BOLTZMANN STATISTICS AND IDEAL MONOATOMIC GAS[1]

The formalism developed in the previous section is powerful, but there are only few cases for which we have the mathematical sophistication to actually evaluate the partition functions. In this section, we will perform the explicit calculation of partition functions for the case of a system of non-interacting particles. The reason we can perform the calculation for this case is that we can separate the total energy of the system (the ***Hamiltonian***, in statistical mechanics terminology) as a sum of independent contributions. There are many other examples in physics in which the Hamiltonian, by a proper and clever selection of variables, can be written as a sum of individual terms. Although these individual terms need not be Hamiltonians for actual individual molecules, they are nevertheless used to define the so-called quasi-particles, which mathematically behave like independent real particles (photons, phonons in solids etc). First, let us consider the canonical partition function for a system of ***distinguishable*** particles, in which the Hamiltonian can be written as a sum of individual terms. Denote the individual energy states by $\{\varepsilon_j^a\}$, where the superscript denotes the particle (as they are distinguishable), and the subscript denotes the state. In this case, the canonical partition function becomes:

$$Q(N,\underline{V},T) = \sum_j e^{-\underline{U}_j/kT} = \sum_{i,j,k,\ldots} e^{-(\varepsilon_i^a+\varepsilon_j^b+\varepsilon_k^c+\cdots)/kT} =$$

$$= \sum_i e^{-\varepsilon_i^a/kT} \cdot \sum_j e^{-\varepsilon_j^b/kT} \cdot \sum_k e^{-\varepsilon_k^c/kT} \ldots$$

$$= q_a \cdot q_b \cdot q_c \cdots \tag{1}$$

where $$q(\underline{V},T) = \sum_i e^{-\varepsilon_i/kT} \tag{2}$$

Equation (1) shows that if we can write the N-particle Hamiltonian as a sum of independent terms, and if the particles are ***distinguishable***, then the calculation of $Q(N,\underline{V},T)$ reduces to a calculation of $q(\underline{V},T)$. Since calculation of $q(\underline{V},T)$ requires knowledge of only the energy values of an individual particle, its evaluation is quite feasible. In most cases, $\{\varepsilon_i\}$ is a set of molecular energy states; thus $q(\underline{V},T)$ is called a molecular partition function.

If the energy states are the same for all particles, then equation (1) becomes:

$$Q(N,\underline{V},T) = [q(\underline{V},T)]^N \quad \text{(distinguishable particles)} \tag{3}$$

Another useful application of equation (1) is to the molecular partition function itself. Often, the Hamiltonian for an individual molecule can be approximated by a sum of Hamiltonians for the various degrees of freedom for the molecule:

$$\underline{\underline{H}} \approx \underline{\underline{H}}_{\text{translational}} + \underline{\underline{H}}_{\text{rotational}} + \underline{\underline{H}}_{\text{vibrational}} + \underline{\underline{H}}_{\text{electronic}} \Rightarrow \tag{4}$$

---

[1] Material in this section is based on Chapters 4, 5 and 7 of D.A. McQuarrie, "Statistical Thermodynamics", Harper and Row, 1976.

$$\Rightarrow q_{molecule} = q_{translational} \cdot q_{rotational} \cdot q_{vibrational} \cdot q_{electronic} \tag{5}$$

Thus, it is not only possible to reduce an N-body problem to a one-body problem, but it is possible to reduce it further into the individual degrees of freedom of the single particles.

Equation (3) is an attractive result, but atoms and molecules are, in general, not distinguishable. When the particles are indistinguishable, the first sum over i,j,k in equation (1) cannot be immediately decomposed into a product of sums over i,j,k, because a state with $\{\varepsilon_i^a, \varepsilon_j^b, ...\}$ is the same as one with $\{\varepsilon_j^a, \varepsilon_i^b, ...\}$. Assuming that there are many more states than particles, there are N! as many such "identical states" that are included in the sum in eq. (1) for every single real state ($N! = 1 \cdot 2 \cdot 3 \cdot 4 \cdots N$ is the number of possible orderings of N particles). Therefore, the correct expression for the partition function for the case of a system of indistinguishable particles, is:

$$Q(N,\underline{V},T) = \frac{1}{N!}\,[q(\underline{V},T)]^N \quad \text{(indistinguishable particles)} \tag{6}$$

Equation (6) is an extremely important result, since it reduces a many-body problem to a one-body problem. The assumption on which it is based, namely that there are many more states than particles is very well satisfied for all systems with atoms or molecules at room temperatures and above. Near absolute zero, or for particles that are very light (e.g. electrons), this is not so, and the problem becomes more complicated because the quantum nature of the particles must be taken into account explicitly. When this assumption is valid, we say that particles obey ***Boltzmann statistics*** (or the "classical limit").

