Statistical Molecular Thermodynamics

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Video 3.6

The Ensemble Partition Function
**Q Is to Stat Mech As Ψ Is to QM**

The partition function $Q$ plays the central role in statistical thermodynamics. $Q$ depends on the allowed energies for a given system, which may be determined quantum mechanically if the system constituents are microscopic.

$Q$ as we have defined it thus far is referred to as the *canonical partition function* and the ensemble (e.g., of bottles) that we have worked with is termed the *canonical ensemble* ($N$, $V$, and $T$ fixed). Other ensembles will be considered later…

$Q$ is needed to compute macroscopic properties, but for an arbitrary system one needs all of the eigenvalues of its $N$-body Schrödinger equation to construct $Q$, which is rarely practical. Fortunately, $Q$ can be approximated based on results for “individual” molecular energy levels.
Consider \( Q \) in Terms of \( q \)

For a system of *distinguishable, non-interacting, identical* particles the *ensemble* partition function \((Q)\) can be written as a product of the individual *molecular* partition functions \((q)\):

\[
Q(N,V,T) = \sum_i e^{-\left[\varepsilon_1(V) + \varepsilon_2(V) + \cdots + \varepsilon_N(V)\right]_i / k_B T} \\
= \left[ \sum_{j(1)} e^{-\varepsilon_j(V)/k_B T} \right] \left[ \sum_{j(2)} e^{-\varepsilon_j(V)/k_B T} \right] \cdots \left[ \sum_{j(N)} e^{-\varepsilon_j(V)/k_B T} \right] \\
= \left[ q(V,T) \right]^N
\]

because non-interacting

because identical

\( q(V,T) \) requires information about allowed energies of only one *individual* atom/molecule
**Indistinguishability**

\[ Q = \left[ q(V, T) \right]^N \] is a nice result, but only sometimes correct. Atoms/molecules are typically *indistinguishable*.

Example: Given 2 particles, each with energy \( \varepsilon_j \) where only \( \varepsilon_1, \varepsilon_2 \) and \( \varepsilon_3 \) are allowed, how many ways can they be arranged if distinguishable? \( 3^2 = 9 \)

\[
Q = \sum_{j} e^{-\beta E_j} = \sum_{j} \sum_{i} e^{-\beta (\varepsilon_j^{(1)} + \varepsilon_i^{(2)})} = \sum_{j} \sum_{i} e^{-\beta \varepsilon_j^{(1)}} e^{-\beta \varepsilon_i^{(2)}} = \sum_{j} e^{-\beta \varepsilon_j^{(1)}} \sum_{i} e^{-\beta \varepsilon_i^{(2)}} = \underbrace{q^{(1)} q^{(2)}} = q^2 = q^N
\]

If the particles are *indistinguishable*, then some are not actually separate terms in the sum. We should remove the repeats, in which case \( 9 \rightarrow 6 \)

\[
Q = e^{-\beta (\varepsilon_1^{(1)} + \varepsilon_1^{(2)})} + e^{-\beta (\varepsilon_2^{(1)} + \varepsilon_1^{(2)})} + e^{-\beta (\varepsilon_1^{(1)} + \varepsilon_2^{(2)})} + e^{-\beta (\varepsilon_2^{(1)} + \varepsilon_2^{(2)})} + e^{-\beta (\varepsilon_1^{(1)} + \varepsilon_3^{(2)})} + e^{-\beta (\varepsilon_2^{(1)} + \varepsilon_3^{(2)})} + e^{-\beta (\varepsilon_3^{(1)} + \varepsilon_1^{(2)})} + e^{-\beta (\varepsilon_3^{(1)} + \varepsilon_2^{(2)})} + e^{-\beta (\varepsilon_3^{(1)} + \varepsilon_3^{(2)})}
\]
Fermionic Behavior

\[ Q = e^{-\beta(\epsilon_1^{(1)} + \epsilon_1^{(2)})} + e^{-\beta(\epsilon_2^{(1)} + \epsilon_2^{(2)})} + e^{-\beta(\epsilon_3^{(1)} + \epsilon_3^{(2)})} + e^{-\beta(\epsilon_1^{(1)} + \epsilon_2^{(1)})} + e^{-\beta(\epsilon_1^{(1)} + \epsilon_3^{(1)})} + e^{-\beta(\epsilon_2^{(1)} + \epsilon_3^{(1)})} \]

If moreover no two particles can be in the same state, then \(6 \rightarrow 3\) (fermion statistics)

Even for bosons, where two indistinguishable particles can be in the same state, it will be very unlikely to find two particles in the same state if the number of available states is much, much greater than the number of particles. This is generally true for translational energy levels of atoms and molecules at typical temperatures and pressures.

In that case, essentially all of the overcounting of unallowed terms in \(Q = [q(V,T)]^N\) comes from failure to consider permutational symmetry in the labeling of the particle states.
**Permutational Symmetry**

\[ Q(N,V,T) = \sum_{i} e^{-[\epsilon_1(V) + \epsilon_2(V) + \cdots + \epsilon_N(V)]_i/k_B T} \]

If all energy levels are different:
- can take on any of \( N \) values
- can take on any of \((N-1)\) values
- can take on only 1 value

So, there are \( N! \) ways to make the same contribution to \( Q \), and if we choose to take \( Q \) as the product of molecular partition functions \( q \), each allowed to take on the various values, we will overcount this one term \( N! \) times.

To a good approximation, then, we should instead use:

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

For a system where:

\[ \frac{N}{V} \left( \frac{h^2}{8mk_B T} \right)^{3/2} \ll 1 \]

is valid, then the particles in the system obey statistics.

**H₂ gas at 1 bar, 300 K?**

\[
\frac{N}{V} = \frac{P}{k_B T} = \frac{10^5 \text{ Pa}}{(1.381 \times 10^{-23} \text{ J} \cdot \text{K}^{-1})(300 \text{ K})} = 2.414 \times 10^{25} \text{ m}^{-3}
\]

\[
\left( \frac{h^2}{8mk_B T} \right)^{3/2} = \left[ \frac{\left(6.626 \times 10^{-34} \text{ J} \cdot \text{s}\right)^2}{(8)(3.35 \times 10^{-27} \text{ kg})(1.381 \times 10^{-23} \text{ J} \cdot \text{K}^{-1})(300 \text{ K})} \right]^{3/2} = 2.486 \times 10^{-31} \text{ m}^3
\]

\[
\frac{N}{V} \left( \frac{h^2}{8mk_B T} \right)^{3/2} = 6.00 \times 10^{-6}
\]