equation 4.4 that calculating the partition function for a system allows us to determine the entropy of that system. Since, as we will see later, knowing the entropy of a system allows us to determine several thermodynamic properties of a system, calculating the partition function for a system permits a thermodynamic description of that system.

## 4.1 Partition Function for Systems of Particles

Entropy and mean energy are both extensive variables. Thus, for a system of  $N$  particles obeying Boltzmann statistics<sup>2</sup>, the entropy of the system is found by multiplying Equation 4.3 by  $N$ .

$$\mathcal{S}_B = N \ln(Z) + N \beta \bar{\epsilon}$$

As discussed in Section 1.3, if the mean energy of a single particle is  $\bar{\epsilon}$ , the product of  $N$  and  $\bar{\epsilon}$  is the mean energy of a system of  $N$  particles, denoted by  $\bar{E}$ .

$$\mathcal{S}_B = \ln(Z^N) + \beta \bar{E} \quad \rightarrow \quad \mathcal{S}_B = \ln(Z_B) + \beta \bar{E}$$

We can think of this expression for  $\mathcal{S}_B$  as system equivalent expression to Equation 4.3. In this case, the partition function for the system of  $N$  particles, denoted as  $Z_B$ , is the partition function for a single particle raised to the power  $N$ .

$$Z_B = \left( \sum_n e^{-\beta \epsilon_n} \right)^N \quad (4.5)$$

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<sup>2</sup>Recall that the derivation of Equation 4.3 relied upon Equation 3.15 and Equation 3.16, which describe a Boltzmann statistics.

Furthermore, since the multiplicity for a system described by Maxwell-Boltzmann statistics differs from the multiplicity of a system described by Boltzmann statistics by  $N!$ , we have

$$\Omega_{MB} = \frac{\Omega_B}{N!} \rightarrow \ln \Omega_{MB} = \ln \Omega_B - \ln N!$$

Thus, from Equation 3.7 we have

$$\mathcal{S}_{MB} = \mathcal{S}_B - \ln N! \rightarrow \mathcal{S}_{MB} = \ln(Z_B) + \beta \bar{E} - \ln N!$$

$$\mathcal{S}_{MB} = \ln \left( \frac{Z_B}{N!} \right) + \beta \bar{E} \rightarrow \mathcal{S}_{MB} = \ln Z_{MB} + \beta \bar{E}$$

$$Z_{MB} = \frac{1}{N!} \left( \sum_n e^{-\beta \epsilon_n} \right)^N \quad (4.6)$$

Of course, we can also write the summations in Equation 4.5 and Equation 4.6 in terms of the energies of the accessible states by including the associated degeneracy.

$$Z_B = \left( \sum_i g_i e^{-\beta \epsilon_i} \right)^N \quad Z_{MB} = \frac{1}{N!} \left( \sum_i g_i e^{-\beta \epsilon_i} \right)^N$$

### Additional Discussion

Let's begin by considering a system of 2 particles that can occupy the accessible states of a system. The partition function for this system can be written as

$$Z = \left[ \sum_r e^{-\beta \epsilon_r} \right] \left[ \sum_s e^{-\beta \epsilon_s} \right]$$

The variables  $r$  and  $s$  in this expression denote the two different particles. In other words, the first summation in this expression corresponds to one particle being in an accessible state of the system, with the index  $r$  denoting the state, and the second summation to the other particle being in an accessible state of the system, with the variable  $s$  denoting the state. Expanding this expression yields

$$Z = \sum_r e^{-2\beta \epsilon_r} + \sum_r \sum_{\substack{s \\ s \neq r}} e^{-\beta(\epsilon_r + \epsilon_s)}$$

The first term in this equation corresponds to terms where  $r = s$ , *i.e.*, both particles are in the same state. The second term in this equation corresponds to terms where  $r \neq s$ , the particles are in different states. If the particles are identical (*i.e.*, the particles are *indistinguishable* from one another), we could not distinguish a situation where  $r = 1$  and  $s = 2$  from a situation where  $r = 2$

and  $s = 1$ . Both would correspond to one particle in state 1 and one particle in state 2. To correct for this double counting occurring when the particles are identical, we need to divide the corresponding summation by  $2!$ .

$$Z = \sum_r e^{-2\beta\epsilon_r} + \frac{1}{2!} \sum_r \sum_{\substack{s \\ s \neq r}} e^{-\beta(\epsilon_r + \epsilon_s)}$$

In general, the partition function for a system consisting of  $N$  particles will consist of two contributions. One corresponding to all  $N$  particles being in the same state and one corresponding to all  $N$  particles being in different states. This second term must be divided by  $N!$  if the particles are identical.

