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):

$$Q(N,V,T) = \sum_i e^{-\left[\varepsilon_1(V)+\varepsilon_2(V)+\cdots+\varepsilon_N(V)\right]_i / k_\mathrm{B}T}$$

because non-interacting

$$= \left[\sum_{j(1)} e^{-\varepsilon_{j(1)}(V)/k_\mathrm{B}T}\right]\left[\sum_{j(2)} e^{-\varepsilon_{j(2)}(V)/k_\mathrm{B}T}\right]\cdots\left[\sum_{j(N)} e^{-\varepsilon_{j(N)}(V)/k_\mathrm{B}T}\right]$$

because identical

$$= \left[q(V,T)\right]^N$$

$q(V,T)$ 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 ε_j where only ε_1, ε_2 and ε_3 are allowed, how many ways can they be arranged if distinguishable? $3^2 = 9$

$$Q = \sum_j e^{-\beta E_j} = \sum_j^3 \sum_i^3 e^{-\beta\left(\varepsilon_j^{(1)} + \varepsilon_i^{(2)}\right)} = \sum_j^3 \sum_i^3 e^{-\beta\varepsilon_j^{(1)}} e^{-\beta\varepsilon_i^{(2)}} = \sum_j^3 e^{-\beta\varepsilon_j^{(1)}} \sum_i^3 e^{-\beta\varepsilon_i^{(2)}} = q^{(1)} q^{(2)} = q^2 = q^N$$

$$Q = \underset{1\;1}{e^{-\beta\left(\varepsilon_1^{(1)}+\varepsilon_1^{(2)}\right)}} + \underset{1\;2}{e^{-\beta\left(\varepsilon_2^{(1)}+\varepsilon_2^{(2)}\right)}} + \underset{1\;3}{e^{-\beta\left(\varepsilon_3^{(1)}+\varepsilon_3^{(2)}\right)}} + \underset{2\;1}{e^{-\beta\left(\varepsilon_1^{(1)}+\varepsilon_2^{(2)}\right)}} + \underset{2\;2}{e^{-\beta\left(\varepsilon_1^{(1)}+\varepsilon_3^{(2)}\right)}} + \underset{2\;3}{e^{-\beta\left(\varepsilon_2^{(1)}+\varepsilon_3^{(2)}\right)}} + \underset{3\;1}{e^{-\beta\left(\varepsilon_3^{(1)}+\varepsilon_1^{(2)}\right)}} + \underset{3\;2}{e^{-\beta\left(\varepsilon_2^{(1)}+\varepsilon_1^{(2)}\right)}} + \underset{3\;3}{e^{-\beta\left(\varepsilon_3^{(1)}+\varepsilon_2^{(2)}\right)}}$$

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

$$Q = \underset{1\;1}{e^{-\beta\left(\varepsilon_1^{(1)}+\varepsilon_1^{(2)}\right)}} + \underset{1\;2}{e^{-\beta\left(\varepsilon_2^{(1)}+\varepsilon_2^{(2)}\right)}} + \underset{1\;3}{e^{-\beta\left(\varepsilon_3^{(1)}+\varepsilon_3^{(2)}\right)}} + \underset{2\;2}{e^{-\beta\left(\varepsilon_1^{(1)}+\varepsilon_2^{(2)}\right)}} + \underset{2\;3}{e^{-\beta\left(\varepsilon_1^{(1)}+\varepsilon_3^{(2)}\right)}} + \underset{3\;3}{e^{-\beta\left(\varepsilon_2^{(1)}+\varepsilon_3^{(2)}\right)}}$$

Fermionic Behavior

$$Q = \underset{1\ 1}{e^{-\beta\left(\varepsilon_1^{(1)}+\varepsilon_1^{(2)}\right)}} + \underset{1\ 2}{e^{-\beta\left(\varepsilon_2^{(1)}+\varepsilon_2^{(2)}\right)}} + \underset{1\ 3}{e^{-\beta\left(\varepsilon_3^{(1)}+\varepsilon_3^{(2)}\right)}} + \underset{2\ 2}{e^{-\beta\left(\varepsilon_1^{(1)}+\varepsilon_2^{(2)}\right)}} + \underset{2\ 3}{e^{-\beta\left(\varepsilon_1^{(1)}+\varepsilon_3^{(2)}\right)}} + \underset{3\ 3}{e^{-\beta\left(\varepsilon_2^{(1)}+\varepsilon_3^{(2)}\right)}}$$

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

$$Q = \underset{1\ 2}{e^{-\beta\left(\varepsilon_1^{(1)}+\varepsilon_2^{(2)}\right)}} + \underset{1\ 3}{e^{-\beta\left(\varepsilon_1^{(1)}+\varepsilon_3^{(2)}\right)}} + \underset{2\ 3}{e^{-\beta\left(\varepsilon_2^{(1)}+\varepsilon_3^{(2)}\right)}}$$

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

$$Q(N,V,T) = \sum_i e^{-[\varepsilon_1(V)+\varepsilon_2(V)+\cdots+\varepsilon_N(V)]_i / k_B T}$$

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.

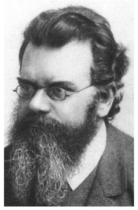
To a good approximation, then, we should instead use:

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

Translation Energy Density

For a system where:

$$\frac{N}{V}\left(\frac{h^2}{8mk_BT}\right)^{3/2} << 1$$

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

H_2 gas at 1 bar, 300 K?

$$\frac{N}{V}=\frac{P}{k_BT}=\frac{10^5\ \text{Pa}}{\left(1.381\times10^{-23}\ \text{J}\bullet\text{K}^{-1}\right)\left(300\ \text{K}\right)}=2.414\times10^{25}\ \text{m}^{-3}$$

$$\left(\frac{h^2}{8mk_BT}\right)^{3/2}=\left[\frac{\left(6.626\times10^{-34}\ \text{J}\bullet\text{s}\right)^2}{(8)\left(3.35\times10^{-27}\ \text{kg}\right)\left(1.381\times10^{-23}\ \text{J}\bullet\text{K}^{-1}\right)\left(300\ \text{K}\right)}\right]^{3/2}=2.486\times10^{-31}\ \text{m}^3$$

$$\boxed{\frac{N}{V}\left(\frac{h^2}{8mk_BT}\right)^{3/2}=6.00\times10^{-6}}$$