Chapter 5 Statistical Mechanics in Molecular Simulations

5.1 Introduction

In Chapter 4 the Maxwell-Boltzmann velocity and energy distributions were derived for non-interacting ideal gas molecules using a set of intuitive and physically appealing arguments. It is not clear how this approach can be extended to systems with interacting molecules or systems which interact with their environment. For such systems, the probability distribution for the N-molecule energy cannot be decomposed to a product of one-particle energy distributions,

\[ P_N(E) \neq P_1(e_1)P_1(e_2)\cdots P_1(e_N). \] (5.1)

For the case of systems with interacting molecules, the concept of the ensemble of systems was introduced by Ludwig Boltzmann in Vienna between the years 1870 and 1896 [Boltzmann] and developed and generalized in 1902 by J. Willard Gibbs at Yale University [Gibbs]. The ensemble was initially used to describe the time evolution of the distributions of systems in classical mechanical phase space under a given set of external constraints.

The derivation of the actual form of the probability distribution functions for interacting systems remained until after the discovery of the principles of quantum mechanics. Quantum mechanics initially provided guidance in determining proper rules for “counting’ the number of classical states (as for example in the Sackur-Tetrode analysis) [Grimus] and ultimately allowed the determination of the discrete quantum mechanical states of a system. The introduction of discrete states into the analysis made the calculation of the probability distributions in interacting systems much easier to perform. After deriving the quantum mechanical forms for the probability distributions, the expressions can be “translated” into a classical mechanical limit which is appropriate for continuous position and conjugate velocity variables of molecular dynamics simulations. The usefulness of the statistical mechanical relations to molecular dynamics and Monte Carlo simulation methodology is discussed in briefly in Sec. 5.9, but becomes much clearer in Chapters 6 and 10.

Up to this point, only mechanically isolated systems with fixed total energy have been considered. The use of ensembles allows coupling of the system with the environment through heat exchange, pressure equalization, molecule exchange, or other mechanisms. The coupling the system to the environment introduces external, non-microscopic thermodynamic factors into the distribution function. This was also seen in Chapter 4 where the macroscopic thermodynamic quantity of temperature is introduced into the distribution function of the microscopic mechanical variables of speed and energy by connecting the predictions of the velocity distribution to the macroscopic ideal gas law. By extending the scope of the calculated N-molecule probability distribution functions to include systems with interactions among molecules and coupling with external environment, the applicability of the statistical mechanical results is greatly enhanced.

In Chapter 4, we used a bottom up approach to derive the N-molecule energy distribution of the ideal gas system starting from a one-molecule energy distribution. Using the convolution of one-molecule energy distribution functions, the distributions of the total energy for larger collections of molecules were constructed, culminating in the N-molecule energy distribution \( P_N(E_N) \). In the ensemble approach, the formalism allows
us to calculate the $N$-molecule distribution function $P_N(E_N)$ directly. Based on the nature of the interactions in the system, the approach uses a top down approach to extract probability distributions for smaller subsets of molecules.

A critical assumption needed to relate the predictions of the ensemble approach to the behaviour of actual systems and molecular dynamics simulations is the so-called ergodic (from Greek: ergon (work) + hodos (way)) hypothesis, according to which, the probability for observing a state in an ensemble of systems reflects the relative amount of time an individual system spends in that state. In other words, we can predict the average time behavior of a system of interest by making predictions on the behavior of an ensemble of the system of interest and vice versa. We revisit this important assumption after the distribution functions for interacting systems are described.

5.2 Discrete states in quantum mechanical systems

In simple systems with interaction potentials similar to those discussed in Chapter 1, classical mechanics allows the calculation of the energy $\varepsilon$ of an object if its position $\mathbf{r}$ and conjugate momentum $\mathbf{p}$ (the phase space variables) are specified at an initial time. The set of $\{\mathbf{r}, \mathbf{p}\}$ define the classical state of the system. The phase space trajectory gives the constant energy pathway in phase space over which the motion occurs for that particular interaction. A continuous range of energies are accessible for objects in classical mechanical systems and each value of energy corresponds to a unique phase space trajectory. In complex many-body systems, the phase space variables are positions $\mathbf{r}_i$ and their conjugate momentum $\mathbf{p}_i$ for all objects $i$ in the system. Each state $\{\mathbf{r}_i, \mathbf{p}_i\}$ is associated with a constant energy, $E$, and a unique phase space trajectory over which it moves. In the many-body systems with complex interactions we may not be able to explicitly determine the energy or the phase space trajectory, but nonetheless, these entities exist and are useful in describing the behavior of the system.

In quantum mechanics, stationary behaviors of molecules are determined by the time-independent Schrödinger equation,

$$\hat{H}\psi_n(\mathbf{r}) = (\hat{K} + \hat{U}(\mathbf{r}))\psi_n(\mathbf{r}) = E_n\psi_n(\mathbf{r}),$$

as described in Sec.2.2.1. The solutions to this equation consists of a set of discrete quantum states characterized by wave functions $\psi_n(\{\mathbf{r}\})$ and their corresponding energy levels $E_n$. The wave function determines the probability of finding the atoms in the molecule at specific locations or it can be transformed to give the probability that atoms in the molecule have certain values of momentum. In quantum mechanics, even though the energy of a state is known, the position and momentum cannot be determined with infinite precision in the form of a trajectory, as was the case in classical mechanics. Similar to the classical mechanical case, in complex $N$-molecule interacting systems, it may not be possible to determine the discrete energies and wave functions which make up the state of the system, but such quantized energy states values exist. The existence of these $N$-molecule states is sufficient to derive general expressions for the probability distributions of systems among available states. Once the expressions for the probability distributions are determined, in statistical mechanics the focus shifts to introducing simplifications to the description of the $N$-molecule energy states. Alternatively, the quantum mechanical relations for the probability distribution are transformed to their corresponding classical limits, in which case the complex $N$-molecule energies can be
either simplified or directly determined by numerical calculations in molecular dynamics or Monte Carlo simulations.

Two simple quantum mechanical systems for which discrete states can be determined are the particle in a box, which is a model for an ideal gas, and the quantum mechanical harmonic oscillator.

The ideal gas is an isolated collection of $N$ molecules where the sum of the energies of the individual molecules gives the total system energy of $E_N$. Quantum mechanically, a non-interacting molecule in a rigid cubic box of volume $V$ is described by the particle in a box model. The quantized energy states of a molecule in the cubic box are described by

$$
\varepsilon_n(V) = \frac{\hbar^2}{8mV^{2/3}} \left( n_x^2 + n_y^2 + n_z^2 \right),
$$

(5.3)

where $n_x, n_y, n_z$ are the quantum numbers associated with the translational motion of molecule in the $x$-, $y$-, and $z$-directions, $m$ is the mass of the molecule, and $\hbar$ is Planck’s constant. Each state has an associated wave function given by,

$$
\psi_{n_x,n_y,n_z} = A_{n_x,n_y,n_z} \sin(\pi n_x x / L) \sin(\pi n_y y / L) \sin(\pi n_z z / L)
$$

(5.4)

The three quantum numbers specify the quantum state $\mathbf{n} = \{n_x,n_y,n_z\}$ which determines the form of the wave function $\psi_{\mathbf{n}}$ and energy levels accessible to the molecule. States with different combinations of $\{n_x,n_y,n_z\}$ can have the same energy, in which case they are degenerate. Further details on the particle in a box model are given in Appendix 5.1.

A system with $N$-molecules in non-interacting particle in a box states is characterized by the total energy $E_N$,

$$
E_N = \sum_{\mathbf{v}=1}^{N} \varepsilon_{\mathbf{v}}(V) = \frac{\hbar^2}{8mV^{2/3}} \sum_{\mathbf{v}=1}^{N} \left( n_{x,v}^2 + n_{y,v}^2 + n_{z,v}^2 \right),
$$

(5.5)

where each molecule $\mathbf{v}$ has a quantum state characterized by $\mathbf{n}$.

Three-dimensional harmonic oscillators with frequencies $\nu_x, \nu_y, \nu_z$ (such as atoms oscillating in a solid lattice) have quantum mechanical states with energies given by,

$$
\varepsilon_{\mathbf{n}}(V) = \left( n_x + \frac{1}{2} \right) \hbar \nu_x + \left( n_y + \frac{1}{2} \right) \hbar \nu_y + \left( n_z + \frac{1}{2} \right) \hbar \nu_z,
$$

(5.6)

where $n_i$ is the quantum number associated with the vibrational state of the oscillator and $\nu_i$ is the frequency of that oscillator. Based on symmetries in the structure, degeneracy can be observed in these three-dimensional harmonic oscillator states. Each state has an associated wave function given by,

$$
\psi_{n_x} = \frac{1}{\sqrt{2^{n_x} n_x!}} \left( \frac{\mu_x \nu_x}{\pi \hbar} \right)^{1/4} \frac{1}{\sqrt{2^{n_x} n_x!}} e^{-\mu_x \nu_x^2 / 2 \hbar} H_{n_x} \left( \frac{\mu_x \nu_x}{\hbar} \right),
$$

(5.7)

where $\mu_x$ is the reduced mass of the oscillator in the $x$-direction and $H_n(x)$ are the Hermite polynomials. [Levine]

### 5.3 Distributions of a system among discrete energy states

In Sections 5.3 and 5.4, the conceptual and mathematical formalism associated with ensembles for systems of non-interacting molecules, in particular an ideal gas system, are discussed. This analysis gives results identical to Eq. (4.59) for the probability of
observing an energy $E_N$ for a non-interacting $N$ molecule system. The mathematical formalism is then extended to describe systems with interacting molecules.

In most quantum systems, $N$ molecules can be distributed in many different ways among the one-molecule quantum states to get a specific value of the total energy $E_N$. As an illustration of the distribution of molecules among energy levels, we first examine a model system of non-interacting molecules with quantized energy levels. Consider a system of non-interacting molecules where each molecule has an infinite number of equally spaced energy levels separation by an energy of $\Delta$ such that $\varepsilon_n = n\Delta$ with $n = 0, 1, 2, 3, \ldots$ similar to harmonic oscillator levels. \begin{footnotesize}(Atkins, Nash, Gurney)\end{footnotesize} We consider simple cases with $N = 5$, $7$, and $9$ molecules and assume that in each case, the average energy per molecule is $\langle \varepsilon \rangle = \Delta$ or equivalently the total energy is $E_N = N\Delta$. This information corresponds to knowledge of the macrostate of the system. What are the possible distributions of $N$ molecules among the energy levels such that they satisfy the conditions of the macrostate?