Our conversation at this point diverges into different cases. First, let's consider what is commonly referred to as the *classical regime*. In this case, the probability is very small that any state is occupied by more than one particle. In this situation, most states are empty, a few contain a single particle, and an insignificant number of states contain more than one particle. Thus, in the classical regime, the contribution to the partition function from multiple particles in the same state can be ignored. The partition function for a system of  $N$  particles in the classical regime can thus be described as

$$\begin{aligned} Z &= \frac{1}{N!} \sum_{x_1} \sum_{x_2} \cdots \sum_{x_N} e^{-\beta(\epsilon_{x_1} + \epsilon_{x_2} + \cdots + \epsilon_{x_N})} \\ Z &= \frac{1}{N!} \left( \sum_{x_1} e^{-\beta\epsilon_{x_1}} \right) \left( \sum_{x_2} e^{-\beta\epsilon_{x_2}} \right) \cdots \left( \sum_{x_N} e^{-\beta\epsilon_{x_N}} \right) \\ Z &= \frac{1}{N!} \left( \sum_n e^{-\beta\epsilon_n} \right)^N \end{aligned}$$

When the particles are distinguishable, the factor of  $N!$  is not included. This is identical to what we derived previously. This is expected, of course, as the Maxwell-Boltzmann distribution is the classical limit of the Fermi-Dirac distribution and the Bose-Einstein distribution (Section 3.1.1).

## 4.2 Partition Function for Continuous Distributions

When calculating the partition function, the degeneracy of each energy state must be included. The integral analog of the degeneracy in the summation in Equation 3.16 is called the *density of states*. The density of states is defined to be the number of energy states whose energies lie in the range between  $\epsilon$  and  $\epsilon + d\epsilon$  for a system of volume  $V$ . We can therefore think of the density of states as a probability density.

### Probability Density

Imagine that you are rolling a six-sided die. There are six possible outcomes for each roll and thus the probability of each outcome is one-sixth. We also see that the probability is normalized since the sum of the probabilities for all possible outcomes is one. If we had a ten-sided die, the probability of each outcome would be one-tenth and, as before, the sum of the probabilities for all possible outcomes is one.

But things get a bit more complicated when we move to a continuous situation. Imagine that instead of rolling a die, you had a random number generator. Let's further assume that there is an equal probability of obtaining any result with this random number generator. If we limit ourselves to integers between 1 and 10, we have a probability of one-tenth for each outcome and the sum of the probabilities for all possible outcomes is one. As we move into decimal quantities, such as random numbers between 1.0 and 10.0 or between 1.00 and 10.00, we see that the probability of each outcome continues to decrease. In the limit that we are in a continuous system, the probability of each outcome (generating a specific random number to infinite decimal places) is asymptotically zero. This would then mean that the sum of the probabilities for all outcomes is zero, rather than one. Furthermore, if we declare instead that the probability of any outcome in this continuous system is non-zero, then the sum of the probabilities of all outcomes is infinite and not one. Bummer.

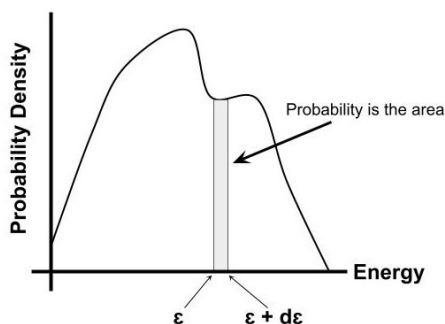


Figure 4.2: The probability of an event is equal to the area under the curve of probability density

We avoid this mess by talking about probability density rather than probability itself. We do not ask for the probability of obtaining a specific outcome, but instead the probability of obtaining an outcome between a range of possible values. As shown in Figure 4.2, we now recast our problem as determining the probability of finding the particle or system with an energy in the range between  $\epsilon$  and  $\epsilon + d\epsilon$  (or equivalently the number of states that have energies in the range between  $\epsilon$  and  $\epsilon + d\epsilon$ ). This probability correctly approaches zero as  $d\epsilon$  approaches zero and we can assure normalcy by setting the area under the



curve to be one. Notice that since the area under the curve is the probability, the vertical axis - and thus also the curve shown - denotes the probability density. Thus, for the example shown in Figure 4.2, the integral of the probability density over all possible energies is equal to one.

