A. Statistical Energy of an Ideal Monatomic Gas

• We have thus far used statistical methods to treat structural and binding equilibria for biopolymers. The question we now address is: how general is this procedure. Do we have enough information to treat all manner of materials using statistical approaches to calculate equilibrium properties?

• For the next several lectures we will explore how well this approach works for simple materials including monatomic and diatomic gases and atomic crystals.

• Here we use the partition function to perform one of the most stunningly successful applications of the statistical approach: the thermodynamic properties of a monatomic ideal gas.

• In general, a gas has a kinetic energy and a potential energy.

\[ \varepsilon = K(v_x, v_y, v_z) + V(x, y, z) \]  

(9.1)

• But a monatomic ideal gas has only kinetic energy. The molecular energy is:

\[ \frac{\varepsilon}{2} = \frac{2}{2m} \left( p_x^2 + p_y^2 + p_z^2 \right) \]

(9.2)

• Let’s calculate the internal energy \( U \) using the partition function derivative equation:

\[ U = k_B T^2 \frac{\partial \ln Q}{\partial T} = U = N k_B T^2 \frac{\partial \ln q}{\partial T} \]

(9.3)

where \( Q = \frac{q^N}{N!} \). The factor of \( N! \) in the denominator indicates the gas molecules are to be treated as indistinguishable. This is reasonable given that ideal gas molecules do not interact and shift positions constantly. Moreover the molecules have available to them a large number of translational energy states so there is virtually no chance two molecules have exactly the same translational energy.

\[ q = \sum_{p_x, p_y, p_z} \exp \left[ -\left( p_x^2 + p_y^2 + p_z^2 \right) / 2mk_B T \right] = \left[ \sum_{p_x} e^{-p_x^2 / 2mk_B T} \right] \times \left[ \sum_{p_y} e^{-p_y^2 / 2mk_B T} \right] \times \left[ \sum_{p_z} e^{-p_z^2 / 2mk_B T} \right] = q_x q_y q_z \]

(9.4)

• We assume translation is equivalent in the \( x, y, z \) directions. Therefore

\[ q_x = q_y = q_z = \sum_{p_x} e^{-p_x^2 / 2mk_B T} \]

(9.5)

• To evaluate this series we assume the momenta are continuously distributed. This means we can replace the series with an integral:
\[ q_x = \int_{-\infty}^{a} dx \int_{-\infty}^{+\infty} dp_x e^{-p_x^2/2mk_BT} \]  

(9.6)

- In the x integral we assume the particles are free to move over a distance a in the x direction.
- Equations 8.6 and 8.7 should give the same result but they differ in an important respect. The partition function in equation 8.6 is dimensionless, whereas in equation 8.7 because of the dx and dp_x terms the partition function has units of momentum times distance. To correct this problem we must divide the partition function in equation 8.7 by a constant with the same units:

\[ q_x = \frac{1}{h} \int_{0}^{a} dx \int_{-\infty}^{+\infty} dp_x e^{-p_x^2/2mk_BT} \]  

(9.7)

- The constant h is called Planck's constant where \( h = 6.62 \times 10^{-34} \text{Js} \) and where a Joule second has units of momentum times distance. This \( 1/h \) factor has a more profound function than simply keeping our units straight. The constant h is the unit increment of distance-momentum. The integral assumes these quantities are varied continuously, but in reality distance and momentum must be countable and so must be incremented discretely. The constant h is the smaller amount that dx dp can be incremented.

- We can now evaluate the partition function:

\[ q_x = \frac{1}{h} \int_{0}^{a} dx \int_{-\infty}^{+\infty} dp_x e^{-p_x^2/2mk_BT} = a \sqrt{\frac{2\pi mk_BT}{h}} \]  

(9.8)

- If we assume translation in the x, y, and z directions are equivalent we find also

\[ q_x = q_y = q_z = a \sqrt{\frac{2\pi mk_BT}{h}} \]  

(9.9)

- Now we use the expression obtained for the translational partition function in equation 9.10 to calculate the internal energy:

\[ U = Nk_B T^2 \frac{\partial}{\partial T} \ln q = Nk_B T^2 \frac{\partial}{\partial T} \ln q_x q_y q_z \]

\[ = Nk_B T^2 \frac{\partial}{\partial T} \left[ \ln \left( \frac{a^3}{h^3} \frac{1}{(2\pi mk_BT)^{3/2}} \right) \right] = Nk_B T^2 \left( \frac{\partial}{\partial T} \ln \frac{V}{h^3} \left( \frac{2\pi mk_BT}{h^3} \right)^{3/2} \right) \]  