The case of the macrostate with five molecules and $E_5 = 5\Delta$ is shown in Figure 5.1. There are seven distinct distributions of molecules among the energy levels, the so-called microstates for a system, which are consistent with the macrostate. These seven distinct distributions satisfy the constraints of the macrostate but may have different properties, such as the velocity distribution for the molecules in the system.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.1.png}
\caption{The seven possible distributions (microstates) of five molecules among available one-molecule quantum states in a hypothetical system with a total energy $E_{\text{tot}} = 5\Delta$. One-molecule quantum states with energies $6\Delta$ or higher are not occupied as they are not consistent with the constraints imposed on the distribution.}
\end{figure}

A more compact notation to describe the distributions is given in Table 5.1 where each distribution is represented as a set of occupancies of the energy levels, $\mathbf{a} = \{a_i\}$, with the occupancy of each quantum state $i$, representing as $a_i$.

\begin{table}[h]
\centering
\caption{The distributions for five molecules among equally spaced levels with a total energy of $5\Delta$. The degeneracies of the microstates are also given.}
\begin{tabular}{|c|c|}
\hline
Distribution $\mathbf{a} = \{a_1,a_2,a_3,a_4,a_5,a_6\}$ & Degeneracy, $W(\mathbf{a})$ (number of microstates) \\
\hline
$\{4,0,0,0,0,1\}$ & 5 \\
$\{3,1,0,0,1,0\}$ & 20 \\
$\{3,0,1,1,0,0\}$ & 20 \\
$\{2,2,0,1,0,0\}$ & 30 \\
\hline
\end{tabular}
\end{table}
The distributions in Figure 5.1 and Table 5.1 do not account for the labeling of the five molecules. For example, the \{4,0,0,0,1\} distribution is composed of five microstates, namely, those with molecule 1, 2, 3, 4, or 5 in the $a_6$ quantum state. These five microstates have identical properties since they only differ in how the identical molecules are distributed among the same levels. The number of microstates for each distribution, $W(a)$, is called the degeneracy or statistical weight of the distribution, which is the number of ways $N$ molecules can be binned among energy levels with $a_1$ in level 1, $a_2$ in level 2, ..., $a_j$ in level $j$. The degeneracy can be calculated by,

$$W(a) = \frac{N!}{a_1!a_2!a_3!\cdots} = \prod a_i!.$$  \hspace{1cm} (5.6)

The values of the degeneracy of each microstate are given in Table 5.1. There are a total of 126 distinct microstates associated with all the distributions in this macrostate. The assumption of equal a priori probabilities used in statistical mechanics states that none of these 126 microstates are preferred over the others. Assigning equal a priori probabilities to the microstates, however, does not mean that all distributions contribute equally to the macrostates. Distributions with larger degeneracies (number of microstates) have a greater probability of being observed than those with smaller degeneracy. The distributions \{2,2,0,1,0,0\} and \{2,1,2,0,0,0\} are the most probable for this system.

The possible distributions and the corresponding degeneracies for the example of seven identical molecules distributed among the same energy levels with a total energy of $E_{tot} = 7\Delta$ are given in Table 5.2. By adding two additional molecules to the system, the numbers of possible distributions and corresponding microstates have increased substantially to 15 and 1716, respectively.

From the assumption of equal a priori probabilities, all 1716 microstates have identical contributions to system properties. The most probable distribution \{3,2,1,1,0,0,0,0\} has the largest degeneracy and the largest statistical weight in the macrostate.

**Table 5.2.** The distributions available for the macrostate of seven molecules with a total energy of $7\Delta$. The degeneracy of each distribution is also given.

<table>
<thead>
<tr>
<th>Distribution $a{a_1, a_2, \ldots, a_7, a_8}$</th>
<th>$W(a)$</th>
<th>Distribution $a{a_1, a_2, \ldots, a_7, a_8}$</th>
<th>$W(a)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>{6,0,0,0,0,0,1}</td>
<td>7</td>
<td>{3,3,0,0,1,0,0,0}</td>
<td>140</td>
</tr>
<tr>
<td>{5,1,0,0,0,1,0}</td>
<td>42</td>
<td>{3,2,1,1,0,0,0,0}</td>
<td>420</td>
</tr>
<tr>
<td>{5,0,1,0,0,1,0}</td>
<td>42</td>
<td>{3,1,3,0,0,0,0,0}</td>
<td>140</td>
</tr>
<tr>
<td>{5,0,0,1,1,0,0}</td>
<td>42</td>
<td>{2,4,0,1,0,0,0,0}</td>
<td>105</td>
</tr>
<tr>
<td>{4,2,0,0,0,1,0}</td>
<td>105</td>
<td>{2,3,2,0,0,0,0,0}</td>
<td>210</td>
</tr>
<tr>
<td>{4,1,1,0,1,0,0}</td>
<td>210</td>
<td>{1,5,1,0,0,0,0,0}</td>
<td>42</td>
</tr>
<tr>
<td>{4,1,0,2,0,0,0}</td>
<td>105</td>
<td>{0,7,0,0,0,0,0,0}</td>
<td>1</td>
</tr>
<tr>
<td>{4,0,2,1,0,0,0}</td>
<td>105</td>
<td>Sum:</td>
<td>1716</td>
</tr>
</tbody>
</table>
The trends described above are enhanced for the distributions of a macrostate with nine molecules in a system with $E_{tot} = 9\Delta$. All possible distributions and the corresponding degeneracy of each case are given in Table 5.3. As the number of molecules increases, the numbers of microstates starts increasing substantially. The most probable distribution with occupancies $\{4,2,2,1,0,0,0,0,0\}$ has the largest degeneracy and the largest statistical weight in the macrostate. The probability for this microstate is significantly greater than many of the other microstates in this macrostate.

Table 5.3. The distributions available for nine molecules with a total energy of $9\Delta$ along with degeneracies of each distribution.

<table>
<thead>
<tr>
<th>Distribution $a{a_1, a_2, \ldots, a_{10}}$</th>
<th>$W(a)$</th>
<th>Distribution $a{a_1, a_2, \ldots, a_{10}}$</th>
<th>$W(a)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>${8,0,0,0,0,0,0,0,0,0}$</td>
<td>9</td>
<td>${5,1,2,0,1,0,0,0,0,0}$</td>
<td>1512</td>
</tr>
<tr>
<td>${7,1,0,0,0,0,0,0,0,0}$</td>
<td>72</td>
<td>${5,1,1,2,0,0,0,0,0,0}$</td>
<td>1512</td>
</tr>
<tr>
<td>${7,0,1,0,0,0,0,1,0,0}$</td>
<td>72</td>
<td>${4,4,0,0,0,1,0,0,0,0}$</td>
<td>630</td>
</tr>
<tr>
<td>${7,0,0,1,0,1,0,0,0,0}$</td>
<td>72</td>
<td>${4,14,0,0,0,0,0,0,0,0}$</td>
<td>630</td>
</tr>
<tr>
<td>${7,0,0,0,1,0,1,0,0,0}$</td>
<td>72</td>
<td>${4,14,1,0,0,0,0,0,0,0}$</td>
<td>2520</td>
</tr>
<tr>
<td>${6,2,0,0,0,0,0,1,0,0}$</td>
<td>252</td>
<td>${4,3,0,2,0,0,0,0,0,0}$</td>
<td>1260</td>
</tr>
<tr>
<td>${6,0,2,0,1,0,0,0,0,0}$</td>
<td>252</td>
<td>${4,22,1,0,0,0,0,0,0,0}$</td>
<td>3780</td>
</tr>
<tr>
<td>${6,1,1,0,0,0,1,0,0,0}$</td>
<td>504</td>
<td>${3,3,3,0,0,0,0,0,0,0}$</td>
<td>1680</td>
</tr>
<tr>
<td>${6,1,0,1,0,1,0,0,0,0}$</td>
<td>504</td>
<td>${3,4,1,1,0,0,0,0,0,0}$</td>
<td>2520</td>
</tr>
<tr>
<td>${6,0,1,1,1,0,0,0,0,0}$</td>
<td>504</td>
<td>${3,5,0,1,0,0,0,0,0,0}$</td>
<td>504</td>
</tr>
<tr>
<td>${6,0,0,3,0,0,0,0,0,0}$</td>
<td>84</td>
<td>${2,6,0,1,0,0,0,0,0,0}$</td>
<td>256</td>
</tr>
<tr>
<td>${5,3,0,0,0,0,1,0,0,0}$</td>
<td>504</td>
<td>${0,9,0,0,0,0,0,0,0,0}$</td>
<td>1</td>
</tr>
<tr>
<td>${5,0,3,1,0,0,0,0,0,0}$</td>
<td>504</td>
<td>Sum</td>
<td>21722</td>
</tr>
<tr>
<td>${5,2,1,0,0,1,0,0,0,0}$</td>
<td>1512</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Direct counting of microstates to determine the most probable distribution is obviously only feasible for systems with small numbers of molecules. However, as the number of molecules increases, the most probable distribution has an overwhelmingly larger contribution to system properties compared to other distributions. For macroscopic systems with the order of $10^{23}$ or so molecules, the most probable distribution has such a overwhelmingly larger probability, that the contributions of other states can effectively be neglected in determining system properties. Thus the task of statistical mechanics of large systems becomes finding a mathematical expression for the number of distributions of the system subject to the physical constraints applied to the macrostate and from that to determine the most probable distribution.

There are two approaches to calculating the most probable distribution of microstates. The conceptually simpler approach, initially developed by Boltzmann, is called the $\mu$-space (for molecule-space) representation.[Boltzmann,Ehrenfest] This approach is only applicable to systems of non-interacting molecules and even in these cases has limitations. This approach is first used in Sec. 5.4 to illustrate the mathematical approach needed to determine the most probable distribution. The second approach, called the $\gamma$-space (gas-space) representation, based on constructing an ensemble of systems was developed conceptually by Gibbs.[Gibbs,Ehrenfest] The $\gamma$-space approach considers distributing the energy among the $N$-molecule states of the entire system. The two methods may appear superficially similar since they use identical mathematical
expressions to determine the most probable distribution, but the ensemble method does not have the limitations of the molecular approach and is valid in systems of interacting molecules.

5.4 Systems with non-interacting molecules: The μ-space approach

Consider the system with \( N \) non-interacting molecules, first equilibrated at temperature \( T \) and then confined in an isolated system with rigid walls as shown in the left hand of Figure 5.2. After equilibration, the total energy of the system is \( E_N \). Each one of these molecules is in a quantum mechanical state \( \psi_j \) and energy \( \epsilon_j \).

Figure 5.2. A representation of \( N \) non-interacting molecules in an isolated system equilibrated at a temperature \( T \). The energy of each molecule in the system is binned according to the available discrete values \( \{ \epsilon_i \} \). After binning is completed, each energy state (bin) \( \epsilon_i \) has an occupancy of \( a_i \).

There can be many microstates with \( N \) molecules distributed among the quantum states \( \epsilon_i \) such that the total system macrostate has an energy \( E_N \). In a process similar to that illustrated in Fig. 5.1 and Tables 5.1 to 5.3, in any particular microstate distribution, there are \( a_1 \) molecules occupying quantum state \( j = 1 \) with energy \( \epsilon_1 \), \( a_2 \) molecules in quantum state \( 2 \) with energy \( \epsilon_2 \), or generally, \( a_i \) molecules in quantum state \( i \) with energy \( \epsilon_i \). This binning of the energies of the individual molecules into corresponding energy values is shown schematically in Fig. 5.2.

The energies of individual molecules are ordered such that \( \epsilon_i \leq \epsilon_{i+1} \). The occupancies of a particular distribution are represented as the set \( \mathbf{a} = \{ a_i \} \) which must satisfy the constraints,
\[
\begin{align*}
\sum_j a_j &= N \\
\sum_j a_j \epsilon_j &= E_N
\end{align*}
\] (5.7)

The degeneracy for a distribution of \( N \) molecules characterized by a set of occupancies \( a_1, a_2, \ldots, \) is calculated from Eq. (5.6). For specific \( N \) and \( E_N \) values, the distribution \( \{ a_i \} \) is not unique and other distributions \( \mathbf{a'} = \{ a'_i \} \) can satisfy the same constraints. As indicated in the discussions above, as \( N \to \infty \), the most probable distribution, \( \mathbf{a^*} = \{ a^*_i \} \) has a much greater probability than other distributions and effectively determines the
properties of the collection or ensemble of molecules. In the most probable distribution, the probability of observing a particular one-molecule state \( i \) is,

\[
P_i = \frac{a_i^*}{N}
\]

and the average of any mechanical property, \( \langle M \rangle \) is determined by,

\[
\langle M \rangle = \sum_j M_j P_j.
\]

To determine the set of occupancies in the most probable distribution, \( a_i^* \), the function \( W(a^*) \) in Eq. (5.6) is maximized with respect to the occupancies \( a_i \) of each state, subject to the constraints given in Eq. (5.7). In finding the maximum degeneracy, the discrete occupancies, \( a_i \), in Eq. (5.6) are treated as being continuous variables. This assumption is valid for macroscopic systems where \( N \) and the \( a_i \) are large. The degeneracy \( W(a) = N!/(a_1!a_2!...\) contains factorials of occupancy numbers and it is not clear how to determine derivatives of factorials. The mathematical trick to overcome the presence of factorials is to realize that since a function and its logarithm have their maxima (and minima) at the same positions, we can determine the maximum of the logarithm, \( \ln W(a) \) instead of the maximum of \( W(a) \). The logarithm of factorials is determined using Stirling’s approximation for factorials of large numbers (named after James Stirling, the Scottish mathematician: 1692-1770) discussed in Appendix 4.4.1, namely, \( \ln n! \sim n\ln n - n \). Using this approximation in Eq. (5.6) gives,

\[
\ln W(a) = N \ln N - N - \sum_j a_j \ln a_j + \sum_j a_j = N \ln N - \sum_j a_j \ln a_j
\]

To optimize \( \ln W(a) \) subject to constraints on the independent variables, we use the method of Lagrange multipliers introduced in Appendix 3.3 of Chapter 3. In this method, the constraint equations, such as those of Eq. (5.7), are multiplied by unknown Lagrange multipliers and added to the original function to be optimized. The maximum of the new function is calculated in the normal manner, treating all variables \( a_i \) as independent.