I realize that you are probably thinking that this discussion is unnecessary as the final result is as expected from converting a summation to an integral.

$$\sum_{x \in S} P(x) = 1 \leftrightarrow \int_s p(x) dx = 1$$

But I believe it is nevertheless important to pause and reflect on what this then means for the variables involved in the calculations. If  $P(x)$  denotes a discrete set of probabilities, then  $p(x)$  denotes the corresponding probability density with the product  $p(x)dx$  denoting the probability. The density of states is analogous to such a probability density.

### Density of States

So how does one calculate a density of states? A good place to start is with quantum mechanics. Let's revisit the solution to a particle in an infinite square well. The energy of that particle was given by

$$\epsilon_n = \frac{\hbar^2 k_n^2}{2m}$$

Where the variable  $k_n$  is defined in terms of the width of the well  $L$ .

$$k_n = \frac{n\pi}{L} \quad n = 1, 2, 3, 4, \dots$$

It follows that each value of  $k_n$  is separated by  $\frac{\pi}{L}$ . Now let's assume that we have a 2-dimensional well. In that case, the variable  $k_n$  in the equation for the energy of the particle would be

$$k_n^2 = k_x^2 + k_y^2$$

Where  $k_x$  and  $k_y$  represent solutions for the Schrödinger equation along the two different dimensions of the box, denoted as  $x$  and  $y$ . Furthermore,

$$k_x = \frac{n_x \pi}{L} \quad n_x = 1, 2, 3, 4, \dots$$

$$k_y = \frac{n_y \pi}{L} \quad n_y = 1, 2, 3, 4, \dots$$

Now since the energy depends on  $k_n^2$  and  $k_n^2 = k_x^2 + k_y^2$ , there are different combinations of  $k_x$  and  $k_y$  that associated with the same value of  $k_n$  and therefore with the same energy. This is the degeneracy that we address with the density of states of the system.

We can use this example to visualize the density of states using Figure 4.3. In this figure, each dot corresponds to a solution of the Schrödinger equation for

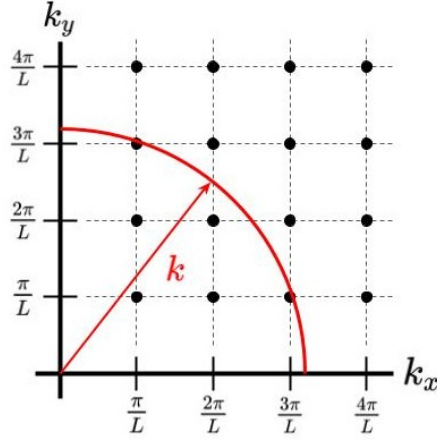


Figure 4.3: The probability of an event is equal to the area under the curve of probability density

this system and the red semicircle corresponds to a particular value of  $k_n$ . The density of states is related to the number of dots (*i.e.*, the number of solutions) enclosed by this curve. If each dot is separated by a distance  $\frac{\pi}{L}$ , then the area of each dot can be modeled as  $(\frac{\pi}{L})^2$ . Since the area bounded by semicircular arc is  $\frac{1}{4}\pi k^2$ , the number of points contained within the area bounded by the semicircular arc is

$$\Gamma(k) = \frac{\frac{1}{4}\pi k^2}{(\frac{\pi}{L})^2} \rightarrow \Gamma(k) = \frac{L^2 k^2}{4\pi}$$

The density of states is the derivative of  $\Gamma(k)$  with respect to  $k$ .

$$\frac{d}{dk}\Gamma(k) = D(k)dk = \frac{L^2 k}{2\pi} dk$$

We now recognize  $D(k)dk$  as the number of states (*i.e.*, the number of solutions of the Schrödinger equation) between  $k$  and  $k + dk$ , and therefore  $D(k)$  as a probability density.

We refer to plots such as that in Figure 4.3 as describing the solutions of the system in  $k$ -space. This is identical to the  $k$ -space you talked about in quantum mechanics and pretty much the same thing as the phase space you talked about in classical mechanics that was described in terms of the generalized coordinates  $p$  and  $q$ . Please also note that we include the factor of  $\frac{1}{4}$  in this calculation so that we consider only positive values of  $k_x$  and  $k_y$ . Since negative values of  $k_x$  and/or  $k_y$  would lead to solutions that are not linearly independent of those corresponding to positive values of  $k_x$  and  $k_y$ .

