

where

$$\sigma_i^{(n)} = \begin{cases} +1, & \text{antialigned moment} \\ -1, & \text{aligned moment.} \end{cases} \quad (103)$$

The calculation of the partition function requires a sum over all possible states, which requires enumeration of all possible sets of values of the σ_i :

$$Z = \sum_{\sigma_1} \sum_{\sigma_2} \dots \sum_{\sigma_N} e^{-\beta \sum_i \sigma_i \mu B}. \quad (104)$$

You can see that direct evaluation of the sum is quite a daunting task, particularly if N is a macroscopically large number like 10^{23} .

One way to simplify the sum would be to change it from a sum over microstates to a sum over energies, using the ability to express the energy in the simpler form $(N_{\uparrow} - N_{\downarrow})\mu B$ together with our previous knowledge of the multiplicities of the energies (macrostates) of the two-state paramagnet.

It is much simpler to make use of the factorizability of the partition function. While it is straightforward to demonstrate explicitly the reduction to factorized form for this system, we'll just use what we already know: if the energy decomposes into a sum of independent contributions, the partition function factors into a product of partition functions that can be calculated independently for each contribution to the energy. Thus:

$$Z = Z^{(1)} Z^{(2)} \dots Z^{(N)} = Z_{1 \text{ moment}}^N, \quad (105)$$

where the last equality follows from that fact that all the moments are the same, so they each have the same individual contribution to the partition function. That contribution is very easy to calculate:

$$\begin{aligned} Z_{1 \text{ moment}} &= \sum_{\sigma} e^{-\beta \sigma \mu B} \\ &= e^{\beta \mu B} + e^{-\beta \mu B} \\ &= 2 \cosh(\beta \mu B). \end{aligned} \quad (106)$$

The full partition function for the system is then simply

$$Z = Z_{1 \text{ moment}}^N = [2 \cosh(\beta \mu B)]^N. \quad (107)$$

[EOC, Fri. 3/31/2006, #32]

There's one additional complication that we need to consider in some cases. If the constituents (particles) of the system are indistinguishable, then the enumeration of the states of the system must take that into account. In an ideal gas of identical molecules, for example, there is no way to distinguish the molecules from each other, so a state with any pair of them interchanged is really no different from the state without that interchange. But we know how to handle that situation from our previous experience:

a sum obtained without regard to indistinguishability can be corrected by dividing by $N!$, the number of permutations of the particles.

That works so long as the individual particles never occupy the same state. For example, suppose a two-particle system in which each particle can be in one of two states and both particles are allowed to be in the same state. The possible states of that system could be described by the index pairs $(1, 1)$, $(1, 2)$, $(2, 1)$, and $(2, 2)$ if we assumed the particles to be distinguishable. For indistinguishable particles, the states $(1, 2)$ and $(2, 1)$ are really the same, and that double counting could be eliminated by dividing the count by 2. But the states $(1, 1)$ and $(2, 2)$ were not double counted in the original enumeration that assumed distinguishable particles, so dividing the entire count by two would overcorrect, giving two states rather than the correct number, three. This dilemma is avoided if we limit ourselves to systems of indistinguishable particles that cannot occupy the same single-particle states, so that the $N!$ correction is accurate. The ideal gas is an example of such a system, since the low density, which is required in order to consider the particles to be noninteracting, makes the likelihood of multiple occupancy very low.

By the way, we didn't have to worry about the correction for the two-state paramagnet because, even though the moments themselves are indistinguishable, they are presumed to be locked into a crystal lattice whose sites are distinguishable by their positions. This effectively labels each of the moments with a unique coordinate triplet.

HW Problem. Schroeder problem 6.44, p. 251.

Reading assignment. Schroeder, section 7.1.

0.1.7 The partition function of the ideal gas

We'll quantize the translational motion of the constituents of this system in exactly the same way we did in our calculation of the multiplicity of the ideal gas long ago. That is, we'll use periodic boundary conditions to impose quantization of the allowed translational momenta of the molecules without actually putting the molecules in a real confining box.¹ This gives us traveling-wave solutions to the Schrödinger equation,

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}) = E\psi(\mathbf{r}), \quad (108)$$

that satisfy the periodic boundary conditions

$$\psi(\mathbf{r} + \mathbf{R}) = \psi(\mathbf{r}). \quad (109)$$

Here

$$\mathbf{R} = (n_x\hat{\mathbf{x}} + n_y\hat{\mathbf{y}} + n_z\hat{\mathbf{z}})L, \quad (110)$$