In the case of Eq. (5.6), introducing undetermined multipliers \( \alpha \) and \( \beta \), occupancies are determined in the most probable distribution \( a_i^* \) by solving,

\[
\frac{\partial}{\partial a_i} \left[ N \ln N - \sum_j a_j \ln a_j - \alpha \left( \sum_j a_j - N \right) - \beta \left( \sum_j a_j e_j - E \right) \right] = 0
\]

In the summations of Eq. (5.11), only terms with \( j = i \) give non-zero derivatives. Solving for \( a_i^* \) in Eq. (5.11) gives,

\[
a_i^* = e^{-(1+\alpha)} e^{-\beta e_i} \quad \text{with} \quad i = 1, 2, \ldots
\]

The \( \alpha \) multiplier, which is related to the constraint on the total number of molecules, is determined from the condition that the sum of all occupied states is equal to the total number of molecules in the system,

\[
\sum_i a_i^* = N \Rightarrow e^{-(1+\alpha)} = N/\sum_i e^{-\beta e_i}
\]

Combining Eqs. (5.8) and (5.13) gives the probability of having quantum state \( i \) occupied in the most probable microstate as,

\[
P_i = e^{-\beta e_i} / \sum_j e^{-\beta e_j}.
\]

The \( \beta \) multiplier is introduced for the constraint on the total energy in Eq. (5.7). For the particle in a box / ideal gas system, in Appendix 5.1 we show that \( \beta = 1/kT \). Using the expression for \( \sum_j e^{-\beta e_i} \) derived for the ideal gas system in Eq. (A5.8), the discrete
probability for observing a molecule in particle in a box state \( i \) in the most probable distribution is,

\[
P_i = \left( \frac{\hbar^2}{2\pi mkT} \right)^{3/2} \frac{1}{V} e^{-\epsilon_i / kT}
\]

(5.15)

This can be compared to Eq. (4.49) for the classical energy distribution of a molecule from the Maxwell-Boltzmann distribution.

The collection of molecules in Fig. 5.2 is analogous to an ensemble. Each molecule can be considered to be in a constant temperature “bath” made up of other molecules in the system.

Key to deriving Eq. (5.15) is the assumption that individual molecules have discrete molecular states required for the counting scheme shown in Fig. 5.2 and Eq. (5.7) to be valid. It is not clear how the derivation can be extended to systems with interacting molecules where the discrete states involve more than single molecules and a counting scheme similar to that given in Eq. (5.7) no longer holds. We will see that the same mathematical methodology can be adapted for systems of interacting molecules, if we change the meaning of the states and energies used to describe the system.

### 5.5 Interacting systems and ensembles: The \( \gamma \)-space approach and the canonical ensemble

The quantum mechanical state of \( N \) molecules in a volume \( V \) interacting with known intra- and intermolecular potentials is described by \( N \)-molecule wave functions \( \Psi_n(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \) with corresponding discrete \( N \)-molecule energies, \( E_n \). It may not be possible to directly determine the states of the interacting \( N \)-molecule system, but for present purposes, we only need to know that such discrete quantum states exist.

Consider a system as shown in Fig. 5.3(a), with \( N \) molecules confined in a container of fixed volume \( V \) with heat conducting walls which allow the exchange of energy between the system and its surroundings (called the “bath”) which are at temperature \( T \). Instead of analyzing this set-up with an individual system, we place a collection of \( \mathcal{A} \) replicas of the system (the ensemble of systems) in thermal contact with each other in the large macroscopic thermostated bath at temperature \( T \), as shown in Figure 5.3(b). The bath surrounding the ensemble is infinitely large and the exchange of energy between the system replicas and the bath does not change the temperature of the bath. Each system in the ensemble can exchange energy with both the bath and other systems in the ensemble.

The ensemble and bath are allowed to equilibrate. After equilibration, we remove ensemble of systems from contact with the bath and surround it with a thermally insulating wall, as shown in Figure 5.3(c). In this state, the member systems of the ensemble still exchange energy with each other through their heat conducting walls, but the ensemble as a whole is isolated from the environment. When isolated, the ensemble of systems has a constant total energy \( \mathcal{E} \). The number of systems in the ensemble \( \mathcal{A} \) and the total ensemble energy \( \mathcal{E} \) are not physically measurable quantities since the ensemble is a theoretical construct. These quantities are ultimately eliminated from the final results of the analysis. The total ensemble energy \( \mathcal{E} \) is not related to the energies \( E_j \), of the \( N \)-molecule quantum states of each system.
Introduction to Molecular Simulation  Chapter 5. Statistical Mechanics

![Diagram](image)

**Figure 5.3.** (a) The experimental set-up of a system with constant $N$ and $V$ in contact with a thermostated bath at temperature $T$. For the canonical ensemble, the set-up in (a) is replaced by an ensemble composed of a very large number $A$ of replicas of the target system at constant $N$ and $V$ separated by heat conducting walls placed in the thermostated bath in (b). The member systems of the ensemble are brought into equilibrium with each other and with the bath of temperature $T$. Afterwards, the ensemble is separated from the bath and isolated within a rigid, thermally insulating wall (c). The total energy of the isolated ensemble is taken as $E$.

The key insight in the setup of Fig.5.3(c) is that individual systems in the isolated ensemble are analogous to molecules in the isolated system of Fig. 5.2. The systems in the ensemble interact with each other through the exchange of heat but are otherwise independent. Gibbs exploited this analogy to introduce the concept of the ensemble in the context of classical mechanics. The particular ensemble shown in Fig. 5.3 where member systems all have the same $N$, $V$, and $T$ and can exchange energy is called a canonical ensemble. Based on the constraints on the ensemble, a more descriptive name for the canonical ensemble would be the isothermal-isochoric (or isothermal-isometric) ensemble. The canonical ensemble in Fig. 5.3(c) has a total of $A$ systems and a total ensemble energy of $E$. All member systems of the ensemble have the same set of $N$-molecule eigenstates $\{E_j\}$ which are ordered such that $E_j \leq E_{j+1}$.

In the ensemble, the systems are distributed among their accessible quantum states such that there are $A_1$ systems in the $N$-molecule quantum state with energy $E_1$, $A_2$ systems in the quantum state with energy $E_2$, or generally, $A_j$ systems in the state with energy $E_j$.

The ensemble is characterized by a set of distributions with occupancy numbers $A_i$, represented in vector form as $A = \{A_i\}$. Any distribution of the system among the states must satisfy the conditions,

$$\begin{align*}
\sum_j A_j &= A \\
\sum_j A_j E_j &= E
\end{align*}$$

(5.16)

The ensemble was designed so that the total energy of the ensemble $E$ is a simple sum of the energies of the non-interacting member systems. The situation is analogous to that of Eq. (5.7) where the system is made of non-interacting molecules.

Each distinguishable system 1, ..., $A$ in the ensemble can be identified and its quantum state determined. For an ensemble distribution characterized by occupancies $A$, the number of ways of assigning the systems so there are $A_1$ systems in state $\Psi_1$ with energy $E_1$, $A_2$ in state $\Psi_2$ with energy $E_2$, and so on, is calculated from,
\[
W(\mathcal{A}) = \frac{\mathcal{A}!}{A_1!A_2!A_3!\cdots} = \frac{\mathcal{A}!}{\prod_j A_j!}.
\] (5.17)

For specific \(\mathcal{A}\) and \(E\) values, the distribution \(\mathcal{A}\) is not unique and other distributions \(\mathcal{A}' = \{A'_1, A'_2, \ldots\}\) can also satisfy the constraints of Eq. (5.16). As \(\mathcal{A} \to \infty\), the most probable distribution \(\mathcal{A}^*\) has such a higher probability than all other distributions that it alone effectively determines the properties of the ensemble. The analysis to find the distribution of quantum states in the most probable distribution follows the mathematical form given in the discussion after Eq. (5.7). In the most probable distribution, the probability of observing an \(N\)-molecule quantum state \(i\) is,

\[
P_i = \frac{A_i^*}{\mathcal{A}}
\] (5.18)

and the ensemble average of any mechanical property \(M\) can be determined by Eq. (5.9). To determine the set of \(A_i^*\), we maximize \(\ln[W(\mathcal{A})]\) subject to the constraints of Eq. (5.16), by defining the function \(\Lambda(\{A_i\}; \alpha, \beta)\) with Lagrange multipliers \(\alpha\) and \(\beta\),

\[
\Lambda(\{A_i\}; \alpha, \beta) = \mathcal{A} \ln \mathcal{A} - \sum_j A_j \ln A_j - \alpha \left( \sum_j A_j - \mathcal{A} \right) - \beta \left( \sum_j A_j E_j - \mathcal{E} \right)
\] (5.19)

In writing Eq. (5.19), we used Stirling’s approximation for the factorials in Eq. (5.17). In an arbitrarily large ensemble with \(\mathcal{A} \to \infty\), the \(A_j\) can be treated as continuous variables. In the most probable distribution, the occupancy of state \(i\), \(A_i^*\) can be determined in the presence of the constraints from,

\[
\frac{\partial}{\partial A_i^*} \left[ \mathcal{A} \ln \mathcal{A} - \sum_j A_j^* \ln A_j - \alpha \left( \sum_j A_j^* - \mathcal{A} \right) - \beta \left( \sum_j A_j^* E_j - \mathcal{E} \right) \right] = 0
\] (5.20)

which gives,

\[
A_i^* = e^{-(1+\alpha)} e^{-\beta E_i} \quad \text{for } i = 1, 2, \ldots
\] (5.21)

The \(\alpha\) multiplier is determined by applying the constraint on the number of systems in the ensemble, \(\sum_i A_i^* = \mathcal{A}\) in Eq. (5.21),

\[
\sum_i A_i^* = \mathcal{A} = e^{-(1-\alpha)} \sum_i e^{-\beta E_i}
\] (5.22)

Substituting \(A_i^*\) in Eq. (5.18) gives the expression for the probability of having the system in quantum state \(i\) in the most probable distribution,

\[
P_i = \frac{A_i^*}{\mathcal{A}} = \frac{e^{-\beta E_i(N,V)}}{\sum_j e^{-\beta E_j(N,V)}} = \frac{e^{-\beta E_i(N,V)}}{Q(N,V,\beta)}.
\] (5.23)

The last equality defines the canonical partition function \(Q(N,V,\beta)\), as named by Charles G. Darwin and Ralph Fowler. [Darwin] The original German name given by Max Planck to this quantity is the Zustandssumme (“state sum” or “sum-over-states”) is more descriptive of its content. [Planck] The canonical probability distribution in Eq. (5.23) decays exponentially as the energy of states \(E_i(N,V)\) increases. The rate of decay depends on the temperature such that at higher temperatures there is a greater probability of high energy states begin occupied.

