Statistical thermodynamics
Lectures 7, 8

Quantum ↔ classical

Energy levels ↔ Bulk properties

Various forms of energies.

Everything turns out to be controlled by temperature

Ref. Atkins 7th or 8th edition
Albery, Silbey, Bawendi 4th edition
Need for statistical thermodynamics
Microscopic and macroscopic world
Energy states
Distribution of energy population
Principle of equal $a$ priori probabilities

Configuration - instantaneous
$n_1, n_2, \ldots$ molecules exist in states with energies $\varepsilon_0, \varepsilon_1, \ldots$
$N$ is the total number of molecules
{N,0,0,…} and {N-2, 2,0,…} are configurations
Second is more likely than the first

$\varepsilon$  

0  

Reference to zero

Fluctuations occur
{1,1}, {2,0}, {0,2}
Weight of a configuration = how many times the configuration can be reached.
A configuration \(\{3,2,0,0,\ldots\}\)

*First ball of the higher state can be chosen in \(N\) ways, because there are \(N\) balls*

*Second ball can be chosen in \(N-1\) ways as there are \(N-1\) balls*

*But we need to avoid \(A,B\) from \(B,A\).*

Thus total number of distinguishable configurations is, \(\frac{1}{2} [N(N-1)]\)

\[ W = \frac{N!}{n_0!n_1!n_2!\ldots} \]

\(W\) is the weight of the configuration.

How many ways a configuration can be achieved.
\[ \ln W = \ln \frac{N!}{n_0! \cdot n_1! \cdot n_2! \ldots} \]

\[ = \ln N! - \ln(n_0! \cdot n_1! \cdot n_2! \ldots) \]

\[ = \ln N! - (\ln n_0! + \ln n_1! + \ln n_2! \ldots) \]

\[ = \ln N! - \sum_i \ln n_i! \]

\[ \ln x! \approx x \ln x - x \text{ Stirling’s approximation} \]

\[ \ln W = (N \ln N - N) - \sum_i (n_i \ln n_i - n_i) = N \ln N - \sum_i n_i \ln n_i \]
Which is the dominating configuration having maximum weight?

Generalized approach is to set $dW = 0$

There are problems as any configuration is not valid.

1. Energy is constant. $\sum_i n_i \varepsilon_i = E$
2. Constant molecules. $\sum_i n_i = N$

Populations in the configuration of greatest weight depends on the energy of the state.

\[
\frac{n_i}{N} = \frac{e^{-\beta \varepsilon_i}}{\sum_i e^{-\beta \varepsilon_i}}
\]

Boltzmann distribution

$i$ is a sum over available states

\[
\beta = \frac{1}{kT}
\]

Temperature gives the most probable populations
**Boltzmann distribution – population**, \( p_i = \frac{e^{-\beta \varepsilon_i}}{q} \)

Another form of \( q \):

\[
q = \sum_i e^{-\beta \varepsilon_i}
\]

\[
q = \sum_{\text{levels}} g_i e^{-\beta \varepsilon_i}
\]

Molecular partition function

There are several ways of looking at \( i \)

1. Partition function is the number of available states.
2. Partition function is the number of thermally accessible states.
3. How molecules are ‘partitioned’ into available states.

How to look at thermodynamic properties?

When number of states is finite, we will not get \( \infty \).

\[
\lim_{T \to 0} q = g_0
\]

Because, \( \varepsilon_0 = 0 \)

For all higher levels \( \varepsilon \) is finite.

\( e^{-\beta \varepsilon} = 1 \). \( e^{-x} \) is 0 when \( x \) is \( \infty \).

\[
\lim_{T \to \infty} = \infty
\]

All terms will reduce to 1.

\( e^{-x} \) is 1 when \( x \) is 0

1. Partition function is the number of available states.
2. Partition function is the number of thermally accessible states.
3. How molecules are ‘partitioned’ into available states.
Evaluation of molecular partition function

\[ 1 + x + x^2 + x^3 + \ldots = \frac{1}{1-x} \]

\[ q = 1 + e^{-\beta \varepsilon} + e^{-2\beta \varepsilon} + e^{-3\beta \varepsilon} + \ldots = \frac{1 + e^{-\beta \varepsilon} + (e^{-\beta \varepsilon})^2 + (e^{-\beta \varepsilon})^3 + \ldots}{1 - e^{-\beta \varepsilon}} \]

Fraction of molecules in energy levels is,
\[ p_i = e^{-\beta \varepsilon_i}/q = (1 - e^{-\beta \varepsilon_i}) e^{-\beta \varepsilon_i} \]

Discussion of figure, next slide

For a two level system,
\[ p_0 = \frac{1}{1 + e^{-\beta \varepsilon}} \]
\[ p_1 = e^{-\beta \varepsilon}/q = e^{-\beta \varepsilon}/(1 + e^{-\beta \varepsilon}) \]

As \( T \to \infty \), both \( p_0 \) and \( p_1 \) go to \( \frac{1}{2} \).