<u>The translational partition function</u>

In this section, we will evaluate the translational partition function. From quantum mechanics, the energy states of a particle of mass m in a cubic "box" of dimensions L×L×L are

$$\varepsilon_{n_x,n_y,n_z} = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2) \quad n_x,n_y,n_z = 1,2,3,\cdots \tag{7}$$

where $h = 6.6262 \cdot 10^{-27}$ erg·s is Planck's constant.

We substitute this into equation (2) to get

$$q_{trans}(\underline{V},T) = \sum_{n_x,n_y,n_z=1}^{\infty} e^{-\beta\varepsilon_{n_x,n_y,n_z}} = \left(\sum_{n=1}^{\infty} \exp\left(-\frac{\beta h^2 n^2}{8mL^2}\right)\right)^3 \tag{8}$$

This summation cannot be evaluated in closed form, that is, cannot be expressed in terms of any simple analytic function. This does not present a serious difficulty, however, for the following reason: The successive terms in this summation differ so little from each other that the terms vary essentially continuously, and the summation can, for all practical purposes, be replaced by an integral. If we do this, equation (8) becomes:

$$q_{trans}(\underline{V},T) = \left(\int_0^\infty \exp\left(-\frac{\beta h^2 n^2}{8mL^2}\right) dn \right)^3 = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \underline{V} \tag{9}$$

where we have replaced L^3 with $\underline{V}$, and have used $\int_0^\infty \exp(-x^2)\,dx = \frac{\sqrt{\pi}}{2}$

The quantity $(h^2/2\pi mkT)^{1/2}$ that occurs in the translational partition function has units of length and is usually denoted by Λ. In this notation, eq. (9) can be written as

$$q_{trans} = \underline{V}/\Lambda^3 \tag{10}$$

The length Λ can be given the following physical interpretation. The average translational kinetic energy of an ideal gas molecule can be calculated immediately from eqs (9) and the definition of an ensemble average,

$$\langle\varepsilon_{trans}\rangle = \frac{\Sigma\ \varepsilon_i \cdot \exp(-\beta\varepsilon_i)}{q} \tag{11}$$

as:

$$\langle\varepsilon_{trans}\rangle = kT^2 \left(\frac{\partial \ln q_{trans}}{\partial T} \right)_{\underline{V},N} \tag{12}$$

we find that $\langle\varepsilon_{trans}\rangle = 3/2\ kT$, and since $\varepsilon_{trans} = p^2/2m$, where p^2 is the momentum of a particle, we can say that the average momentum is essentially $(mkT)^{1/2}$. Thus, Λ is essentially h/p, which is equal to the De Broglie wavelength of the particle. Consequently, Λ is called the thermal De Broglie wavelength. The condition for the application of classical Boltzmann statistics is that the thermal De Broglie wavelength must be small compared to the relevant intermolecular length scale. For a dilute gas, relevant length scales are the average distance between particles, $\rho^{-1/3}$, and σ (the diameter of particles).

Thermodynamic functions

The Helmholtz energy of an ideal monoatomic gas is given by

$$\underline{A}(N,\underline{V},T) = -\ kT\ \ln Q = -\ NkT\ \ln\left(\left(\frac{2\pi mkT}{h^2} \right)^{3/2} \frac{\underline{V}\cdot e}{N} \right) \tag{15}$$

For most systems, the electronic contribution to $\underline{A}$ is negligible. The thermodynamic energy $\underline{U}$ is

$$\underline{U} = kT^2\ (\partial \ln Q/\partial T)_{N,\underline{V}} = -\ \frac{3}{2}\ NkT \tag{16}$$

The pressure is

$$P = kT\ (\partial \ln Q/\partial \underline{V})_{N,T} = NkT/\underline{V} \tag{17}$$

The pressure equation results because $q(\underline{V},T)$ is of the form $f(T)\cdot\underline{V}$, and is correct even if the electronic contributions to the partition function are not negligible (since the electronic partition function is independent of volume).