Although Eq. (5.23) is similar in form to Eq. (5.14), in the latter, energy states \(e_j\) are single-molecule energy states for a system of non-interacting molecules, while in Eq. (5.23), \(E_j\) is the \(N\)-molecule energy state for a system of interacting molecules. The \(a_j^*\) in
Eq. (5.12) are the number of molecules in the $N$-molecule system in state $e_j$, while $A_j^*$ are the number of systems in the hypothetical $\beta$-system ensemble in the state $E_j$.

The average energy for members of the ensemble, $E_j(N,V)$ is,

$$
\langle E(N,V,\beta) \rangle = \sum_j P_j E_j(N,V) = \frac{\sum_j E_j(N,V)e^{-\beta E_j(N,V)}}{\sum_i e^{-\beta E_i(N,V)}},
$$

(5.24)

where the total molecule number and volume dependence of the energy states is explicitly shown.

To find the value of $\beta$ in this general case, the predictions of statistical mechanics are compared with known thermodynamic relations. The thermodynamic relation between pressure and energy of a system, $P = -(\partial E/\partial V)_N$, allows us to write the pressure corresponding to each quantized state $j$ as, $P_j = -[\partial E_j(N,V)/\partial V]_N$. The expectation value of the pressure in the ensemble is thus,

$$
\langle P(N,V,\beta) \rangle = \sum_j P_j = -\frac{\sum_j \left( \frac{\partial E_j(N,V)}{\partial V} \right) e^{-\beta E_j(N,V)}}{\sum_i e^{-\beta E_i(N,V)}}.
$$

(5.25)

The ensemble averages of energy and pressure in Eqs. (5.24) and (5.25) are taken to be equal to the thermodynamic averages of the internal energy and pressure in a macroscopic system.

The thermodynamic equation of state relates the volume derivative of the internal energy to the pressure and temperature derivative of the pressure, [Zemansky, Moore, Atkins]

$$
\left( \frac{\partial E}{\partial V} \right)_{T,N} = -P - \frac{1}{T} \left( \frac{\partial P}{\partial 1/T} \right)_{N,V}.
$$

(5.26)

In Appendix 5.2, by comparing the statistical mechanical relations in Eqs. (5.24) and (5.25) with the thermodynamic relation of Eq. (5.26), it is proven that the $\beta$ Lagrange multiplier is proportional to the inverse of the temperature, $\beta = 1/kT$ where $k$ is the Boltzmann constant.

Relating the probabilistic statistical mechanical analysis of the microscopic system to the macroscopic thermodynamic relation allows the Lagrange multiplier $\beta$ in Eq. (5.23) to be identified with the macroscopic variable temperature. The coupling of the ensemble of systems to the thermostat bath to give a constant ensemble energy of $E$ introduces a non-mechanical Lagrange multiplier related to temperature in the description of the system. Note that in the final expression for the probability of observing a system in a particular quantum state $j$, the theoretical properties attributed to the ensemble, namely the number of replicas of the system in the ensemble $A$, and the total ensemble energy $E$, do not appear.

In addition to the sum-over-states form of the canonical partition function in Eq. (5.23), the partition function can also be written as a sum over energy levels,

$$
Q(N,V,E) = \sum_j e^{-E_j(N,V)/kT} = \sum_E \Omega(N,V,E)e^{-E(N,V)/kT}.
$$

(5.27)

where $\Omega(N,V,E)$ is the degeneracy of the energy level $E$. Note that the degeneracy generally increases, while the exponential term $\exp(-E/kT)$ decays as the energy
increases. All systems of the canonical ensemble have the same number of molecules \( N \), volume \( V \), and temperature \( T \). These quantities are the characteristic thermodynamic quantities of the canonical ensemble.

5.5.1 Thermodynamics quantities

In determining thermodynamic variables from the partition function, it is more convenient to use the logarithm of the canonical partition function,

\[
\ln Q(N,V,T) = \ln \left( \sum_j e^{-E_j(N,V)/kT} \right)
\]

With this definition, average values of the energy and pressure for systems in the canonical ensemble given in Eqs. (5.24) and (5.25), respectively, can be written in simplified form as,

\[
\langle E(N,V,T) \rangle = kT^2 \left( \frac{\partial \ln Q(N,V,T)}{\partial T} \right)_{N,V}
\]

and,

\[
\langle P(N,V,T) \rangle = kT \left( \frac{\partial \ln Q(N,V,T)}{\partial V} \right)_{N,T}
\]

Having determined the average mechanical properties of energy and pressure in the systems in the ensemble, we next determine statistical mechanical interpretations of heat and work. The complete differential of the average energy defined using Eq. (5.9) is,

\[
d\langle E \rangle = \sum_j P_j dE_j + \sum_j E_j dP_j
\]

Equation (5.31) shows there are two ways to change the average energy of an ensemble of systems. First, energy levels of the system can be changed without changing occupancies of the different states. Changing the volume of a system, for example, perturbs the energy levels of a quantum mechanical system from \( E_j \) to \( E_j + dE_j \). If \( A_j \) systems in ensemble are in state \( E_i \), the total contribution to the energy change as a result of the change of volume is \( \sum_j A_j dE_j \). This energy change in the ensemble is associated with the total work done on the ensemble as a result of the change in volume, and the ensemble average work done on the system is, \( \delta w_{rev} = \sum_j P_j dE_j \).

The second way to change the average energy of the ensemble is to vary the occupancy numbers of the states from \( A_j \) to \( A_j + dA_j \), while keeping the energy levels unchanged. In this case, the change of energy in the ensemble for state \( j \) is \( E_j dA_j \), which averaged over the entire ensemble becomes, \( \sum_j E_j dP_j \).

Thermodynamically, heat transfer between the system and surroundings is the difference between the total energy change and work done on/by the system,

\[
\delta q_{rev} = d\langle E \rangle - \delta w_{rev} = d\langle E \rangle - \sum_j P_j dE_j
\]

By comparing Eqs. (5.31) and (5.32), we identify the change in energy related to the change in occupancy numbers in the ensemble as the heat transfer to/from the system,

\[
\delta q_{rev} = \sum_i E_i dP_i
\]
From the expression for heat, a statistical mechanical expression for the entropy of the ensemble can be derived. The function \( \ln Q(N,V,T) \) given in Eq. (5.28) depends on the temperature and energy states \( E_j \) of the system. The complete derivative of \( \ln Q(T, \{ E_j \}) \) is,

\[
\frac{\partial \ln Q}{\partial T} = \frac{1}{kT} dT - \frac{1}{kT} \sum_j P_j dE_j. 
\]

(5.34)

where Eqs. (5.23) and (5.24) are used to identify terms in Eq. (5.34). From Eq. (5.34),

\[
d(\ln Q + \langle E \rangle/kT) = d\ln Q + d\langle E \rangle/kT - 1/kT^2 \langle E \rangle dT = \left( d\langle E \rangle - \sum_j P_j dE_j \right)/kT.
\]

(5.35)

Comparing Eqs. (5.32) and (5.35) we identify,

\[
\frac{\delta q_{rev}}{kT} = d(\ln Q + \langle E \rangle/kT).
\]

(5.36)

From thermodynamics, we know heat is not an exact differential and the heat transfer between the system and the surroundings depends on the path taken from the initial state to a final state. However, from Eq. (5.36) \( \delta q_{rev}/kT \) is the exact differential of \( d(\ln Q + \langle E \rangle/kT) \) which implies that \( 1/kT \) is an integration factor for the heat. We therefore identify \( \delta q_{rev}/kT = d(\ln Q + \langle E \rangle/kT) \) as the entropy change \( dS \). Using Eq. (5.36),

\[
S = \frac{\langle E \rangle}{T} + k \ln Q + \text{const}. 
\]

(5.37)

or in terms of the partition function,

\[
S = kT \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} + k \ln Q. 
\]

(5.38)

Knowing the entropy, the relations between other thermodynamic variables and the canonical ensemble partition function can be determined. Equations (5.29) and (5.38) are combined to write the Helmholtz free energy, \( A = E - TS \),

\[
A(N,V,T) = -kT \ln Q(N,V,T). 
\]

(5.39)

The Helmholtz free energy which is the thermodynamic potential for systems with fixed \( N, V, \) and \( T, \) is related to the canonical ensemble partition function. The Helmholtz free energy in differential form,

\[
da = -pdV - SdT - \mu dN. 
\]

(5.40)

along with Eq. (5.39) gives an easy way of deriving Eqs. (5.30), (5.37), and (5.38).

### 5.5.2 Fluctuations in thermodynamic quantities in the canonical ensemble

It is important to determine the fluctuations in the predicted thermodynamic quantities between different systems predicted for the canonical ensemble. Through the ergodic hypothesis discussed at the end of this chapter, these fluctuations are related to the fluctuations in the time measures of the quantities for a single system. We demonstrate below that for large systems with interacting molecules, similar to the case of an ideal gas discussed in Sec. 4.4.3, the ratios of the standard deviation to the average value of variables are of the order of \( N^{-1/2} \).

Equations (5.9), (5.23), and (5.24) give the expression for the variance for the average energy in a canonical ensemble,
\[ \sigma_E^2 = \langle E^2(N,V,T) \rangle - \langle E(N,V,T) \rangle^2 = \sum_j E_j^2 e^{-E_j/kT} \left( \frac{\sum_j e^{-E_j/kT}}{\sum_i e^{-E_i/kT}} \right)^2 \]  

(5.41)

On the other hand, calculating the heat capacity at constant volume, \( (\partial E/\partial T)_{N,V} = C_V \), for the canonical ensemble relates the variance of the energy distribution to a physically measurable quantity,

\[ C_V = \frac{d}{dT} \langle E(N,V,T) \rangle = \frac{1}{kT^2} \sigma_E^2. \]  

(5.42)

The standard deviation of the energy distribution depends on the temperature-dependent heat capacity at constant volume which includes all the effects of kinetic energy and intra- and intermolecular interactions. The heat capacity for an ideal gas at each temperature is \( \alpha(T)Nk \) where \( \alpha \) is a temperature dependent factor related to the internal degrees of freedom of the molecule at the given temperature, and the average energy \( \langle E \rangle \) is of the order of \( \alpha NkT \). \cite{Hill1986,McQuarrie}

Similar orders of magnitude hold for solids and liquid phases where in addition to kinetic energy, the heat capacity also captures effects of intermolecular interactions. Therefore,

\[ \frac{\sigma_E}{\langle E \rangle} = \left( kT^2 C_V \right)^{1/2} \frac{O(NkT)^{1/2}}{O(NkT)} = \frac{1}{\sqrt{N}} \]  

(5.43)

Equation (5.43) shows that for systems with interacting molecules, the ratio of \( \sigma_E/\langle E \rangle \) becomes vanishingly small for systems with large numbers of molecules \( N \) and macroscopic energy effectively becomes a single value.

From Eqs. (5.23) and (5.27), the probability of observing a system with interacting molecules in the ensemble with a particular energy level is,

\[ P(E) = \frac{\Omega(E)e^{-E/kT}}{\sum_E \Omega(E)e^{-E(V)/kT}} \]  

(5.44)

Writing the Taylor expansion of the expression for probability with respect to the average energy, the probability distribution for the energy, neglecting terms of the order of \( O(N^{-2}) \) or smaller, is a narrow Gaussian function centered on the average energy. \cite{McQuarrie}

\[ P(E) = P(\langle E \rangle)\exp \left[ -\frac{(E - \langle E \rangle)^2}{kT^2 C_V} \right]. \]  

(5.45)

The energy distribution for a many-molecule system with interactions maintains the same Gaussian form as the energy distribution of the ideal gas, Eq. (4.59).