	$D(k)dk$	$D(\epsilon)d\epsilon$
1-D	$\left(\frac{L}{2\pi}\right) dk$	$\left(\frac{L}{\hbar} \sqrt{\frac{m}{8\epsilon}}\right) d\epsilon$
2-D	$\left(\frac{Ak}{2\pi}\right) dk$	$\left(\frac{mA}{2\pi\hbar^2}\right) d\epsilon$
3-D	$\left(\frac{V k^2}{2\pi^2}\right) dk$	$\left(\frac{V}{\pi^2\hbar^3} \sqrt{\frac{m^3\epsilon}{2}}\right) d\epsilon$

Table 4.1: Densities of states for different dimensionalities

This density of states can also be written in terms of the corresponding energy.

$$\epsilon = \frac{\hbar^2 k^2}{2m} \rightarrow k = \sqrt{\frac{2m\epsilon}{\hbar^2}} \rightarrow dk = \left(\sqrt{\frac{m}{2\hbar^2\epsilon}}\right) d\epsilon$$

$$D(\epsilon)d\epsilon = \frac{L^2}{2\pi} \left(\sqrt{\frac{2m\epsilon}{\hbar^2}}\right) \left(\sqrt{\frac{m}{2\hbar^2\epsilon}}\right) d\epsilon$$

$$D(\epsilon)d\epsilon = \left(\frac{mL^2}{2\pi\hbar^2}\right) d\epsilon$$

The density of states for this system is independent of the energy of the system. That makes sense as the energy depends on  $k^2$  and the surface area in  $k$ -space also depends on  $k^2$ . It also then follows that we should probably expect a different density of states for a system with a different dimensionality. This is, indeed, the case as shown in Table 4.1.

We can use a density of states to convert the summation in Equation 3.16 into an integral.

$$Z = \int e^{-\beta\epsilon} D(\epsilon) d\epsilon$$

### Continuous Systems

It is common to express the Boltzmann factor in the calculation of a partition function in terms of the Hamiltonian of the system, which is a function of the generalized positions and generalized momenta of the particles in the system. It follows that the integral with respect to  $d\epsilon$  can be represented as an integral with respect to the generalized positions and generalized momenta too. For example, building on the derivation presented previously, the density of states in 3-dimensions would be

$$D(k)dk = \frac{d}{dk} \left[ \frac{1}{8} \left( \frac{4}{3} \pi k^3 \right) \right] \rightarrow D(k)dk = \frac{d}{dk} \left[ \frac{L^3 k^3}{6\pi^2} \right] \rightarrow D(k)dk = \frac{L^3 k^2}{2\pi^2} dk$$

We recognize  $L^3$  as the volume  $V$  of the 3-dimensional well (*i.e.*, the 3-dimensional box) in which the particle is located.

$$D(k)dk = \frac{Vk^2}{2\pi^2} dk$$

Let's now express this in terms of momentum states of the particle.

$$p = \hbar k \quad \rightarrow \quad D(p)dp = \frac{V \left(\frac{p}{\hbar}\right)^2}{2\pi^2} \left(\frac{dp}{\hbar}\right)$$

$$D(p)dp = \frac{Vp^2}{2\pi^2\hbar^3} dp$$

We can also rewrite this equation by substituting  $\hbar = \frac{h}{2\pi}$ .

$$f(p)dp = \frac{Vp^2}{2\pi^2 \left(\frac{h}{2\pi}\right)^3} dp \quad \rightarrow \quad f(p)dp = \frac{V4\pi p^2}{h^3} dp$$

This looks a lot like what we would derive using the Jacobian (Section A.1), but there is this additional factor of  $h^3$  floating around. What is that doing there? Well, we remember that the units of  $h$  are the same as the units of the product of  $p$  and  $q$ . Thus, if we think of  $(dp_x dx)(dp_y dy)(dp_z dz)$  as denoting a cube in phase space, we can think of the size of a *quantum cube* of this phase space is  $h^3$ . In this case, the product

$$\left(\frac{dp_x dx}{h}\right) \left(\frac{dp_y dy}{h}\right) \left(\frac{dp_z dz}{h}\right) = \frac{dx dy dz dp_x dp_y dp_z}{h^3}$$

is a dimensionless quantity. Similarly,  $\frac{V4\pi p^2}{h^3} dp$  is also a dimensionless quantity. We can therefore think of the partition function as a normalized measure of the volume in phase space occupied by the canonical ensemble.