Consequences?
Approximations: Partition functions are often complex. Analytical expressions cannot be obtained in several cases. Approximations become very useful.

For example, partition function for one dimensional motion

\[
E_n = \frac{n^2 \hbar^2}{8mX^2} \quad n = 1, 2, \ldots
\]

\[
\epsilon_n = (n^2 - 1)\epsilon 
\]

\[
\epsilon = \frac{\hbar^2}{8mX^2}
\]

\[
q_x = \sum_{n=1}^{\infty} e^{-(n^2 - 1)\beta\epsilon}
\]

\[
q_x = \int_{1}^{\infty} e^{-(n^2 - 1)\beta\epsilon} \, dn \quad \text{energy levels are close, sum becomes an integral}
\]

No big difference, if we take the lower limit to 0 and replace \(n^2 - 1\) to \(n^2\).

\[
q_x = \left[ \frac{1}{\beta\epsilon} \right]^{1/2} \int_{0}^{\infty} e^{-x^2} \, dx = \frac{1}{\beta\epsilon} \left[ \frac{\pi}{2} \right]^{1/2} = \left[ \frac{2\pi m}{\hbar^2\beta} \right]^{1/2} X
\]

Substitute, \(X^2 = n^2\beta\epsilon\), \(dn = dx/(\beta\epsilon)^{1/2}\)

\[
q_x = \left[ \frac{2\pi m}{\hbar^2\beta} \right]^{1/2} X
\]

Substitute for \(\epsilon\)
Independent motion in three dimensions

\[ \varepsilon_{n_1n_2n_3} = \varepsilon_{n_1}(X) + \varepsilon_{n_2}(Y) + \varepsilon_{n_3}(Z) \]

Energy is a sum of independent terms

\[ q = \sum_{\text{all } n} e^{-\beta \varepsilon(X)} n_1 e^{-\beta \varepsilon(Y)} n_2 e^{-\beta \varepsilon(Z)} n_3 \]

\[ = \left( \sum_{n_1} e^{-\beta \varepsilon(X)} n_1 \right) \left( \sum_{n_2} e^{-\beta \varepsilon(Y)} n_2 \right) \left( \sum_{n_3} e^{-\beta \varepsilon(Z)} n_3 \right) \]

\[ = q_x q_y q_z \]

\[ q = \left( \frac{2\pi m}{\hbar^2 \beta} \right)^{3/2} \]

\[ q = \frac{V}{\Box^3} \]

\[ = h \left( \frac{\beta}{2\pi m} \right)^{1/2} = \frac{h}{(2\pi mkT)^{1/2}} \]

\[ \Box \] has dimensions of length, thermal wavelength

\[ J = \text{kg m}^{-2} \text{ s}^{-2} \]

Question: How many more quantum states will be accessible for \(^{18}\text{O}_2\) compared to \(^{16}\text{O}_2\), if it were to be confined in a box of 1 cm\(^3\)?
How to get thermodynamics?

All information about the thermodynamic properties of the system is contained in the partition function. Thermal wavefunction.

Total energy

\[ E = \sum_i n_i \varepsilon_i \]

\[ E = \frac{N}{q} \sum_i \varepsilon_i e^{-\beta \varepsilon_i} \]  

Most probable configuration is dominating.

We use Boltzmann distribution.

We know, \( \varepsilon_i e^{-\beta \varepsilon_i} = - \frac{d}{d\beta} e^{-\beta \varepsilon_i} \)

\[ E = - \frac{N}{q} \sum_i \frac{d}{d\beta} e^{-\beta \varepsilon_i} = -N \frac{d}{d\beta} \sum_i e^{-\beta \varepsilon_i} = -N \frac{dq}{d\beta} \]

1. All E's are relative

\( E \) is the value of U relative to \( T = 0 \).

\[ U = U(0) + E \]

\[ U = U(0) - N \frac{\frac{d}{d\beta} \ln q}{v} \]

2. Derivative w.r.t. \( \beta \) is partial as there are other parameters (such as \( V \)) on which energy depends on.

Partition function gives internal energy of the system.
How to get entropy?

For a process, change in internal energy, \( U = U(0) + E \)

\[
U = U(0) + \sum_i n_i \varepsilon_i
\]

*Internal energy changes occur due to change in populations* \((n_i + d n_i)\) *or energy states* \((\varepsilon_i + d \varepsilon_i)\). Consider a general case:

\[
dU = dU(0) + \sum_i n_i d \varepsilon_i + \sum_i \varepsilon_i d n_i
\]

*For constant volume changes, \( dU = \sum_i \varepsilon_i d n_i \)*

\[
dU = dq_{rev} = T dS \quad dS = dU/T = k \beta \sum_i \varepsilon_i d n_i
\]

\[
dS = k \sum_i (\partial \ln W / \partial n_i) d n_i + k\alpha \sum_i d n_i
\]

*Number of molecules do not change. Second term is zero.*

\[
dS = k \sum_i (\partial \ln W / \partial n_i) d n_i = k (d \ln W)
\]

\[
S = k \ln W
\]