(9.10)

- Now we use the relationship \( \frac{\partial}{\partial T} \ln q = \frac{1}{q} \frac{\partial q}{\partial T} \)

\[ U = \frac{Nk_B T^2 h^3}{V \left( \frac{2\pi mk_BT}{h^3} \right)^{3/2}} \frac{\partial}{\partial T} \left[ \frac{V \left( \frac{2\pi mk_BT}{h^3} \right)^{3/2}}{h^3} \right] = \frac{3Nk_B T}{2} \]  

(9.11)

- An explicit form for the Equipartition Principle based on equation 9.2 is

\[ U = U_x + U_y + U_z = \frac{Nk_BT}{2} + \frac{Nk_BT}{2} + \frac{Nk_BT}{2} = \frac{3Nk_BT}{2} \]  

(9.12)

and states that for a system at equilibrium, energy is equally partitioned between the translational, rotational, and vibrational motions. In the case of an ideal monatomic gas energy is equally divided between the x, y, and z translational motions.
The Equipartition Principle in turn predicts the following two properties for ideal monatomic gases.

- Starting with \( q = q_xq_yq_z \)
  \[
  q = \left[ a^2 \frac{2\pi mk_BT}{\hbar} \right]^3 = \frac{a^3}{h^3} (2\pi mk_BT)^{3/2} = \frac{V}{h^3} (2\pi mk_BT)^{3/2} \tag{9.13}
  
- Then from \( dA = TdS - PdV \),
  \[ P = k_BT \frac{\partial}{\partial V} (\ln Q) = k_BT \frac{\partial}{\partial V} (\ln q) = \frac{k_BT}{q} \frac{\partial q}{\partial V} \]
  \[
  = \frac{k_BT}{V (2\pi mk_BT)^{3/2}} \frac{\partial V}{\partial V} = \frac{k_BT}{V (2\pi kmk_BT)^{3/2}} \frac{\partial V}{\partial V} \tag{9.14}
  
which means the Equipartition Principle predicts that ideal monatomic gases obey \( PV = Nk_BT \).

- In addition to predicting that ideal monatomic gases obey the equation \( PV = Nk_BT = nRT \), we also get an expression for the heat capacity:
  \[
  C_v = \left( \frac{\partial U}{\partial T} \right)_V = \frac{\partial}{\partial T} \left( \frac{3Nk_BT}{2} q \right) = \frac{3R}{2} 
  
Or \( C_p = C_v + R = \frac{5R}{2} \approx 20.775 \text{JK}^{-1}\text{mol}^{-1} \)

The heat capacities \( C_p \) for various monatomic gases are compiled in Table 2.2 of Appendix B:

<table>
<thead>
<tr>
<th>Element</th>
<th>Argon</th>
<th>Helium</th>
<th>Krypton</th>
<th>Neon</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_p ) (JK(^{-1}\text{mol}^{-1})</td>
<td>20.79</td>
<td>20.79</td>
<td>20.79</td>
<td>20.79</td>
</tr>
</tbody>
</table>

The Equipartition Principle predicts very accurately the equation of state and heat capacities of monatomic gases. It was considered a fundamental law of nature until the first decade of the 20th century.

B. Statistical Entropy of an Ideal Gas: Sackur-Tetrode Eqn.

- The entropy for an ideal gas can be calculated using equation 9.14, i.e.
  \[
  q_{trans} = \frac{V}{h^3} (2\pi mk_BT)^{3/2} \quad \text{and} \quad S = \frac{U}{T} + k_B \ln \left( \frac{q^N}{N!} \right) \quad \text{and} \quad U = \frac{3Nk_BT}{2}
  
- Combine the expressions for \( S \) and \( U \), then use \( \ln N! = N \ln N - N \) and a little algebra
  \[
  S = \frac{U}{T} + k_B \ln \left( \frac{q_{trans}^N}{N!} \right) = \frac{3Nk_BT}{2} + Nk_B (\ln q_{trans} - \ln N + 1) = \frac{5Nk_BT}{2} + Nk_B \ln \left( \frac{q_{trans}}{N} \right) = Nk_B \ln \left( \frac{q_{trans}^{5/2}}{N} \right) \tag{9.15}
  