A similar calculation for the pressure in a canonical ensemble gives the following formula for the variance,

\[ \sigma_P^2 = \langle P^2 \rangle - \langle P \rangle^2 = kT \left[ \frac{\partial \langle P \rangle}{\partial V} \right]_{N,T} - \frac{\partial \langle P \rangle}{\partial V} \right], \]  

(5.46)

which leads to a narrow pressure distribution with,

\[ \frac{\sigma_P}{\langle P \rangle} = \frac{kT}{\langle P \rangle} \left[ \frac{\partial \langle P \rangle}{\partial V} \right]_{N,T} - \frac{\partial \langle P \rangle}{\partial V} \right] = O(N)^{-1/2}. \]  

(5.47)
For systems with large \( N \) values, the pressure distribution can be shown to be a Gaussian function with a very small relative standard deviation. These relations show that in systems with large numbers of molecules, the pressure is very narrowly distributed. As the pressure of the systems in the ensemble is well-defined, macroscopic behaviors like the existence of an equation of state emerge where in a system a unique \( p \) can be determined once \( V \) and \( T \) are known.

In simulations, other factors such as the numerical algorithm used to solve the equations of motion and the effects of truncation and round off errors affect the probability distribution of thermodynamic quantities, but the results above point to having well defined, single values quantities with known magnitudes of fluctuations.

### 5.5.3 Canonical ensemble for systems with non-interacting molecules

For a system with \( N \) distinguishable non-interacting molecules (for example, an ideal gas), the Hamiltonian representing the energy of the \( N \)-molecule system is separable into a sum of Hamiltonians for individual molecules,

\[
H = \sum_{i=1}^{N} H_i ,
\]

and as a result, the total energy, \( E_{\text{tot},k} \) for the \( N \)-molecule quantum state \( k \) becomes,

\[
E_{\text{tot},k}(N) = \varepsilon_\alpha(1) + \varepsilon_\beta(2) + \cdots + \varepsilon_\zeta(N)
\]

where \( \varepsilon_i(k) \) is the energy for molecule \( k \) in quantum state \( i \). Using this decomposition of the energy, the \( N \)-particle canonical partition function \( Q(N,V,T) \) is factored into a product of one-molecule partition functions, \( q(V,T) \),

\[
Q(N,V,T) = \sum_k e^{-E_k/kT} = \sum_\alpha \sum_\beta \cdots \sum_\zeta e^{-[\varepsilon_\alpha(1)+\varepsilon_\beta(2)+\cdots+\varepsilon_\zeta(N)]/kT}
\]

\[
= \sum_\alpha e^{-\varepsilon_\alpha(1)/kT} \sum_\beta e^{-\varepsilon_\beta(2)/kT} \cdots \sum_\zeta e^{-\varepsilon_\zeta(N)/kT} = q_1 q_2 \cdots q_N
\]

where the \( q_i \) are individual molecule partition functions. If all the distinguishable molecules in the non-interacting system are identical, \( Q = q^N \).

A further simplification arises by noticing that the Hamiltonian (energy) of each molecule can be further decomposed into contributions from non-interacting translational, rotational, vibrational, and electronic degrees of freedom,

\[
h_{\text{mol}} = h_{\text{trans}} + h_{\text{rot}} + h_{\text{vib}} + h_{\text{elec}}.
\]

The same reasoning used to derive Eq. (5.50) can be used to factor the molecular partition function into contributions from the different degrees of freedom,

\[
q_{\text{mol}} = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}}
\]

In this case, the molecule indices \( \alpha, \beta, \ldots \) in Eq. (5.50) become composite indices made up of a combination of translational, rotational, vibrational, and electronic state quantum numbers.

If in the sum of Eq. (5.50) none of the molecules have identical sets of indices, the indistinguishability of the molecules requires the partition function to be written as,

\[
Q(T;\{E_i\}) = \frac{q(T;\{E_i\})^N}{N!} .
\]
5.5.4 A physical interpretation of the canonical partition function

A physical interpretation can be given for the canonical partition function by studying its behavior for a model system. Consider a system with nine quantum states arranged in three energy levels with a separation of $\Delta$, shown in Fig. 5.4(a). In terms of individual states, the partition function for this system is,

$$Q(T; \{E_i\}) = e^{-0/kT} + e^{-0/kT} + e^{-0/kT} + e^{-\Delta/kT} + e^{-\Delta/kT} + e^{-\Delta/kT} + e^{-\Delta/kT} + e^{-\Delta/kT} + e^{-\Delta/kT}.$$  

(5.54)

In terms of energy levels using Eq. (5.27), the partition function is,

$$Q(T; \{E\}) = 3e^{-0/kT} + 2e^{-\Delta/kT} + 4e^{-2\Delta/kT},$$  

(5.55)

where the degeneracies of the energy levels, $\Omega(E)$, are taken from Fig. 5.4(a). This latter representation is more compact and emphasizes physically relevant quantities for this system. Numerical values of the partition function at different temperatures expressed in units of $\Delta/k$ are given in Table 5.4 and plotted in Fig. 5.4(b). The behavior of the partition function at the limiting temperatures is instructive. At $T = 0$, the contribution of terms from the first energy level with $E_1 = 0$ to the partition function is 3 (the degeneracy of the lowest energy state) and all other terms in the partition function are zero. At the limit of $T \to \infty$, exponential terms in the partition function, Eq. (5.55) are 1 and $Q = 9$, which is the total number of states in this system. At intermediate temperatures, the partition function varies between 3 and 9 and its value roughly reflects the number of energetically accessible states at each temperature.

![Figure 5.4](image.png)

Figure 5.4. (a) A model system with nine quantum states arranged in three energy levels separated by energy $\Delta$. (b) The partition function and (c) probabilities for residing in different energy levels for a model system at different temperatures.

The probabilities of occupying each of the three energy levels given by Eq. (5.23) are calculated in Table 5.4 and plotted in Fig. 5.4(c). Since the first level is assigned an energy of 0, the temperature dependence of $P_1$ is entirely determined by the partition function $Q(T)$. At temperatures much less than $\Delta/k$, the probability of occupying energy level 1 is unity and there is a zero probability of having the upper levels occupied. As the temperature rises and approaches $\Delta/k$, the gap between the energy of the first and second
levels, the probability of occupying states of energy level 2 starts to increase and \( Q(T) \) increases to 5. As the temperature further rises, the probability of occupying states of energy level 3 increases and \( Q(T) \) asymptotically approaches 9. Temperature acts as the factor which determines the average energy available to a molecule in the system. With the variation of temperature, the distribution of the systems among the different accessible states changes.

#### Table 5.4. The temperature dependence of the partition function and probabilities of the energy levels for the system shown in Figure 5.4. The temperatures are in units of \( \Delta/k \).  

<table>
<thead>
<tr>
<th>( T ) (( \Delta/k ))</th>
<th>0</th>
<th>0.5</th>
<th>1.0</th>
<th>1.5</th>
<th>2.0</th>
<th>5.0</th>
<th>10</th>
<th>( \infty )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Q(T) )</td>
<td>3</td>
<td>3.34</td>
<td>4.28</td>
<td>5.08</td>
<td>5.68</td>
<td>7.32</td>
<td>8.80</td>
<td>9</td>
</tr>
<tr>
<td>( P_1 = 3e^{-0/kT}/Q )</td>
<td>1</td>
<td>0.90</td>
<td>0.70</td>
<td>0.59</td>
<td>0.53</td>
<td>0.41</td>
<td>0.37</td>
<td>0.33</td>
</tr>
<tr>
<td>( P_2 = 2e^{-\Delta/kT}/Q )</td>
<td>0</td>
<td>0.08</td>
<td>0.17</td>
<td>0.20</td>
<td>0.21</td>
<td>0.22</td>
<td>0.22</td>
<td>0.22</td>
</tr>
<tr>
<td>( P_3 = 4e^{-2\Delta/kT}/Q )</td>
<td>0</td>
<td>0.02</td>
<td>0.13</td>
<td>0.21</td>
<td>0.26</td>
<td>0.37</td>
<td>0.41</td>
<td>0.44</td>
</tr>
</tbody>
</table>

#### 5.6 Other Constraints Coupling the System to the Environment

A canonical (isothermal-isochoric) ensemble is a very large number of replicas of a system all of which are in the same thermodynamic state at constant \( N, V, \) and \( T \). Ensembles with other external constraints can be treated with similar mathematical procedures to derive expressions for the most probable distribution of microstates in these ensembles. The partition function associated with each ensemble is connected naturally to a specific thermodynamic variable.

##### 5.6.1. Isothermal – isobaric ensemble (Fixed \( N, P, \) and \( T \))

A closed system with heat-conducting walls in contact with a pressure-adjusting mechanism, such as pistons and cylinders shown schematically in Fig. 5.5(a), has constant number of molecules \( N \), temperature \( T \), and pressure \( P \). In this system, volume is the dependent variable which changes as the system exchanges heat and work with the environment. Similar to the case of the canonical ensemble shown in Fig. 5.3, instead of a single system in contact with a barostat and heat bath, we construct an ensemble of system replicas called the isothermal-isobaric ensemble in equilibrium with the barostat, heat bath, and with each other, such that they all equilibrate to the same pressure \( P \) and temperature \( T \). The closed systems in the ensemble have heat conducting walls and are connected by mechanisms which allow each system volume to adjust to the pressure, see Fig. 5.5(b). The flexibility of the volume for each system is shown schematically in Fig. 5.5(b) by the piston and cylinder mechanisms connecting each system to its neighbors. The shading in each cylinder represents volume occupied by the substance in each system. After equilibration, the isothermal-isobaric ensemble is separated from the thermostat / barostat mechanism and placed in a rigid container with thermally insulating walls, see Fig. 5.5(c).
Figure 5.5. (a) The experimental set-up of a system with constant \( N \), in contact with a barostat and thermostated bath. The volume of the system is not fixed and adjusted according to the pressure and as a result, its energy states \( \{ E_i \} \) may change. (b) In the isothermal-isobaric ensemble an infinite number of replicas of the target system at constant \( N \) separated by flexible heat conducting walls placed in the thermostated bath and barostat of pressure \( P \). The volume of the individual members of the ensemble may vary during pressure / temperature equilibration. (c) After equilibration, the ensemble is removed and put in a rigid, thermally insulated container with a fixed total volume, \( V \), and total energy \( E \).

The isothermal-isobaric ensemble leads to an expression for the probability of observing a system at a particular volume \( V \) and associated quantum mechanical state \( i \), if the system is maintained at constant \( N \), \( P \), and \( T \). Quantum states of a system can depend on the system volume as shown for the example of a collection of \( N \) ideal gas molecules in a cubic box. The energies of quantum states of the ideal gas of \( N \) molecules are,

\[
E_n(V_k, N) = \frac{\hbar^2}{8mV_k^{2/3}} \sum_{j=1}^{N} \left( n_{V, x}^2 + n_{V, y}^2 + n_{V, z}^2 \right).
\]  

(5.56)

where \( V_k \) is the volume of the cubic box. The index \( n \) represents a collective index for the quantum state of the \( N \)-particle system.

In the isothermal-isobaric ensemble, member systems have different volumes \( V_1, V_2, \ldots, V_k \) (which can change continuously), each with its associated set of quantum states \( E_j(V_k) \). Similar to the procedure used to determine the most probable distribution of microstates in the canonical ensemble, we count the number of systems in the ensemble that are in different quantum states in each distribution. For each volume, \( V_k \), we determine the occupancy, \( A_j(V_k) \), of the member systems of the isothermal-isobaric ensemble with quantum state \( j \). If the total number systems in the ensemble is \( \mathcal{A} \), the degeneracy for a specific distribution \( \mathcal{A} \) is,

\[
W(\mathcal{A}) = \frac{\mathcal{A}!}{\prod_j A_j(V_1)! \prod_j A_j(V_2)! \prod_j A_j(V_3)! \cdots} = \frac{\mathcal{A}!}{\prod_{V_k} (\prod_j A_j(V_k)!)}
\]  

(5.57)

In the denominator of Eq. (5.57), for each volume \( V_k \), we have product of occupancies \( A_j(V_k)! \). The denominator consists of a product of such products for all \( V_k \) values. Each distribution is subject to the additional constraints that total energy \( E \) and the total volume \( V \) of the ensemble are constant (see system in Figure 5.5(c)).
The first equation states that the total number of systems (associated with different volumes and their corresponding quantum states) in the ensemble is constant. The second equation states that the sum of the energies of all systems with different volumes and their associated quantum states is constant. Finally, the third equation states that the sum of volumes of the systems in the ensemble is constant.