But, there is also a more fun way of thinking about this. If we think back to Equation 3.7, we remember that entropy involves counting or otherwise enumerating energy states. This requirement of counting energy states also shows up in our calculation of the partition function. But how does one count energy states if those energy states are distributed continuously, such as the energy states associated with the kinetic energy of a molecule of gas? The quick answer would be to use a histogram. So, we can think of the  $h^3$  as being the size of a 3-dimensional histogram bin in phase space. From this point of view, creating the product  $\left(\frac{dp_x dx}{h}\right) \left(\frac{dp_y dy}{h}\right) \left(\frac{dp_z dz}{h}\right)$  is our attempt to *bin* the continuous space of possible positions and momenta so that we can count the associated energy states.

The partition function for a system of  $N$  particles described by Boltzmann statistics can be written as

$$Z_B = \frac{1}{h^{3N}} \int e^{-\beta \sum_{i=1}^N H(\vec{q}_i, \vec{p}_i)} d^3\vec{q}_1 \cdots d^3\vec{q}_N d^3\vec{p}_1 \cdots d^3\vec{p}_N \quad (4.7)$$

The variable  $H$  is the Hamiltonian for the system, which is a function of the generalized positions  $(d^3q_1 \cdots d^3q_N)$  and generalized momenta  $(d^3p_1 \cdots d^3p_N)$

of the particles in the system. If the particles are indistinguishable (*i.e.*, if the system is described by Maxwell-Boltzmann statistics, the partition function must be corrected by a factor of  $N!$ ).

$$Z_{MB} = \frac{1}{N!h^{3N}} \int e^{-\beta \sum_{i=1}^N H(\vec{q}_i, \vec{p}_i)} d^3\vec{q}_1 \cdots d^3\vec{q}_N d^3\vec{p}_1 \cdots d^3\vec{p}_N$$

We can simplify this a bit further using Stirling's approximation.

$$Z_{MB} = \left( \frac{e}{Nh^3} \right)^N \int e^{-\beta \sum_{i=1}^N H(\vec{q}_i, \vec{p}_i)} d^3\vec{q}_1 \cdots d^3\vec{q}_N d^3\vec{p}_1 \cdots d^3\vec{p}_N \quad (4.8)$$

### Equipartition Theorem

Let's consider a particularly useful situation where the Hamiltonian for our system is quadratic function of position or momentum. For example,

$$H = ap_k^2$$

In this case, the energy states are a function of only one generalized momentum coordinate  $p_k$ . Next, let's assume that the average energy of our system is fixed (*e.g.*, our system is in equilibrium). In this case, we can use the following integrals to denote the number of particles and mean energy of the system.

$$N = \int C e^{-\beta ap_k^2} d^3q_1 d^3q_2 \cdots d^3q_n d^3p_1 d^3p_2 \cdots d^3p_n$$

$$\bar{E} = \int ap_k^2 C e^{-\beta ap_k^2} d^3q_1 d^3q_2 \cdots d^3q_n d^3p_1 d^3p_2 \cdots d^3p_n$$

Let's now determine the mean energy per particle.

$$\frac{\bar{E}}{N} = \frac{\int ap_k^2 C e^{-\beta ap_k^2} d^3q_1 d^3q_2 \cdots d^3q_n d^3p_1 d^3p_2 \cdots d^3p_n}{\int C e^{-\beta ap_k^2} d^3q_1 d^3q_2 \cdots d^3q_n d^3p_1 d^3p_2 \cdots d^3p_n}$$

We can factor out the constant  $C$  and break up the integration into two integrals, one with respect to generalized position and one with respect to generalized momentum.

$$\frac{\bar{E}}{N} = \frac{C \int d^3q_1 d^3q_2 \cdots d^3q_n \int ap_k^2 e^{-\beta ap_k^2} d^3p_1 d^3p_2 \cdots d^3p_n}{C \int d^3q_1 d^3q_2 \cdots d^3q_n \int e^{-\beta ap_k^2} d^3p_1 d^3p_2 \cdots d^3p_n}$$

The factor  $C$  and the integration over generalized position cancel.

$$\frac{\bar{E}}{N} = \frac{\cancel{C} \int \cancel{d^3q_1 d^3q_2 \cdots d^3q_n} \int ap_k^2 e^{-\beta ap_k^2} d^3p_1 d^3p_2 \cdots d^3p_n}{\cancel{C} \int \cancel{d^3q_1 d^3q_2 \cdots d^3q_n} \int e^{-\beta ap_k^2} d^3p_1 d^3p_2 \cdots d^3p_n}$$

$$\frac{\bar{E}}{N} = \frac{\int ap_k^2 e^{-\beta ap_k^2} d^3p_1 d^3p_2 \cdots d^3p_n}{\int e^{-\beta ap_k^2} d^3p_1 d^3p_2 \cdots d^3p_n}$$

