

Calculation of Thermodynamic and Kinetic Properties

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1 Connection Between QM and Thermodynamics

We have focused to this point on the many approaches and details of calculating the *internal electronic energy* of a single molecule, that is, the energy associated with taking infinitely separated constituent nuclei and electrons at rest and forming a molecule:



E^{elec} is typically calculated within the Born-Oppenheimer approximation, i.e. within the approximation that the nuclei are fixed in space at the minimum energy configuration. Even at 0 K, by quantum mechanics the atoms must vibrate about this minimum, and this intrinsic vibration imparts a *zero-point vibrational energy* (ZPVE) to the molecule, and the 0 K internal energy of a molecule is thus:

$$E^0 = E^{\text{elec}} + \text{ZPVE} \quad (2)$$

ZPVE can be calculated reliably within the harmonic approximation, according to

$$\text{ZPVE} = \frac{1}{2} h \sum_{i=1}^{3n-6} \nu_i \quad (3)$$

where ν_i are the harmonic vibrational frequencies, obtained from a vibrational frequency analysis. E^0 is the minimum physically meaningful energy of the molecule.

Energy can be deposited in a molecule in many other ways as well, e.g. as translational and rotational kinetic energy, in excited vibrational modes, in the interaction of a molecule with an external electric or magnetic or gravitational field, or If we assume that the energy in these various degrees of freedom are separable, we can write:

$$E_i = E^0 + E^{\text{trans}} + E^{\text{rot}} + E^{\text{vib}} + E^{\text{elec*}} + E^{\text{ext}} \quad (4)$$

To fully describe microscopic energetic state of a molecule, would have to specify all of these.

Typically, though, we are more interested in the collective properties of many molecules at equilibrium, like the internal energy U or enthalpy H or Gibbs energy G , under some external constraints like temperature T or volume V . These thermodynamic quantities are averages over the energy states of an *ensemble* of molecules. The way this averaging is performed is the realm of *statistical thermodynamics*.

Most important for us will be the *canonical ensemble*, in which the free variables are the number of molecules N , the total volume V , and the temperature T . Offer without proof, in the canonical ensemble the probability for a molecule to be in some energy state E_i above E^0 is given by the Boltzmann factor,

$$P(E_i) \propto e^{-E_i\beta} = e^{-E_i/k_B T}, \quad \beta = 1/k_B T \quad (5)$$

Defines an exponentially decaying probability function for a state to be occupied at some temperature. In a sense, *temperature* is the property of a system following this distribution.

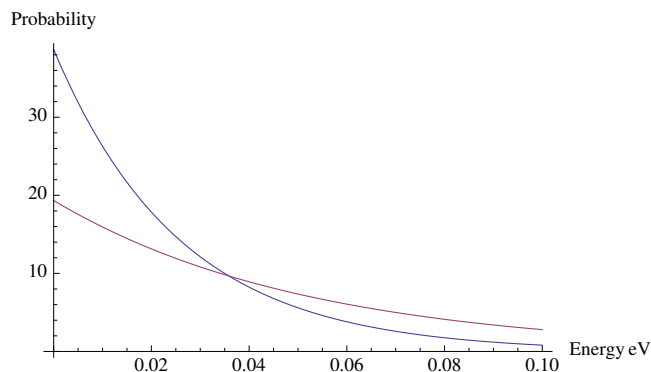


Figure 1: Boltzmann distribution at two different temperatures

1.1 Averages and partition functions

Let's use this to calculate the internal energy U of a molecule at some temperature.

$$U(T) = \frac{\sum_i E_i P(E_i)}{\sum_i P(E_i)} \quad (6)$$

where the denominator ensures that the probability is normalized.

$$U(T) = \frac{\sum_i E_i e^{-E_i \beta}}{\sum_i e^{-E_i \beta}} \quad (7)$$

$$= \frac{\frac{\partial}{\partial \beta} \sum_i e^{-E_i \beta}}{\sum_i e^{-E_i \beta}} \quad (8)$$

$$= - \frac{\partial \ln \sum_i e^{-E_i \beta}}{\partial \beta} \quad (9)$$

The sum over energy states is evidently a special quantity, called the partition function:

$$q = \sum_i e^{-E_i \beta} \quad (10)$$

All thermodynamic quantities can be written in terms of the partition function!