In Eqs. (5.57) and (5.58) to simplify the notation, system volumes are written as discrete variables, whereas in reality, volume changes continuously and Eqs. (5.58) should be written with integrals over the range of possible volumes. With a now familiar procedure, we optimize the logarithm of Eq. (5.57), subject to the constraints of Eq. (5.58). The three constraints appear with corresponding Lagrange multipliers, $\alpha$, $\beta$, and $\delta$. The most probable distribution is determined by finding the maximum of the logarithm of Eq. (5.57) with respect to the occupancy for a specific volume $V_\ell$ and quantum state $i$,

$$\frac{\partial}{\partial A_i(V_\ell)} \left\{ \ln W(A) - \alpha \left( \sum V_k \sum j A_j(V_k) - A \right) - \beta \left( \sum V_k \sum j A_j(V_k) E_j(V_k, N) - \mathcal{E} \right) - \delta \left( \sum V_k \sum j A_j(V_k) V_k - \mathcal{V} \right) \right\} = 0 \tag{5.59}$$

Using Stirling’s approximation and calculating the derivative, the occupancy number for a state with volume $V_\ell$ in quantum state $E_i(V_\ell, N)$ in the most probable distribution of the ensemble becomes,

$$A_i^*(V_\ell) = e^{-(1+\alpha)} e^{-\beta E_i(V_\ell, N)} e^{-\delta V_\ell} \tag{5.60}$$

The constraint that the total number of system replicas in the ensemble is $A$ eliminates the $\alpha$ Lagrange multiplier,

$$\sum A_j^*(V_k) = A = e^{-(1+\alpha)} \sum e^{-\delta V_k} \sum j e^{-\beta E_j(N, V_k)} \tag{5.61}$$

The probability of observing a state $(j, V_k)$ in the ensemble is,

$$P_i(V_\ell) = \frac{A_i^*(V_\ell)}{A} = \frac{e^{-\delta V_\ell} e^{-\beta E_i(V_\ell, N)}}{\sum V_k e^{-\delta V_k} \sum j e^{-\beta E_j(V_k, N)}} = \frac{e^{-\delta V_\ell} e^{-\beta E_i(V_\ell, N)}}{\Delta(N, \beta, \delta)} \tag{5.62}$$

where $\Delta(N, \beta, \delta)$ is the isothermal-isobaric partition function. For systems in a constant temperature-pressure ensemble, there are two exponential terms associated with the probability of observing a certain system volume $V_\ell$ and the probability that at this specific volume, the system has an energy state $E_i(V_\ell)$.

Invoking the macroscopic thermodynamic equation of state,

$$\left( \frac{\partial H}{\partial P} \right)_{T,N} = V + \frac{1}{T} \left( \frac{\partial V}{\partial 1/T} \right)_{N,P} \tag{5.63}$$

in a manner similar to the derivation of the canonical ensemble Lagrangian multipliers in Appendix 5.2, it can be proven that multipliers $\beta = kT$ and $\delta = P/kT$. [McQuarrie, Hill]
The isothermal-isobaric partition function, $\Delta(N, P, T)$, is a function of $N$, $P$, and $T$ and is given as,

$$
\Delta(N, P, T) = \sum_{\ell} e^{-PV_{\ell}/kT} \sum_j e^{-E_j(V_{\ell}, N)/kT} = \sum_{\ell} e^{-PV_{\ell}/kT} \sum_j \Omega(N, V_{\ell}, E) e^{-E_j(V_{\ell}, N)/kT} = \sum_{\ell} \Omega(N, V_{\ell}, E) e^{-pV_{\ell}/kT}
$$

(5.64)

where $\Omega(N, V_{\ell}, E)$ is the degeneracy of the states of energy $E$ with $N$ molecules and volume $V_{\ell}$. In the last equality we used the definition of the canonical (isothermal-isochoric) ensemble partition function.

At temperature $T$ and pressure $P$, the probability that the system has a volume $V_{\ell}$, and is in the discrete state $i$ characterized by energy $E_i(V_{\ell}, N)$ is given by,

$$
P_i(V_{\ell}) = \frac{1}{\Delta(N, T, P)} e^{-PV_{\ell}/kT} e^{\beta E_i(N, V_{\ell})/kT}
$$

(5.65)

The first exponential term in Eq. (5.65) gives the probability that the system has a volume $V_{\ell}$ when at pressure $p$ and temperature $T$, and the second exponential gives the probability of the system of volume $V_{\ell}$ is in the energy state $E_i(V_{\ell}, N)$. The normalization factor in the denominator of Eq. (5.65) is the isothermal-isobaric partition function of Eq. (5.64).

Equation (5.65) shows that the probability of the state decays exponentially as the volume of the system increases. The rate of decay of the probability is such that at lower pressures and higher temperatures there is a greater probability of observing larger system volumes. At a particular volume, the probability that the system is in an energy state $E_i(N, V_{\ell})$ decays exponentially as the energy of the state increases. The rate of decay depends on the temperature such that at higher temperatures there is a greater probability for high energy states to be occupied.

It is more convenient to express the thermodynamic variables in the isothermal-isobaric ensemble in terms of $\ln \Delta(N, T, p)$. Using Eq. (5.64), the average enthalpy for the systems in the ensemble is,

$$
\langle H(N, T, P) \rangle = \sum_{\ell} \sum_i P_i(V_{\ell}) [E_i(V_{\ell}, N) - PV_{\ell}] = kT^2 \left[ \frac{\partial \ln \Delta(N, T, P)}{\partial T} \right]
$$

(5.66)

$$
= \frac{\sum_{V_{\ell}} e^{-PV_{\ell}/kT} \sum_i [E_i(V_{\ell}, N) - PV_{\ell}] e^{-E_j(V_{\ell}, N)/kT}}{\sum_{V_k} e^{-PV_k/kT} \sum_j e^{-E_j(V_k, N)/kT}}
$$

The fluctuations in the average enthalpy are given by,

$$
\sigma_H^2 = \langle H^2(N, T, P) \rangle - \langle H(N, T, P) \rangle^2 = kT^2 \frac{\partial \langle H(N, T, P) \rangle}{\partial T} = kT^2 C_P
$$

(5.67)

Similarly, the average volume for the systems in the ensemble is determined as,

$$
\langle V(N, T, P) \rangle = \sum_{V_k} \sum_j P_j(V_k) V_k = -kT \left[ \frac{\partial \ln \Delta(N, T, P)}{\partial P} \right]
$$

(5.68)

$$
= \frac{\sum_{V_{\ell}} V_{\ell} e^{-PV_{\ell}/kT} \sum_i E_i(V_{\ell}, N) e^{-E_j(V_{\ell}, N)/kT}}{\sum_{V_k} e^{-PV_k/kT} \sum_j e^{-E_j(V_k, N)/kT}}
$$
We can show that, [Hill 1986]

$$\sigma^2_V = \langle V^2 \rangle - \langle V \rangle^2 = -kT \left( \frac{\partial \langle V \rangle}{\partial P} \right)_{N,T}. \quad (5.69)$$

Similar to cases studied above in the canonical ensemble,

$$\frac{\sigma_V}{\langle V \rangle} = \frac{1}{\langle V \rangle} \left[ -kT \left( \frac{\partial \langle V \rangle}{\partial P} \right)_{N,T} \right]^{1/2} = \left( \frac{kT \kappa}{\langle V \rangle} \right)^{1/2} = \frac{1}{\sqrt{N}} \quad (5.70)$$

where $\kappa$ is the isothermal compressibility. The volume distribution in an isothermal-isobaric ensemble is a Gaussian function with small relative standard deviation for systems with large numbers of molecules.

In a manner similar to the proof of Eq. (5.39), it can be shown that the characteristic thermodynamic potential for the isothermal-isobaric ensemble is the Gibbs free energy, [Hill 1986, McQuarrie]

$$G(N, p, T) = H - TS = -kT \ln \Delta(N, p, T). \quad (5.71)$$

The Gibbs free energy is the thermodynamic potential for systems with fixed $N$, $P$, and $T$, and these are the variable of the isothermal-isobaric ensemble partition function.

### 5.6.2. Grand canonical ensemble (Fixed $\mu$, $V$, and $T$)

The grand canonical ensemble models a system which exchanges molecules with a surrounding reservoir and is enclosed in a rigid heat conducting container, see Fig. 5.6(a). The exchange of molecules between the system and reservoir is through the container walls which are permeable to the molecules (represented by the dashed lines in Fig. 5.6(a). This situation arises, for example, when studying the uptake of gas molecules from a reservoir at a specified pressure into a porous solid material. As in previous cases, instead of dealing with a single system, we place a large number of replicas of the system (the ensemble) in contact with the heat bath/molecule reservoir, and in contact with each other, see Fig. 5.6(b). After the temperature and chemical potential of all systems have equilibrated, the ensemble is transferred to a closed, thermally isolated container in Fig. 5.6(c). The isolated ensemble has a total $\mathcal{N}$ replicas of the system, a combined total number of $\mathcal{N}$ molecules in all members of the ensemble, and total ensemble energy $\mathcal{E}$. Thermodynamically, in this equilibrated ensemble, the chemical potential $\mu$, temperature $T$, and volume $V$ are identical in all members. Based on the quantities that are fixed, the grand canonical ensemble may more descriptively be called the isopotential-isothermal-isochoric ensemble.
Figure 5.6. (a) The experimental set-up of a system with fixed $\mu$ and $V$ in contact with a molecule reservoir and thermostat bath. (b) In the grand canonical ensemble, the system in (a) is replaced by an infinite number of replicas of the target system at constant $\mu$, $V$, and $T$ separated by permeable heat conducting walls placed in the thermostat bath. The number of molecules in the individual members of the ensemble may vary during chemical potential / temperature equilibration. (c) After equilibration, the ensemble of systems is placed in a rigid, thermally insulating container with a fixed total volume, $V$, total number of molecules $N$, and total energy $E$.

In the grand canonical ensemble, the energy states of each member system $\{E_j(N_k,V)\}$, depend on the number of molecules $N_k$ in the system. This is illustrated for energy states of a particle in a cubic box. The one-molecule energies of a three-dimensional box of volume $V$ are,

$$E_n(1,V) = \frac{\hbar^2}{8 m V^{2/3}} (n_x^2 + n_y^2 + n_z^2)$$  \hspace{1cm} (5.72)

where the composite index $n$ represents the state with a set of three quantum numbers $n_x$, $n_y$, and $n_z$. The two-molecule states are,

$$E_n(2,V) = \frac{\hbar^2}{8 m V^{2/3}} (n_{1x}^2 + n_{1y}^2 + n_{1z}^2 + n_{2x}^2 + n_{2y}^2 + n_{2z}^2)$$  \hspace{1cm} (5.73)

where in this case the composite index $n$ represents the two-molecule state with a set of six quantum numbers $n_{1x}$, $n_{1y}$, $n_{1z}$, $n_{2x}$, $n_{2y}$, and $n_{2z}$.

