Topics 3&4 - Statistical Calculation of Ideal Gas Thermodynamics

Content & Objectives: Chapters 3 and 4 provide an introduction to statistical mechanics at a level sufficient to enable 1st principles calculations of thermodynamic properties of ideal gases. We will not have time to explore the underlying ideas of statistical mechanics or derive many of the formulas used. Such explorations will have to be done in another context. We will mainly concentrate on learning how to apply the formalism to the specific problem of ideal gas energetics and examining the results so obtained.

Reading: M&S Chapter 3 & 4, MathChapters B & C, Chandler Ch. 3

Other Sources: Basic Ideas of Statistical Mechanics: Hill Ch. 1-2; Chandler Ch. 3-4; Callen Ch. 15-16; SM of Ideal Gases: Hill Ch. 4, 8, 9; D. A. McQuarrie, Statistical Mechanics (Harper & Row, New York, 1976) Ch. 5-8.

Basic Ideas of Statistical Mechanics

Statistical mechanics is founded on a few simple ideas concerning how to represent the behavior of a thermodynamic systems in terms of appropriate “statistical ensembles” together with prescriptions for using averages over such ensembles to calculate thermodynamic quantities of interest.

- Ensemble: A hypothetical collection of systems, each having the same values of the constrained thermodynamic variables as the system of interest, but with members distributed over all accessible quantum states. The three most commonly used ensembles are:

<table>
<thead>
<tr>
<th>ensemble name</th>
<th>type of system</th>
<th>constraints</th>
</tr>
</thead>
<tbody>
<tr>
<td>microcanonical</td>
<td>isolated</td>
<td>$N, V, U$ fixed</td>
</tr>
<tr>
<td>canonical</td>
<td>closed, isothermal</td>
<td>$N, V, T$ fixed</td>
</tr>
<tr>
<td>grand canonical</td>
<td>open, isothermal</td>
<td>$\mu, V, T$ fixed</td>
</tr>
</tbody>
</table>

- Postulate I (“ergodic hypothesis”): The time average of a mechanical property $M$ in the system of interest is equal to the ensemble average of $M$ in the appropriate ensemble.

A “mechanical” property is one whose value can be defined for an individual member of the ensemble (quantum state). Examples are $U, V, P,$ and $N$. (Non-mechanical properties such as $T, S,$ and $\mu$ refer to the ensemble as a whole and are derived by comparison to thermodynamic relations.)

- Postulate II (“postulate of equal a priori probabilities”): In an ensemble representative of an isolated system, members are distributed uniformly over all possible quantum states consistent with the constraints on $N, V,$ and $U$.

These two postulates suffice to determine the probability distributions of all other ensembles as well as the prescriptions for determining thermodynamic quantities from a knowledge of the characteristic function of the ensemble, its “partition function”. A summary of the basic relations in various ensembles is provided on the following page.
Table 1: Summary of Thermodynamic Quantities in Several Ensembles

Microcanonical Ensemble: $\Omega(N,V,U)$

$$S(N,V,U) = k_B \ln \Omega$$

$$\frac{1}{k_B T} = \left( \frac{\partial \ln \Omega}{\partial U} \right)_{N,V}$$

$$\frac{P}{k_B T} = \left( \frac{\partial \ln \Omega}{\partial V} \right)_{N,U}$$

$$\frac{\mu}{k_B T} = -\left( \frac{\partial \ln \Omega}{\partial N} \right)_{U,V}$$

Canonical Ensemble: $Q(N,V,T)$

$$A(N,V,T) = -k_B T \ln Q$$

$$S = k_B \ln Q + k_B T \left( \frac{\partial \ln Q}{\partial T} \right)_{V,N}$$

$$P = k_B T \left( \frac{\partial \ln Q}{\partial V} \right)_{N,T}$$

$$\mu = -k_B T \left( \frac{\partial \ln Q}{\partial N} \right)_{V,T}$$

$$U = k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{V,N} = -\left( \frac{\partial \ln Q}{\partial \beta} \right)_{V,N}$$

$$C_v / k_B = \beta^2 \left( \frac{\partial^2 \ln Q}{\partial \beta^2} \right)_{V,N}$$