1.2 Harmonic oscillator example

Harmonic oscillator is a reasonable model of a molecular vibration. Energy spectrum given by

$$E_v = (v + 1/2)h\nu, \quad v = 0, 1, 2, \dots \quad (11)$$

Let's define the energy quantum $h\nu = \epsilon_0$ and reset the energy scale so that zero is at $1/2h\nu$:

$$E_v = v\epsilon_0, \quad v = 0, 1, 2, \dots \quad (12)$$

$$q(T) = \sum_{v=0}^{\infty} e^{-v\epsilon_0 \beta} \quad (13)$$

$$= \frac{1}{1 - e^{-\epsilon_0 \beta}} \quad (14)$$

where we take advantage of the fact that the sum is a geometric series to evaluate it in closed form.

Plot partition function vs T , increasing function.

Internal energy:

$$U(T) = -\frac{\partial \ln q}{\partial \beta} \quad (15)$$

$$= \frac{\epsilon_0}{e^{\epsilon_0 \beta} - 1} \quad (16)$$

Heat capacity:

Entropy

2 Molecular Ideal Gas

Nice example above for a simple model. To get thermodynamics of an ideal gas, in principle need to sum over all the types of energy states (translational, rotational, vibrational, ...) of every molecule. Seemingly impossible task. One simplification is if we can write energy as sum of energies of individual elements (molecules) of system:

$$E_j = \epsilon_j(1) + \epsilon_j(2) + \dots + \epsilon_j(N) \quad (17)$$

$$Q(N, V, T) = \sum_j e^{-E_j \beta} \quad (18)$$

$$= \sum_j e^{-(\epsilon_j(1) + \epsilon_j(2) + \dots + \epsilon_j(N))\beta} \quad (19)$$

If molecules/elements of system can be distinguished from each other (like atoms in a fixed lattice), expression can be factored:

$$Q(N, V, T) = \left(\sum_j e^{-\epsilon_j(1)\beta} \right) \dots \left(\sum_j e^{-\epsilon_j(N)\beta} \right) \quad (20)$$

$$= q(1) \dots q(N) \quad (21)$$

$$\text{Assuming all the elements are the same:} \quad (22)$$

$$= q^N \quad (23)$$

If *not* distinguishable (like molecules in a liquid or gas, or electrons in a solid), problem is difficult, because identical arrangements of energy amongst elements should only be counted once. Approximate solution, good almost all the time:

$$Q(N, V, T) = q^N / N! \quad (24)$$

Sidebar: “Correct” factoring depends on whether individual elements are fermions or bosons, leads to funny things like superconductivity and superfluidity.

This $q(V, T)$ is the *molecular partition function*, and is calculated by summing over the individual energy states of a single molecule (starting at E_0).

Further simplified by factoring into contributions from various ($3N$) molecular degrees of freedom:

$$q(V, T) = \left(\sum_{\text{trans}} e^{-e_{\text{trans}}\beta} \right) \left(\sum_{\text{rot}} e^{-e_{\text{rot}}\beta} \right) \left(\sum_{\text{vib}} e^{-e_{\text{vib}}\beta} \right) \left(\sum_{\text{elec}} e^{-e_{\text{elec}}\beta} \right) \quad (25)$$

$$= q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}} \quad (26)$$

$$U = E_0 + U_{\text{trans}} + U_{\text{rot}} + U_{\text{vib}} + U_{\text{elec}} \quad (27)$$

Similarly for other thermodynamic quantities, for example,

$$C_v = \left(\frac{\partial U}{\partial T} \right)_V = C_{v,\text{trans}} + C_{v,\text{rot}} + C_{v,\text{vib}} + C_{v,\text{elec}} \quad (28)$$

Have to somehow *model* these motions and have to use our quantum mechanical results to parameterize the models.

2.1 Translational partition function

Need a model molecules freely translating about in a box. How about the *particle in a box*?

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2}, \quad n = 1, 2, 3, \dots \quad (29)$$

Have to construct partition function for one molecule. For gas molecules at normal conditions, energy spacing is tiny. Spare the details, but find that q_{trans} can be written in terms of a *thermal wavelength* Λ :

$$\Lambda = \frac{h}{\sqrt{2\pi m k_B T}} \quad (30)$$

$$q_{\text{trans}} = \frac{V^\circ}{\Lambda^3} \quad (31)$$

Λ depends only a molecule mass (that's easy!) and is of the order the box dimensions at which quantization is evident. Typically a tiny number (e.g. 1.7×10^{-11} m for Ar in a 1 liter volume at 298 K. q_{trans} is, on the other hand, enormous: lots of translational freedom. V° defines the standard state volume.

Given this, can find all translational contributions to thermodynamics. S_{trans} gives the Sackur-Tetrode equation: the absolute entropy of a monatomic gas.

2.2 Rotational partition function

Model molecule as a rigidly rotating body. Body has three orthogonal moments of inertia I determined by the molecular structure.