In the grand canonical ensemble, the occupancy of a $N_k$-molecule systems in state $j$ is $A_j(N_k)$. The number of ways the members of the ensemble can be distributed among systems with $N_k$ molecules in states $j$ is given by,

$$W(\{A\}) = \prod_j A_j(1)! \prod_j A_j(2)! \prod_j A_j(3)! \cdots = \frac{A!}{\prod_{N_k} \prod_j A_j(N_k)!}.$$  \hspace{1cm} (5.74)

Each distribution of the ensemble of systems must satisfy the constraints,
To find the occupancies in the most probable microstate, we maximize $\ln W(\{A\})$ with respect to the $A_i(N_\ell)$, subject to the constraints of Eq. (5.75) to get,

$$A_i^*(N_\ell) = e^{-(1+\alpha)} e^{-\beta E_i(N_\ell, V)} e^{-\gamma N_\ell}$$

where $\gamma$ is the Lagrange multiplier for the third constraint in Eq. (5.76). Summing over the number of molecules in each system $N_k$ and states $j$ allows us to eliminate the $\alpha$ multiplier,

$$\sum_{N_k} \sum_j A_j^*(N_k) = \mathcal{A} = e^{-(1+\alpha)} \sum_{N_k} e^{-\gamma N_k} \sum_j e^{-\beta E_j(V, N_k)}$$

The probability of observing an ensemble system with $N_\ell$ molecules in a state $i$ is therefore,

$$P_i(N_\ell) = \frac{A_i^*(N_\ell, V)}{\mathcal{A}} = \frac{e^{-\gamma N_\ell} e^{-\beta E_i(N_\ell, V)}}{\sum_{N_k} e^{-\gamma N_k} \sum_j e^{-\beta E_j(N_k, V)}} \Xi(V, \beta, \gamma),$$

where $\Xi(V, \beta, \gamma)$ is the grand canonical partition function. The grand canonical partition function can also be written in terms of $N$-molecule energy levels,

$$P_E(N_\ell) = \frac{A_E^*(N_\ell)}{\mathcal{A}} = \frac{e^{-\gamma N_\ell} \Omega(E, N_\ell) e^{-\beta E(N_\ell, V)}}{\sum_{N_k} e^{-\gamma N_k} \sum_{E} \Omega(E, N_k) e^{-\beta E(N_k, V)}}.$$ 

The probability in Eq. (5.79) has two exponential decay terms with respect to the number of molecules in the system and the energy levels associated with each number of molecules. Systems with larger number of molecules also have larger degeneracies for their energy levels which compensates for the energy and molecule number exponential decay terms. Therefore systems with a smaller number of molecules are not necessarily favored.

The macroscopic thermodynamic relation,

$$TdS = dE + pdV - \mu dN$$

for an open system at fixed volume, can be used in a procedure similar to that given in Appendix 5.2 for the canonical ensemble to identify the unknown Lagrange multipliers as $\beta = 1/kT$ and $\gamma = -\mu/kT$ where $\mu$ is the chemical potential of the molecules in the reservoir. [Hill 1986, McQuarrie] This gives the following expression for the grand canonical partition function $\Xi(\mu, V, T)$,
where $\lambda = \exp(\mu/kT)$ is the absolute activity for molecules in the open system at the $T$ and $V$ of the experiment. The grand canonical ensemble is characterized by the thermodynamic quantities $\mu$, $T$, and $V$. Expressions for mechanical properties $\langle E \rangle$, $\langle N \rangle$, and $\langle p \rangle$ are obtained from Eq. (5.81). [McQuarrie] Thermodynamic relations show that the product $pV$ is the characteristic potential of the grand canonical ensemble,

$$pV = kT \ln \Xi(\mu,V,T),$$

and the entropy of the grand canonical ensemble is given as,

$$S = \langle E \rangle / T + \mu \langle N \rangle / kT + k \ln \Xi.$$

The relative magnitude of the standard deviation in the number of molecules in the system is,

$$\sigma_N^2 = \langle N^2 \rangle - \langle N \rangle^2 = kT^2 \left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{V,T} = \left( \frac{\langle N \rangle^2}{V} kT \right),$$

where we used the thermodynamic relation

$$\left( \frac{\partial \mu}{\partial \langle N \rangle} \right)_{V,T} = -\frac{V^2}{N^2} \left( \frac{\partial \rho}{\partial V} \right)_{N,T}. \quad (5.84)$$

The relative magnitude of the standard deviation in the number of molecules in the system is,

$$\frac{\sigma_N}{\langle N \rangle} = \left( \frac{kT \kappa}{V} \right)^{1/2} = O(N)^{-1/2}, \quad (5.85)$$

which shows that for systems with large numbers of molecules, most systems will have very close to the same number of molecules. The distribution of molecule numbers in the systems of the grand canonical ensemble is a Gaussian with a small standard deviation relative to the average,

$$P(N) = P(\langle N \rangle) \exp \left[ -\frac{(N - \langle N \rangle)^2}{2kT \left( \frac{\partial \langle N \rangle}{\partial \mu} \right)_{V,T}} \right]. \quad (5.86)$$

These relations show that in a molecular simulation (in particular, a Monte Carlo simulation for an open system), if there are a sufficient number of molecules ($N$) and we perform the simulation over a sufficiently long time (so as to effectively satisfy ergodicity, see below), the thermodynamic quantities derived are single valued Gaussian functions with only small deviations from the mean.

### 5.6.3. Microcanonical ensemble (Fixed $N$, $V$, and $E$)

The microcanonical ensemble is a collection of thermodynamically isolated systems with constant numbers of molecules, volumes, and total energy, see Figure 5.7. The quantum states for this fixed energy state are shown as $E_j$. Based on the quantities that are fixed, the microcanonical ensemble may more descriptively be called the isoenergy-isochoric ensemble.
In the microcanonical ensemble, all systems have \( N \) molecules, a volume \( V \), and the corresponding energy \( E \). The degeneracy of this state is \( \Omega(N, V, E) \). Each of the system states \( i \) of energy \( E \) have an equal probability of being observed in the ensemble,

\[
P_i = \frac{\tilde{A}_i}{\mathcal{A}} = \frac{1}{\Omega(N, V, E)}. \tag{5.90}
\]

In this case, the ensemble is constructed to be large enough that the probability of each state is represented according to the degeneracy. It can be shown that the entropy for the isolated system is the logarithm of the degeneracy which is number of states accessible to the system at energy \( E \), \([\text{Hill 1987, McQuarrie}]\)

\[
S = k \ln \Omega(N, V, E). \tag{5.91}
\]

Entropy is the characteristic function of the microcanonical ensemble.

### 5.7. Classical statistical mechanics

Classical statistical mechanics was originally formulated through the Liouville equation to study the time evolution of the phase space distribution of an ensemble of points representing a physical system, \([\text{Bagchi,McQuarrie}]\). The phase space distribution was determined in such a way as to obey the thermodynamic constraints (constant temperature, constant pressure, etc.) applied on the system.

After the development of the quantum mechanical formulation of equilibrium statistical mechanics, expressions for the partition function were derived based on counting of states available to the system subject to the applied constraints. Semi-classical limits to the expressions for the partition function and probabilities of observing specific states were then derived based on an equivalency of quantum states and finite cells in the phase space of the system. These semi-classical expressions provide conditions that molecular simulations must fulfill in order to be consistent with statistical mechanical and thermodynamics relations.

In subsections that follow, we first outline the general reasoning involved in deriving the semi-classical expressions for the partition function and probabilities in the canonical ensemble and then write the forms for partition functions and probabilities for other ensembles.

#### 5.7.1 The canonical ensemble

![Figure 5.7.](image-url)
The quantum mechanical partition function is a sum over states available to the system, \( Q(N,V,T) = \sum_j e^{-E_j/kT} \). The Heisenberg uncertainty principle states that the uncertainty corresponding to each coordinate and its conjugate momentum must follow the relation, \( dpdq \geq h/2\pi \), so the smallest phase space element for each degree of freedom that can be specified has a volume related to \( h/2\pi \). Therefore, a \( N \)-molecule quantum mechanical state \( j \) in the semi-classical limit corresponds to a volume element in phase space expressed in the units of Planck’s constant \( h \), in particular, \( (dp_1dq_1\cdots dp_Ndq_N)/h^{3N} \).

In the semi-classical limit, the quantum sum over states for a \( N \)-molecule system can be shown to go to an integral over phase space,[Hill1986,Tuckerman] \( N!h^{3N} \sum_j e^{-E_j/kT} \rightarrow \int\cdots\int e^{-\mathcal{H}((\mathbf{p},\mathbf{q}))}/kTd\mathbf{p}_1d\mathbf{q}_1\cdots d\mathbf{p}_N d\mathbf{q}_N \), \( (5.93) \)

where \( \mathcal{H}(\mathbf{p},\mathbf{q}) = \mathcal{H}(p_1,q_1, \ldots, p_{3N}, q_{3N}) \) is the classical Hamiltonian for the system. The \( N! \) in Eq. (5.93) takes into account the indistinguishability of the molecules, particularly that there are \( N! \) ways of distributing \( N \) molecules into each selection of phase space elements. The degeneracy of the quantum mechanical energy levels, \( \Omega(E) \), corresponds to the area of the phase-space sub-surface composed of phase space volume elements which have the same energy \( E \).

We can derive a classical form of the canonical partition function by using Eq. (5.93). Defining \( C_0 = 1/(N!h^{3N}) \), the classical form of the partition function is written as, \( Q_{\text{class}}(N,V,T) = C_0\int\cdots\int e^{-\mathcal{H}((\mathbf{q},\mathbf{p}))}/kT d\mathbf{q}_1d\mathbf{p}_1 \cdots d\mathbf{q}_N d\mathbf{p}_N \). \( (5.94) \)

For a system of \( N \) molecules, the classical Hamiltonian is a sum of kinetic and potential energies, \( \mathcal{H}((\mathbf{q},\mathbf{p})) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + U(q_1,\ldots,q_N) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + U((\mathbf{q})) \). \( (5.95) \)

If we substitute the Hamiltonian into Eq. (5.94), the momentum and coordinate integrals in the classical partition function can be separated, \( Q_{\text{class}} = C_0\int\cdots\int e^{-\sum_{i=1}^{N} \frac{p_i^2}{2m} \pm \sum_{i=1}^{N} \frac{p_i^2}{2m} }/kT d\mathbf{p}_1 \cdots d\mathbf{p}_N \int\cdots\int e^{-U((\mathbf{q}))}/kT d\mathbf{q}_1 \cdots d\mathbf{q}_N \). \( (5.96) \)

Regardless of the presence of intermolecular interactions in the system, the momentum integral in the partition function always has the same form. Evaluating the momentum integrals (see Eq. (A4.46) of Appendix 4.4.3) gives,

\[ Q_{\text{class}} = C_0 (2\pi mkT)^{3N/2} \int e^{-U((\mathbf{q}))}/kT d\mathbf{q}_1 \cdots d\mathbf{q}_N = C_0 (2\pi mkT)^{3N/2} Z_N. \] \( (5.97) \)

Equation (5.97) defines the classical \textit{configurational integral} \( Z_N \), which incorporates all the complexity of the intermolecular interactions of the system.

In the semi-classical expression for the probability distribution among phase space points for the canonical ensemble, \( P_{\text{class}}((\mathbf{q},\mathbf{p});T) \), the momentum and position dependent parts are independent,
\begin{align*}
P_{\text{class}}(\{q_i, p_i\}; V, T) &= \frac{C_Q e^{-(p_1^2 / 2m + \ldots + p_N^2 / 2m)/kT} e^{-U(\{q_i\})/kT}}{C_Q \int p e^{-(p_1^2 / 2m + \ldots + p_N^2 / 2m)/kT} \, dp_1 \ldots dp_N \int V e^{-U(\{q_i\})/kT} \, dq_1 \ldots dq_N} \\
&= \left( \frac{1}{2\pi mkT} \right)^{3N/2} e^{-\sum_i p_i^2 / 2mkT} \frac{1}{Z_N} e^{-U(\{q_i\})/kT} \quad (5.98)
\end{align*}

From Eq. (5.98), the one molecule momentum (speed) distribution, \( P(p_i) \propto \exp(-p_i^2 / 2m) \), is consistent with the Maxwell-Boltzmann distribution for the speed. The analysis of the spatial probability distributions in the configurational integral forms the basis of the theory of non-ideal gases and liquids which is discussed briefly in Chapter 7.
Appendix 5.1 Quantum mechanical description and determination of the Lagrange multiplier $\beta$ and pressure for an ideal gas.