Equation 9.15 is called the Sackur-Tetrode equation and when combined with \( q_{trans} = \frac{V}{h^3} (2\pi mk_BT)^{3/2} \) we can predict all thermodynamic properties of monatomic ideal gases taught in Chem 452...
  - Dependence of \( S \) on changes in \( V \) and \( T \):
\[
dS = \left( \frac{\partial S}{\partial V} \right)_T dV + \left( \frac{\partial S}{\partial T} \right)_V dT \tag{9.16}
\]

- Now use the Sackur-Tetrode equation \( S = Nk_B \ln \left( \frac{q_{\text{trans}} e^{5/2}}{N} \right) \)

\[
\left( \frac{\partial S}{\partial V} \right)_T = \frac{\partial}{\partial V} \left[ Nk_B \left( \ln V + \text{constant} \right) \right] = \frac{Nk_B}{V}
\]

\[
\left( \frac{\partial S}{\partial T} \right)_V = \frac{\partial}{\partial T} \left[ Nk_B \left( \ln T^{3/2} + \text{constant} \right) \right] = \frac{3Nk_B}{2T} \tag{9.17}
\]

- Use equation 9.17 and 9.18 to obtain the familiar result:

\[
dS = \left( \frac{\partial S}{\partial V} \right)_T dV + \left( \frac{\partial S}{\partial T} \right)_V dT = Nk_B \frac{dV}{V} + \frac{3Nk_B}{2T} dT
\]

\[
\therefore \Delta S = Nk_B \ln \left( \frac{V_2}{V_1} \right) + \frac{3Nk_B}{2} \ln \left( \frac{T_2}{T_1} \right) = nR \ln \left( \frac{V_2}{V_1} \right) + nC_V \ln \left( \frac{T_2}{T_1} \right) \tag{9.18}
\]

C. Chemical Potential and Standard States for an Ideal Gas

- The partition function for translations can also be used to obtain expressions for free energies and the chemical potential. Start with the Helmholtz free energy:

\[
A = -k_B T \ln Q = -Nk_B T \left( \ln q - \ln N + 1 \right) = -Nk_B T \ln \left( \frac{q e}{N} \right) \tag{9.19}
\]

- Equation 9.20 works for anything. The chemical potential of a molecule with partition function \( q \) is

\[
\mu = \left( \frac{\partial A}{\partial N} \right)_{V,T} = \frac{\partial}{\partial N} \left[ -Nk_B T \ln \left( \frac{q e}{N} \right) \right] = -k_B T \frac{\partial}{\partial N} \left[ N \ln \left( q e \right) - N \ln N \right] = -k_B T \left[ \ln \left( q e \right) - \ln N - 1 \right] = -k_B T \ln \left( \frac{q}{N} \right) \tag{9.20}
\]

- Again, equation 9.21 works for anything. But now we put our expression for the translational partition function into 9.21

\[
\mu = -k_B T \ln \left( \frac{q}{N} \right) = -k_B T \ln \left( \frac{V}{N} \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \right) = -k_B T \ln \left( \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \right) \tag{9.21}
\]

\[
= k_B T \left[ \ln \left( \frac{h^3}{\left( 2\pi m k_B T \right)^{3/2} k_B T} \right) + \ln P \right] = \mu^* + k_B T \ln P = k_B T \ln \left( \frac{P}{P^*} \right)
\]

- Equation 9.22 clearly defines the standard state chemical potential and pressure:

\[
\mu^* = k_B T \ln \left( \frac{h^3}{\left( 2\pi m k_B T \right)^{3/2} k_B T} \right) \quad \text{and} \quad P^* = \frac{\left( 2\pi m k_B T \right)^{3/2} k_B T}{h^3} \tag{9.22}
\]
D. The Gibbs Paradox

- An exercise called the Gibbs Paradox illustrates the care that must be taken in constructing the statistical entropy for gases. Assume a chamber filled with an ideal monatomic gas is separated into two volumes by a partition as shown in Figure 9.1.