The entropy $\underline{S}$ and the chemical potential are, respectively:

$$\underline{S} = (\underline{U} - \underline{A})/T = Nk \ln \left(\left(\frac{2\pi mkT}{h^2}\right)^{3/2} \frac{\underline{V}\cdot e^{5/2}}{N} \right) \tag{18}$$

$$\mu = -kT \, (\partial \ln Q/\partial N)_{\underline{V},T} = -kT \ln(q/N) =$$

$$= -kT \ln \left(\left(\frac{2\pi mkT}{h^2}\right)^{3/2} kT \right) + kT\ln P \tag{19}$$

We can rewrite equation (19) as

$$\mu = \mu_0(T) + kT\ln P \tag{20}$$

which is the familiar expression of μ for an ideal gas from classical thermodynamics. The difference is that now $\mu_0(T)$ is no longer a mysterious, ill-defined function of temperature.

<u>Classical translational partition function and the Maxwell-Boltzmann distribution</u>

Equation (9) gives the translational partition function of an ideal gas from summing over all possible quantum states. The same result can be obtained from a classical description of the system. The classical Hamiltonian of a monoatomic gas is simply the kinetic energy:

$$\underline{\underline{H}} = 1/(2m) \; (p_x^2 + p_y^2 + p_z^2) \tag{21}$$

where p_x, p_y, p_z are the momenta of the particle in the x-, y- and z- directions and m is the mass of the particle.

The partition function can be written as the integral over phase space of the Hamiltonian:

$$q_{class} = \iiiint\!\!\iint \exp\left(- \frac{\beta(p_x^2 + p_y^2 + p_z^2)}{2m} \right) dp_x dp_y dp_z dx dy dz \tag{22}$$

The integral over dxdydz simplifies to the volume of the container, and the integrations over momenta in the three spacial dimensions are equivalent:

$$q_{class} = \underline{V} \left(\int_{-\infty}^{+\infty} \exp(-\beta p^2/2m)\, dp \right)^3 = (2\pi mkT)^{3/2} \, \underline{V} \tag{23}$$

which is the same result as equation (9), with the difference being the lack of a factor of h^3 in equation (23). Clearly, we cannot expect Planck's constant to pop up in a purely classical treatment! The probability $\mathcal{P}$ that the single particle momentum has the magnitude p is:

$$\mathcal{P}(p) = \frac{\exp(-\beta p^2/2m)}{(2\pi mkT)^{3/2}} \tag{24}$$

Equation (24) is usually called the Maxwell-Boltzmann distribution. The translational partition function for *any* system (and not just for an ideal gas) has the same form as shown above, because the potential energy of an interacting system depends only on positions of particles, and thus can be separated from the kinetic energy. Particles in gases, liquids, and solids thus have the same distributions of momenta (velocities), provided that the system is thermally equilibrated. Equation (24) can be used to calculate various averages of kinetic parameters. For example, the average magnitude of the momentum of a particle is

$$\langle p \rangle = \frac{\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} p \exp(-\beta p^2/2m)\, dp_x dp_y dp_z}{(2\pi mkT)^{3/2}} =$$

$$\frac{\int_0^{\pi}\int_0^{2\pi}\int_0^{\infty} p^3 \sin\theta \exp(-\beta p^2/2m)\, dp\, d\varphi\, d\theta}{(2\pi mkT)^{3/2}} = \frac{4\pi \int_0^{\infty} p^3 \exp(-\beta p^2/2m)\, dp}{(2\pi mkT)^{3/2}} =$$

$$\frac{2\pi \int_0^{\infty} p^2 \exp(-\beta p^2/2m)\, dp^2}{(2\pi mkT)^{3/2}} = \frac{2\pi (2mkT)^2}{(2\pi mkT)^{3/2}} = (8mkT/\pi)^{1/2} \tag{25}$$