The integral over all generalized momenta other than  $p_k$  also cancels. We next set the limits of the integrals to cover all possible values of  $p_k$ .

$$\frac{\bar{E}}{N} = \frac{\int_{-\infty}^{\infty} ap_k^2 e^{-\beta ap_k^2} dp_k}{\int_{-\infty}^{\infty} e^{-\beta ap_k^2} dp_k}$$

We now consult our trusty table of integrals.

$$\int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}} \quad \int_{-\infty}^{\infty} x^2 e^{-ax^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{a^3}}$$

$$\frac{\bar{E}}{N} = \frac{\frac{a}{2} \sqrt{\frac{\pi}{(\beta a)^3}}}{\sqrt{\frac{\pi}{\beta a}}} \rightarrow \frac{\bar{E}}{N} = \frac{1}{2\beta}$$

Each quadratic term in the expression for the energy of the system contributes  $\frac{1}{2\beta}$  to the average energy per molecule of the system. This result is referred to as the *equipartition theorem* as it describes how the average energy is partitioned equally to these quadratic energy states.

For example, a 3-dimensional ideal gas (*i.e.*, a gas for which the only energy possessed by the molecules is translational kinetic energy) would have an average energy per molecule of  $\bar{\epsilon} = 3 \left( \frac{1}{2\beta} \right) = \frac{3}{2\beta}$ . If this gas consisted of  $N$  molecules, the total average energy of the gas would be  $\bar{E} = N\bar{\epsilon} = \frac{3N}{2\beta}$ .

### 4.3 Summary

- The mean energy of a particle is determined from the partition function for that particle.

$$\bar{\epsilon} = -\frac{\partial}{\partial \beta} \ln(Z)$$

- Entropy can be determined from the partition function.

$$S = \ln(Z) + \beta \bar{E} \quad S = \ln(Z) - \beta \left( \frac{\partial \ln(Z)}{\partial \beta} \right)$$

- The partition function for a system of  $N$  classical and distinguishable particles is

$$Z_B = \left( \sum_n e^{-\beta \epsilon_n} \right)^N \quad Z_B = \left( \sum_i g_i e^{-\beta \epsilon_i} \right)^N$$

$$Z_B = \frac{1}{h^{3N}} \int e^{-\beta \sum_{i=1}^N H(\vec{q}_i, \vec{p}_i)} d^3 \vec{q}_1 \cdots d^3 \vec{q}_N d^3 \vec{p}_1 \cdots d^3 \vec{p}_N$$

	$D(k)dk$	$D(\epsilon)d\epsilon$
1-D	$\left(\frac{L}{2\pi}\right) dk$	$\left(\frac{L}{h} \sqrt{\frac{m}{8\epsilon}}\right) d\epsilon$
2-D	$\left(\frac{Ak}{2\pi}\right) dk$	$\left(\frac{mA}{2\pi h^2}\right) d\epsilon$
3-D	$\left(\frac{V k^2}{2\pi^2}\right) dk$	$\left(\frac{V}{\pi^2 h^3} \sqrt{\frac{m^3 \epsilon}{2}}\right) d\epsilon$

Table 4.2: Densities of states for different dimensionalities

- The partition function for a system of  $N$  classical and indistinguishable particles is

$$Z_{MB} = \frac{1}{N!} \left( \sum_n e^{-\beta \epsilon_n} \right)^N \quad Z_{MB} = \frac{1}{N!} \left( \sum_i g_i e^{-\beta \epsilon_i} \right)^N$$

$$Z_{MB} = \left( \frac{e}{N h^3} \right)^N \int e^{-\beta \sum_{i=1}^N H(\vec{q}_i, \vec{p}_i)} d^3 \vec{q}_1 \dots d^3 \vec{q}_N d^3 \vec{p}_1 \dots d^3 \vec{p}_N$$

- The partition function for a continuous distribution can be calculated using the density of states of the system.

$$Z = \int e^{-\beta \epsilon} D(\epsilon) d\epsilon$$

- **Equipartition Theorem:** Each quadratic term in the expression for the energy of the system contributes  $\frac{1}{2\beta}$  to the average energy per molecule of the system.