Grand Canonical Ensemble: $\Xi(\mu,V,T)$

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

$$S = k_B \ln \Xi + k_B T \left( \frac{\partial \ln \Xi}{\partial T} \right)_{V,\mu}$$

$$N = k_B T \left( \frac{\partial \ln \Xi}{\partial \mu} \right)_{V,T}$$

$$P = k_B T \left( \frac{\partial \ln \Xi}{\partial V} \right)_{\mu,T}$$

Some Handy Relations between $T$ and $\beta$:

$$\beta = \frac{1}{k_B T}$$

$$\frac{\partial}{\partial \beta} = -k_B T^2 \frac{\partial}{\partial T}$$

$$\frac{\partial}{\partial T} = -k_B \beta^2 \frac{\partial}{\partial \beta}$$
We will be concerned primarily with the canonical \((N, V, T)\) ensemble, because it provides the most convenient route to ideal gas properties. The probability law describing how members are distributed among quantum states within this ensemble is the well-known **Boltzmann distribution law**:

\[
p_i = \frac{1}{Q} \exp\left\{ -E_i(V, N)/k_B T \right\}
\]

where \(i\) designates a unique quantum state of the system, \(E_i\) its energy (generally a function of \(N\) and \(V\)) and \(k_B\) is Boltzmann’s constant, \(k_B = R/N_A\).

\(Q\) is the **canonical partition function** (or partition sum) of the system:

\[
Q(N,V,T) \equiv \sum_i \exp\left\{ -E_i(V, N)/k_B T \right\}
\]

**Aside:** The exponential temperature dependence characteristic of the Boltzmann distribution can be derived from the uniform distribution postulated in II by considering the states of a system coupled to a thermal reservoir which together form an isolated super-system.

Mechanical quantities \(M\) of a system in thermal equilibrium can be calculated by averaging (denoted by brackets “\(<>\)”) over the Boltzmann probability distribution:

\[
M(N,V,T) = <M_i> = \sum_i p_iM_i
\]

In the case of the internal energy \(U\) and pressure \(P\), manipulations using relations such as

\[
\sum_i e^{-\beta E_i} = -\frac{\partial}{\partial \beta} \sum_i e^{-\beta E_i} = -\frac{\partial Q}{\partial \beta}
\]

lead to:

\[
U = <E_i> = \left( \frac{\partial \ln Q}{\partial \beta} \right)_{V,N} = k_B T^2 \left( \frac{\partial \ln Q}{\partial T} \right)_{V,N}
\]

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

Because it is directly measurable (whereas absolute energies like \(U\) are not) a related quantity of more immediate interest is the **constant volume heat capacity**:

\[
C_V \equiv \left( \frac{\partial U}{\partial T} \right)_{N,V} = k_B \beta^2 \left( \frac{\partial^2 \ln Q}{\partial \beta^2} \right)_{N,V}
\]

Note that the quantity \(\beta = 1/k_B T\) appears in these and many other expressions because it is often easier derive relationships when \(Q\) is expressed as a function \(\beta\) rather than as a function of \(T\) (as a result of simpler dependence of \(Q\) on \(\beta Q(N,V,\beta) \equiv \sum_i e^{-\beta E_i(V,N)}\)).
(Aside: In later chapters we will discuss the fact that the Helmholtz free energy $A$ is a natural function of the variables $N$, $V$, and $T$. For this reason the partition function in the canonical ensemble is directly related to $A$ via $A(N,V,T) = -k_B T \ln Q$. A number of the other thermodynamic relations that follow from this association are also shown in Table 1.)

### Independent Subsystems & Distinguishability

- It often happens that the Hamiltonian of a system can be decomposed into a sum of contributions from independent subsystems, $\hat{H} = \hat{H}_1(1) + \hat{H}_2(2) + \hat{H}_3(3) + \ldots$ where “1” refers to some set of coordinates describing the 1st subsystem, etc. In such cases the energy can also be written as a sum of the energies of the individual subsystems $E = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \ldots$ and the total partition function conveniently factorizes into a simple product $Q = q_1q_2q_3\ldots$, at least when the subsystems are distinguishable.