A particle in a three-dimensional cubic box with side $L$ has the potential energy,

$$U(x, y, z) = \begin{cases} 
0 & \text{for } -L/2 \leq x, y, z < L/2; \\
\infty & \text{elsewhere}.
\end{cases}$$  \hspace{1cm} (A5.1)

The states of the particles in a box are a set functions characterized by the integer quantum numbers $n_x$, $n_y$, and $n_z$ [Levin, McQuarrie]

$$\psi_{n_x,n_y,n_z} = A_{n_x,n_y,n_z} \sin(\pi n_x x / L) \sin(\pi n_y y / L) \sin(\pi n_z z / L)$$  \hspace{1cm} (A5.2)

The energies of these states are,

$$\epsilon_{n_x,n_y,n_z} = \frac{\hbar^2}{8mV^{2/3}} \left(n_x^2 + n_y^2 + n_z^2\right) \hspace{1cm} n_x, n_y, n_z = 1, 2, 3, \ldots$$  \hspace{1cm} (A5.3)

In systems with sufficient symmetry (usually in systems with greater than one dimension), degenerate states with different combinations of quantum numbers can have the same value of energy. For example in a cubic particle in a box system, the three quantum states,

$$\begin{align*}
\psi_{2,1,1} &= A_{2,1,1} \sin(2\pi x / L) \sin(\pi y / L) \sin(\pi z / L) \\
\psi_{1,2,1} &= A_{1,2,1} \sin(\pi x / L) \sin(2\pi y / L) \sin(\pi z / L), \\
\psi_{1,1,2} &= A_{1,1,2} \sin(\pi x / L) \sin(\pi y / L) \sin(2\pi z / L)
\end{align*}$$  \hspace{1cm} (A5.4)

are degenerate with an energy of $6\hbar^2/8mV^{2/3}$.

The degeneracy of particle in a box states with high energy can be estimated with a method outlined below. The energy for one molecule in a three-dimensional cubic box given in Eq. (A5.3) can be written as,

$$\epsilon(n_x, n_y, n_z) = \frac{\hbar^2}{8mV^{2/3}} n^2$$  \hspace{1cm} (A5.5)

with $n^2 = n_x^2 + n_y^2 + n_z^2$. Consider a discrete three-dimensional Cartesian space with axes corresponding to the quantum numbers $n_x$, $n_y$, and $n_z$. Each integer point in this space represents an energy value $\epsilon$ according to Eq. (A5.5).

The total number of points within a radius $\leq n$ is equal the number of states $\phi(\epsilon)$ with energy $\leq \epsilon$, see Figure A5.1. The total number of discrete lattice points within a radius $n$ is related to the volume of a sphere of that radius. Therefore, using Eq. (A5.5),

$$\phi(\epsilon) \approx \frac{1}{3} \left(\frac{\pi}{6} mV^{1/3}\right) V^{3/2}$$  \hspace{1cm} (A5.6)

The number of states with energy between the shell $\epsilon$ and $\epsilon + \Delta\epsilon$ is the degeneracy of the energy which can be obtained from,

$$\omega(\epsilon + \Delta\epsilon) = \frac{d\phi(\epsilon)}{d\epsilon} \Delta\epsilon = 2\pi \left(\frac{2m}{\hbar^2}\right)^{3/2} V^{1/2} \Delta\epsilon.$$  \hspace{1cm} (A5.7)
Figure A5.1. The discrete states of a particle in a two-dimensional box represented by the grid of integers in two-dimensional Cartesian space. The total number of states in the system with an energy less than \( \varepsilon \) is equal the number of points within the sphere of radius \( \varepsilon \). The degeneracy of any energy state is the number of lattice points within a shell of thickness \( \Delta \varepsilon \) at the radius of \( \varepsilon \).

For a particle in a box, as the quantum numbers increase, the energy levels become more closely spaced and the sum in the partition function can be approximated by an integral over continuous energy levels. The integral can be evaluated using the expression for the degeneracy of the particle in a box states given in Eq. (A5.7),

\[
q(T) = \sum_{\varepsilon} e^{-\beta \varepsilon} \approx \int_0^{\infty} \omega(\varepsilon) e^{-\beta \varepsilon} d\varepsilon = \frac{\pi}{4} \left( \frac{8m}{\hbar^2} \right)^{3/2} V \int_0^{\infty} e^{\frac{1}{2} \varepsilon} e^{-\beta \varepsilon} d\varepsilon
\]

(A5.8)

In evaluating the integral in Eq. (A5.8), we used the Eq. (A4.42) of Chapter 4.

The expression for the average pressure for each state is given in Eq. (5.25) as,

\[
\langle P(N,V,\beta) \rangle = N \sum_j P_j (V) = -N \sum_j \frac{\partial E_j (V) / \partial V}{e^{-\beta E_j (V)}}
\]

(A5.9)

If we calculate the derivative of the energy of state \( j \) with respect to volume from Eq. (A.5.5), and approximate the resulting sum by an integral, we get,

\[
\langle P(N,V,\beta) \rangle = \frac{N}{3V} \sum_j \frac{e_j (V) e^{-\beta E_j (V)}}{e^{-\beta E_j (V)}} \approx \frac{2N}{3V} \int_0^{\infty} e^{\omega(\varepsilon)} e^{-\beta \varepsilon} d\varepsilon = \frac{N}{V\beta}
\]

(A5.10)

where Eqs. (A4.42) and (A4.43) of Chapter 4 were used. Equating the statistical mechanical prediction for the pressure with the ideal gas law allows us to identify \( \beta = 1/kT \).
Appendix 5.2 Determination of the Lagrange multiplier $\beta$ in systems with interacting molecules

Our goal is to construct quantities corresponding to the thermodynamic derivatives in Eq. (5.26). Differentiating the ensemble average energy, Eq. (5.24) with respect to volume gives,

$$\left( \frac{\partial \langle E(N,V,\beta) \rangle}{\partial V} \right)_{N,\beta} = \sum_j \left( \frac{\partial E_j(N,V)}{\partial V} \right) e^{-\beta E_j(N,V)} - \beta \sum_j E_j(N,V) \left( \frac{\partial E_j(N,V)}{\partial V} \right) e^{-\beta E_j(N,V)} + \frac{\sum_j E_j(N,V) e^{-\beta E_j(N,V)}}{\sum_i e^{-\beta E_i(N,V)}} \times \frac{\beta \sum_k \left( \frac{\partial E_k(N,V)}{\partial V} \right) e^{-\beta E_k(N,V)}}{\sum_i e^{-\beta E_i(N,V)}}$$

which is simplified using Eqs. (5.24) and (5.25) to

$$\left( \frac{\partial \langle E \rangle}{\partial V} \right)_{N,\beta} = - \langle p \rangle + \beta \langle E p \rangle - \beta \langle E \rangle \langle p \rangle.$$  \hspace{1cm} (A5.11)

The pressure derivative with respect to $\beta$ is also determined using Eq. (5.25),

$$\left( \frac{\partial \langle P \rangle}{\partial \beta} \right)_{N,V} = - \sum_j \left( \frac{\partial E_j(N,V)}{\partial V} \right) E_j(N,V) e^{-\beta E_j(N,V)}$$

$$- \frac{\sum_i \left( \frac{\partial E_i(N,V)}{\partial V} \right) e^{-\beta E_i(N,V)} \sum_k E_k(N,V) e^{-\beta E_k(N,V)}}{\left[ \sum_i e^{-\beta E_i(N,V)} \right]^2}.$$  \hspace{1cm} (A5.13)

Using the definitions of the expectation values, Eq. (A5.13) simplifies to,

$$\left( \frac{\partial \langle p \rangle}{\partial \beta} \right)_{N,V} = - \langle E p \rangle + \langle E \rangle \langle p \rangle.$$  \hspace{1cm} (A5.14)

Combining Eqs. (A5.12) and (A5.14) gives,

$$\left( \frac{\partial \langle E \rangle}{\partial V} \right)_{N,\beta} = - \langle p \rangle - \beta \left( \frac{\partial \langle p \rangle}{\partial \beta} \right)_{N,V}.$$  \hspace{1cm} (A5.15)

Comparing this statistical mechanical result with the thermodynamic relation Eq. (5.26) allows us to deduce that $\beta \approx 1/T$ which is conventionally written as $\beta = 1/kT$. This procedure does not identify $k$, but this can be done by comparing the predictions of statistical mechanical relations to a specific substance, such as an ideal gas.

Appendix 5.3. Summary of statistical mechanical formulas

Canonical (isothermal-isochoric; isothermal-isometric) ensemble partition function, $Q(N,V,T)$
\[ A = -kT \ln Q(N,V,T) \]
\[ dA = -SdT - p\,dV + \mu dN \]
\[ S = k \ln Q + kT \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} \]
\[ E = kT^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{N,V} \quad \text{with} \quad \sigma_E = (kT^2 C_V)^{1/2} \]

\[ P = kT \left( \frac{\partial \ln Q}{\partial V} \right)_{N,T} \quad \text{with} \quad \sigma_P = kT \left[ \left( \frac{\partial \langle P \rangle}{\partial V} \right)_{N,T} - \langle \frac{\partial P}{\partial V} \rangle \right] \]
\[ \mu = -T \left( \frac{\partial \ln Q}{\partial N} \right)_{V,T} \]

Isothermal-isobaric ensemble partition function, \( \Delta(N,p,T) \)
\[ G = -kT \ln \Delta(N,P,T) \]
\[ dG = -SdT + dP + \mu dN \]
\[ S = k \ln \Delta + kT \left( \frac{\partial \ln \Delta}{\partial T} \right)_{N,P} \]
\[ H = kT^2 \left( \frac{\partial \ln \Delta}{\partial T} \right)_{N,P} \quad \text{with} \quad \sigma_H = (kT^2 C_P)^{1/2} \]
\[ V = -kT \left( \frac{\partial \ln \Delta}{\partial P} \right)_{N,T} \quad \text{with} \quad \sigma_V = \left[ -kT \left( \frac{\partial \langle V \rangle}{\partial P} \right)_{N,T} \right]^{1/2} = (\langle V \rangle kT \kappa)^{1/2} \]
\[ \mu = -kT \left( \frac{\partial \ln \Delta}{\partial N} \right)_{P,T} \]

Grand canonical (isopotential-isochoric-isothermal) ensemble partition function, \( \Xi(\mu,V,T) \)
\[ PV = -kT \ln \Xi(\mu,V,T) \]
\[ d(PV) = SdT + P\,dV + \mu dN \]
\[ S = k \ln \Xi + kT \left( \frac{\partial \ln \Xi}{\partial T} \right)_{\mu,V} \]
\[ E = kT^2 \left( \frac{\partial \ln \Xi}{\partial T} \right)_{V,\mu} \]
\[ P = kT \left( \frac{\partial \ln \Xi}{\partial V} \right)_{\mu,T} \]
$N = kT \left( \frac{\partial \ln \Xi}{\partial \mu} \right)_{V,T}$ with $\sigma_N = \left( \frac{kT}{N} \right)^{1/2}$

Microcanonical (isochoric-isoenergy) ensemble partition function $\Omega(N, V, E)$

$S = k \ln \Omega(N, V, E)$

$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$

$\frac{1}{kT} = \left( \frac{\partial \ln \Omega}{\partial E} \right)_{N,V}$; $P = kT \left( \frac{\partial \ln \Omega}{\partial V} \right)_{N,E}$; $\mu = -kT \left( \frac{\partial \ln \Omega}{\partial N} \right)_{V,E}$