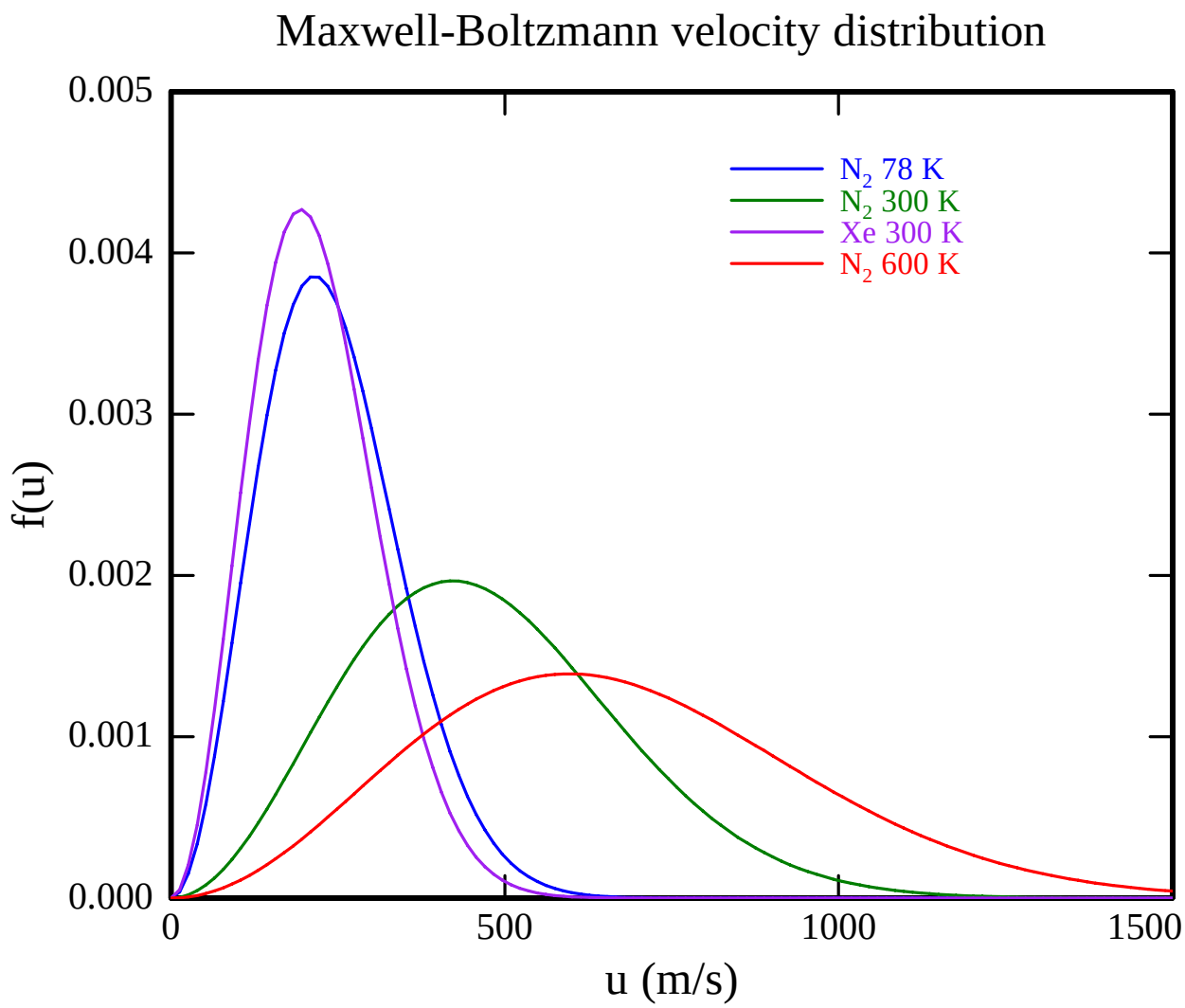
From equation (24), by substituting $p = u \cdot m$, the probability of a given velocity u is:

$$\mathcal{P}(u) = \frac{\exp(-\beta m u^2/2)}{(2\pi kT/m)^{3/2}}$$

The fraction of molecules, f(u), with velocities between u and u+du is obtained by taking into account that there are more states at higher velocities; more formally, transforming to spherical coordinates and integrating over φ and θ:

$$\mathcal{P}(u)\, du = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} u^2 \exp(-mu^2/2kT)\, du \tag{26}$$

which is called the Maxwell-Boltzmann distribution of molecular velocities.

A graph of the Maxwell-Boltzmann distribution for N_2 at different temperatures

is shown in the graph below.