- If the subsystems happen to be individual molecules, $q$ is termed the **molecular partition function** $q$, which governs the probability of a molecule being a particular single-molecule quantum state $i$ in the same way that $Q$ specifies the probability distribution of the whole system:

$$q(V,T) = \sum_i \exp\{-\varepsilon_i(V)/k_B T\} \quad p_i = \frac{e^{-\varepsilon_i/k_B T}}{Q}$$

The state label $i$ here denotes all of the quantum states of a single molecule, which may themselves be separable into different independent degrees of freedom.

- If one has a system of $N$ identical but distinguishable molecules (or subsystems), the total partition function of the $N$-molecule system is simply

$$Q(N,V,T) = q(V,T)^N \quad \text{(distinguishable molecules)}$$

- However, molecules are typically not distinguishable. Their indistinguishability destroys the independence of single-molecule states which enables $Q$ to be simply factorized. The reason is that the total wavefunction of an $N$-particle system must possess definite symmetry with respect to exchange of identical particles, as tabulated below:

<table>
<thead>
<tr>
<th>Spin</th>
<th>Particle class</th>
<th>$\Psi$ symmetry</th>
<th>State Occupation</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>half integral</td>
<td>fermion</td>
<td>-</td>
<td>0 or 1</td>
<td>$e^-, H^+, n$</td>
</tr>
<tr>
<td>integral</td>
<td>boson</td>
<td>+</td>
<td>0, 1, 2, …</td>
<td>$\alpha, h\nu, ^4\text{He}$</td>
</tr>
</tbody>
</table>

Systems of identical particles in these two classes follow distinctly different statistics called **Fermi-Dirac** and **Bose-Einstein statistics**. Luckily, the molecular gases of interest in thermodynamics are nearly always “dilute” in the sense that the number of single-particle states greatly exceeds the number of particles. In this case the vast majority of $N$-particle states are ones in which no single-particle state is more than singly occupied.
• In this limiting situation the statistics for fermions and bosons both degenerate into the much simpler case of “Boltzmann statistics” wherein

\[ Q(N, V, T) = \frac{q(V, T)^N}{N!} \]  

(Boltzmann statistics)

• The applicability of Boltzmann statistics is tied to the number of translational states available per molecule. It depends on the number density \( \rho \) and the thermal deBroglie wavelength

\[ \Lambda = \left( \frac{\hbar^2}{2\pi mk_b T} \right)^{1/2} \]

Boltzmann statistics are applicable when \( \rho \Lambda^3 << 1 \). Some examples of the magnitude of \( \Lambda \) and this test factor are listed below:

<table>
<thead>
<tr>
<th>System*</th>
<th>( T / \text{K} )</th>
<th>( \Lambda / \text{Å} )</th>
<th>( \rho \Lambda^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>He(l)</td>
<td>4</td>
<td>4.3</td>
<td>2.1</td>
</tr>
<tr>
<td>He(g)</td>
<td>4</td>
<td>4.3</td>
<td>.15</td>
</tr>
<tr>
<td>He(g)</td>
<td>100</td>
<td>.87</td>
<td>4.7\times10^{-5}</td>
</tr>
<tr>
<td>H(_2)(l)</td>
<td>20</td>
<td>2.7</td>
<td>.41</td>
</tr>
<tr>
<td>H(_2)(g)</td>
<td>20</td>
<td>2.7</td>
<td>7.3\times10^{-3}</td>
</tr>
<tr>
<td>H(_2)(g)</td>
<td>100</td>
<td>1.2</td>
<td>1.3\times10^{-4}</td>
</tr>
<tr>
<td>Ne(l)</td>
<td>27</td>
<td>.75</td>
<td>.014</td>
</tr>
<tr>
<td>Ne(g)</td>
<td>27</td>
<td>.75</td>
<td>1.1\times10^{-4}</td>
</tr>
<tr>
<td>Kr(l)</td>
<td>127</td>
<td>.36</td>
<td>7.3\times10^{-5}</td>
</tr>
<tr>
<td>e(^-) in Na(s)</td>
<td>300</td>
<td>140</td>
<td>2.0\times10^{+3}</td>
</tr>
</tbody>
</table>