![Figure 9.1: A chamber filled with an ideal monatomic gas is divided into two separate volumes by a partition (dotted line). The pressures in the two chambers are equal as shown.](image)

- If the partition is removed and the gases in the two volumes mix, does the entropy increase? Let us use the statistical entropy equation to determine this and let at first \( Q = q^N \)

First let us calculate the entropies of the separate chambers:

\[
S_1 = \frac{U_1}{T} + k_B \ln Q_1 = \frac{3N_1k_B}{2} + k_B \ln q_1^N = \frac{3N_1k_B}{2} + N_1k_B \ln V_1 + \text{cons} \tan t
\]

\[
S_2 = \frac{U_2}{T} + k_B \ln Q_2 = \frac{3N_2k_B}{2} + k_B \ln q_2^N = \frac{3N_2k_B}{2} + N_2k_B \ln V_2 + \text{cons} \tan t
\]

where \( q = \frac{V}{h^3}(2\pi mk_BT)^{3/2} \)

(9.23)

- Now if the partition is removed we can likewise calculate the resulting entropy:

\[
S_{1+2} = \frac{U_{1+2}}{T} + k_B \ln Q_{1+2} = \frac{3(N_1 + N_2)k_B}{2} + (N_1 + N_2)k_B \ln (V_1 + V_2) + \text{cons} \tan t
\]

where \( Q_{1+2} = q^{N_1+N_2} \), \( q = \frac{(V_1 + V_2)^{3/2}}{h^3}(2\pi mk_BT)^{3/2} \)

(9.24)

Now we calculate the difference between the entropies:

\[
\Delta S = S_{1+2} - S_1 - S_2 = (N_1 + N_2)k_B \ln (V_1 + V_2) - N_1k_B \ln V_1 - N_2k_B \ln V_2
\]

\[
= N_1k_B \ln \frac{V_1 + V_2}{V_1} + N_2k_B \ln \frac{V_1 + V_2}{V_2} > 0
\]

(9.25)

- The entropy has increased as a result of mixing two volumes of identical gas molecules. However, this is not physically reasonable because mixing identical
gas molecules does not result in an increase in distinguishable microstates. Therefore the entropy change should be zero. The entropy would only increase if the particles in the left and right chambers were distinguishable.

- This is called the Gibbs Paradox and it is resolved by including the correction of $N!$: $Q = \frac{q^N}{N!}$. Now define the separate entropies:

$$S_1 = \frac{U_1}{T} + k_B \ln Q_1 = \frac{3N_1k_B}{2} + k_B \ln \left(\frac{q_{N_1}^N}{N_1!}\right) = \frac{5N_1k_B}{2} + N_1k_B \ln \left(\frac{V_1}{N_1}\right) + \text{cons} \tan t$$

$$S_2 = \frac{U_2}{T} + k_B \ln Q_2 = \frac{5N_2k_B}{2} + N_2k_B \ln \left(\frac{V_2}{N_2}\right) + \text{cons} \tan t$$

$$S_{1+2} = \frac{5(N_1+N_2)k_B}{2} + k_B \left(\frac{N_1+N_2}{N_1+N_2}\right) \ln \left(\frac{V_1 + V_2}{(N_1+N_2)}\right) + \text{cons} \tan t$$

(9.26)

- Now again we calculate the entropy change:

$$\Delta S = S_{1+2} - S_1 - S_2 = k_B \left(\frac{N_1+N_2}{N_1+N_2}\right) \ln \left(\frac{V_1 + V_2}{(N_1+N_2)}\right)$$

$$-N_1k_B \ln \left(\frac{V_1}{N_1}\right) - N_2k_B \ln \left(\frac{V_2}{N_2}\right) = k_BN_1 \ln \left(\frac{V_1 + V_2}{(N_1+N_2)}\right) + k_BN_2 \ln \left(\frac{V_1 + V_2}{(N_1+N_2)}\right)$$

(9.27)

- However, because the densities in the left and right hand chambers were equal, the final density after the partition is removed is unchanged. Therefore:

$$\frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N_1+N_2}{V_1 + V_2}$$

(9.28)

- Equation 9.28 means both logarithms in equation 9.27 are $\ln(1)=0$ so that $\Delta S=0$.

- The factor of $N!$ in the partition function definition $Q = \frac{q^N}{N!}$ assures the indistinguishability of the particles and must be incorporated into the statistical entropy expression for ideal gases.