¹Note that Schroeder does the latter, so his calculation is a bit different.

with $L^3 = V$, the volume of the macroscopic “box,” and the n_i are integers, which may be negative or zero, as well as positive. The solutions are plane waves,

$$\psi(\mathbf{r}) = \left(\frac{1}{L}\right)^{3/2} e^{i\mathbf{p}\cdot\mathbf{r}/\hbar}, \quad (111)$$

where the momentum is required to be of the form

$$\mathbf{p} = \frac{\hbar}{L}(K_x\hat{\mathbf{x}} + K_y\hat{\mathbf{y}} + K_z\hat{\mathbf{z}}) \quad (112)$$

with integral quantum numbers K_i , in order to satisfy the periodic boundary conditions. Thus, the translational kinetic energy of each particle is

$$E_{\text{tr}} = \frac{p^2}{2m} = \frac{\hbar^2}{2mL^2}(K_x^2 + K_y^2 + K_z^2). \quad (113)$$

We will allow the constituents to be polyatomic, so, in addition to the translational motion, each molecule may also undergo rotational and/or vibrational motion. For the vibrational motion, the energies are of the form

$$E_{\text{vib}} = \sum_i \left(n_i + \frac{1}{2}\right) \hbar\omega_i, \quad (114)$$

where i indexes the independent modes of vibration of the molecule. And for the rotational motion, the energies are of the form

$$E_{\text{rot}} = \sum_{i=1}^3 j_i(j_i + 1) \frac{\hbar^2}{2I_i}, \quad (115)$$

where i indexes the three principal axes of inertia of the molecule.

Since the particles of an ideal gas are noninteracting, the total energy of the gas can then be found by adding contributions from all the molecules:

$$E_{\text{tot}} = \sum_{i=1}^N E_i = \sum_{i=1}^N (E_{\text{tr},i} + E_{\text{rot},i} + E_{\text{vib},i}). \quad (116)$$

This means the partition function factors, taking the form

$$Z = \frac{1}{N!} Z_1^N, \quad (117)$$

where Z_1 is the partition function of a single molecule, and the factor $1/N!$ is needed to account for the indistinguishability of the molecules. Furthermore, the single-molecule partition function factors into translational, rotational, and vibrational parts:

$$Z_1 = Z_{\text{tr}} Z_{\text{rot}} Z_{\text{vib}}, \quad (118)$$

each of which can be obtained by adding up the corresponding Boltzmann factors:

$$\begin{aligned}
Z_{\text{tr}} &= \sum_{K_x, K_y, K_z} e^{-\beta E_{\text{tr}}(K_x, K_y, K_z)} \\
Z_{\text{rot}} &= \sum_{\substack{j_1, j_2, j_3 \\ m_1, m_2, m_3}} e^{-\beta E_{\text{rot}}(j_1, j_2, j_3)} \\
Z_{\text{vib}} &= \sum_{n_1, n_2, \dots} e^{-\beta E_{\text{vib}}(n_1, n_2, \dots)}.
\end{aligned} \tag{119}$$

There is another contribution as well, coming from the electronic states of the molecule, or of the atom in a monatomic gas. However, electronic excitations are generally of much higher energy than rotational and vibrational excitations, hence they are well above kT at typical temperatures, so that their Boltzmann factors are negligible—they are frozen out. This means we can usually ignore the corresponding factor Z_{elect} in the single-molecule partition function unless the ground state is degenerate. In the latter case, we can take Z_{elect} to be just the multiplicity of the ground state, Ω_{gnd} .

Now, let's take a closer look at the translational contributions:

$$\begin{aligned}
Z_{\text{tr}} &= \sum_{K_x=-\infty}^{\infty} \sum_{K_y=-\infty}^{\infty} \sum_{K_z=-\infty}^{\infty} e^{-\beta h^2 (K_x^2 + K_y^2 + K_z^2) / 2mL^2} \\
&= \left(\sum_{K=-\infty}^{\infty} e^{-\beta h^2 K^2 / 2mL^2} \right)^3.
\end{aligned} \tag{120}$$

Even this contribution to Z_1 factors into identical contributions from each dimension, as we should expect, since the energy decomposes into additive contributions from each dimension.