*liquids and gases are at their saturation pressures

• Note that He and H\(_2\) are “quantum fluids” in the sense that under critical conditions they do not strictly obey Boltzmann statistics. It is for this reason that they do not follow the same corresponding states correlations as other simple fluids (i.e. why \( \omega \neq 0 \)). But He and H\(_2\) at higher temperatures, and all other fluids under virtually all conditions can be considered “classical” and treated with Boltzmann statistics.
Statistics of Ideal Gases

- For an ideal gas (when $\rho \Lambda^3 << 1$) the total system partition function $Q(N,V,T)$ can be written in terms of the partition function of an individual molecule as $Q(N,V,T) = q(V,T)^N / N!$. Furthermore, the molecular hamiltonian and thus the energies of individual molecules can be approximately decomposed into a sum of contributions from translational, rotational, vibrational, and electronic motions: $\varepsilon \cong \varepsilon_{\text{trans}} + \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}} + \varepsilon_{\text{el}}$.

This separability of the energy allows the partition function for a system of $N$ ideal gas molecules to be written:

$$ Q = \{q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{el}}\}^N / N! $$

The partition functions for the different modes of motion can be individually evaluated by summing over the appropriate energy level expressions provided in Chapter 1. The results are:

- **translation:**
  $$ q_{\text{trans}}(V,T) = \left(\frac{2\pi M k_B T a^2}{\hbar^2}\right)^{3/2} = \frac{V}{\Lambda^3} $$
  - $a$ is the length of the cubic confining box and $V$ is its volume
  - $M$ is the total mass of the molecule

Derivation of this expression makes use of a classical or high-temperature approximation wherein a sum over discrete quantum states is replaced by an integral. In the case of translational states, $\Delta \varepsilon / k_B T$ is always <<1 and this “approximation” is essentially exact.

- **rotation:**
  $$ q_{\text{rot}}(T) \cong \frac{1}{\sigma} \left(\frac{T}{\Theta_{\text{rot}}}\right) $$
  (linear molecules)

  $$ q_{\text{rot}}(T) \cong \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_{\text{rot}}^A \Theta_{\text{rot}}^B \Theta_{\text{rot}}^C}\right)^{1/2} $$
  (nonlinear molecules)

  - $\Theta_{\text{rot}}, \Theta_{\text{rot}}^A$, etc. are rotational temperatures related to the moments of inertia, $I, I_A$, by:
    $$ \Theta_{\text{rot}} = \frac{\hbar^2}{2 I k_B}, \quad \Theta_{\text{rot}}^A = \frac{\hbar^2}{2 I_A k_B}, \text{ etc.} $$

  - $\sigma$ is the symmetry number of the molecule – the number of indistinguishable orientations it can adopt

As in the translational case, derivation of these expressions also entails high-temperature or classical approximations. Rotational energy spacings are usually small compared to $k_B T$ and this approximation is usually sufficient. When it is not, series expansions of the sort:

$$ q_{\text{rot}}(T) \cong \frac{1}{\sigma} \left(\frac{T}{\Theta_{\text{rot}}}\right) \left[1 + \frac{1}{3} \left(\frac{\Theta_{\text{rot}}}{T}\right) + \frac{1}{15} \left(\frac{\Theta_{\text{rot}}}{T}\right)^2 + \frac{4}{315} \left(\frac{\Theta_{\text{rot}}}{T}\right)^3 + \ldots\right] (T > \Theta_{\text{rot}}) $$
can be used for greater accuracy.

**vibration:**

\[
q_{\text{vib}}(T) = \prod_{i=1}^{f_{\text{vib}}} q_{\text{ho}}^{(i)} = \prod_{i=1}^{f_{\text{vib}}} \frac{e^{-\Theta_{\text{vib}}^{(i)}/2T}}{1 - e^{-\Theta_{\text{vib}}^{(i)}/T}}
\]

- \(f_{\text{vib}}\) is the number of vibrational modes in the molecule (\(f_{\text{vib}} = 3N - 5\) for a linear molecule and \(3N-6\) for a nonlinear molecule)
- \(q_{\text{ho}}^{(i)}\) indicates that the harmonic oscillator approximation is used for each mode \(i\)
- \(\Theta_{\text{vib}}^{(i)}\) is the **vibrational temperature** of mode \(i\):

\[
\Theta_{\text{vib}}^{(i)} = \frac{h \nu_i}{k_B}
\]

Since vibrational energy spacings are usually larger than or comparable to \(k_B T\), high-temperature or classical approximations are usually inappropriate. The above expression is the result of an exact sum over quantum states of the harmonic oscillator. However, for sufficiently high \(T\) or low \(\nu\) the partition function of a single harmonic mode becomes similar to that for a rotation:

\[
q_{\text{ho}}^{(i)} = \frac{e^{-\Theta_{\text{vib}}^{(i)}/2T}}{1 - e^{-\Theta_{\text{vib}}^{(i)}/T}} \Rightarrow \frac{T}{\Theta_{\text{vib}}^{(i)}} \Rightarrow 0
\]

**electronic:**

\[
q_{\text{el}}(T) = g_{\text{el}} e^{D_e/k_B T} + g_{\text{el}}^2 e^{-\epsilon_{\text{el}}/k_B T} + ...
\]

- \(D_e\) is the equilibrium ground state energy of the molecule. It appears here because the separated atoms are chosen to define the zero of energy for the molecule.
- \(g_{\text{el}}\) and \(\epsilon_{\text{el}}\) are the degeneracy and energy of electronic state \(i\)

Since electronic energy spacings are so much larger than \(k_B T\) under most conditions, usually only 1st term of this sum is needed.

**Using the general relation between the internal energy and \(Q(N,V,T)\) discussed previously, the energy and heat capacity of an ideal polyatomic gas can be written as a sum of translational, rotational, vibrational, and electronic contributions:**

\[
\frac{U}{Nk_B T} = \frac{3}{2} + \frac{f_{\text{rot}}}{2} + \sum_{i=1}^{f_{\text{vib}}} \frac{\Theta_{\text{vib}}^{(i)}/2T}{e^{\Theta_{\text{vib}}^{(i)}/T} - 1} - \frac{D_e}{k_B T}
\]

\[
\frac{C_v}{Nk_B} = \frac{3}{2} + \frac{f_{\text{rot}}}{2} + \sum_{i=1}^{f_{\text{vib}}} \left( \frac{\Theta_{\text{vib}}^{(i)}}{T} \right)^2 \frac{e^{-\Theta_{\text{vib}}^{(i)}/T}}{(1 - e^{-\Theta_{\text{vib}}^{(i)}/T})^2}
\]

- \(f_{\text{rot}}\) is the number of rotational degrees of freedom of the molecule (\(f_{\text{rot}} = 2\) for a linear molecule and 3 for a nonlinear molecule)
Because evaluation of the translational and rotational partition functions employed the classical approximation, the contributions of these modes to the energy and heat capacity take on their classical or *equipartition values* of $\frac{1}{2} k_B T$ and $\frac{1}{2} k_B$ per degree of freedom. If vibrational modes could be treated in this fashion (i.e. using $q_{\text{vib}}^{(i)} \equiv T / \Theta_{\text{vib}}^{(i)}$) they would each contribute the limiting high temperature value of $k_B T$ per mode.

The temperature dependence of $C_v(T)$ under most conditions arises solely from the “activation” of quantal vibrations that have energy spacings near to $k_B T$. The temperature dependence of a single harmonic mode is illustrated at the right. The temperature dependence of $C_v(T)$ in a polyatomic gas reflects a superposition of a number ($f_{\text{vib}}$) of such curves.

Constant pressure heat capacities of some ideal gases are shown below ($C_p = C_v + Nk_B$).