Recall that L is a macroscopic distance, so that the spacing between the energies is very small compared to $kT = 1/\beta$. This means that for all but the lowest temperatures, we can approximate the sum by an integral:

$$\begin{aligned}
Z_{\text{tr}}^{1/3} &\approx \int_{-\infty}^{\infty} e^{-\beta h^2 K^2 / 2mL^2} dK \\
&= \int_{-\infty}^{\infty} e^{-\alpha K^2} dK \\
&= \left(\frac{\pi}{\alpha} \right)^{1/2},
\end{aligned} \tag{121}$$

where

$$\alpha = \frac{\beta h^2}{2mL^2} = \frac{h^2}{2mkTL^2}. \tag{122}$$

Thus, the translational part of the single-molecule partition function is

$$Z_{\text{tr}} = \left(\frac{2\pi mkTL^2}{h^2} \right)^{3/2}. \tag{123}$$

This is a dimensionless quantity, of course, and it is customary to write it in terms of the ratio of two lengths:

$$Z_{\text{tr}} = \left(\frac{L}{\ell_Q} \right)^3, \quad (124)$$

where

$$\ell_Q = \frac{h}{\sqrt{2\pi mkT}}. \quad (125)$$

To interpret the quantity ℓ_Q it is helpful to recall that the quantum-mechanical deBroglie wavelength of a free particle is

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}}, \quad (126)$$

where p is its momentum, and E is its kinetic energy. Clearly, ℓ_Q is of a similar form, with the product πkT playing the role of the energy. Thus, it is sometimes called the *thermal deBroglie wavelength*. Schroeder calls it the *quantum length*.

The translational partition function can also be expressed as a ratio of volumes:

$$Z_{\text{tr}} = \frac{V}{v_Q}, \quad (127)$$

where $V = L^3$ is the volume of the macroscopic container, and $v_Q = \ell_Q^3$ can be termed the *quantum volume*. Note well that

$$\ell_Q \ll L \quad \text{and} \quad v_Q \ll V, \quad (128)$$

except at very low temperatures or for very small confinement volumes.

Putting all the pieces together, we get the partition function for the entire gas:

$$\begin{aligned} Z &= \frac{1}{N!} (Z_{\text{tr}} Z_{\text{rot}} Z_{\text{vib}} Z_{\text{elect}})^N \\ &= \frac{1}{N!} \left(\frac{V}{v_Q} Z_{\text{int}} \right)^N, \end{aligned} \quad (129)$$

where

$$Z_{\text{int}} = Z_{\text{rot}} Z_{\text{vib}} Z_{\text{elect}}. \quad (130)$$

With this, it is now straightforward to calculate the thermodynamic properties of an ideal gas in thermal contact with a reservoir, just as it was after we obtained the multiplicity of the isolated ideal gas and from it the Sackur-Tetrode expression for its entropy. One notable difference is that we have included internal degrees of freedom here, which we did not do for the isolated gas.

The first step in obtaining thermodynamic properties is to find the free energy:

$$\begin{aligned}
 F &= -kT \ln Z \\
 &= -kT \ln \left[\frac{1}{N!} \left(\frac{V}{v_Q} Z_{\text{int}} \right)^N \right] \\
 &= -kT \left[N \left(\ln \frac{V}{v_Q} + \ln Z_{\text{int}} \right) - \underbrace{\ln N!}_{\approx N \ln N - N} \right] \quad (131) \\
 &\approx -NkT \left(\ln \frac{V}{v_Q} - \ln N + 1 \right) \underbrace{-kTN \ln Z_{\text{int}}}_{\equiv F_{\text{int}}}.
 \end{aligned}$$

Other thermodynamic quantities follow from that.

[EOC, Mon. 4/3/2006, #33; HW10 closed, due Mon. 4/10/2006]

Exercise. Calculate the entropy of an ideal gas from the free energy

$$F = -NkT \left(\ln \frac{V}{v_Q} - \ln N + 1 \right) + F_{\text{int}}. \quad (132)$$

Don't try to assume anything about the form of F_{int} .

Also, show that the Sackur-Tetrode expression for the entropy is recovered for the monatomic ideal gas if the energy is fixed at the mean energy dictated by the reservoir temperature.

0.1.8 Epilog

It's worthwhile now to revisit the distinction between the circumstances of this formalism based on the partition function or the free energy and the previous formalism based on the multiplicity or the entropy.

- Multiplicity/entropy: The system is isolated, so its energy U is fixed. The entropy is given by

$$S = k \ln \Omega = S(U, V, N). \quad (141)$$

The temperature can be obtained from the entropy by differentiation:

$$T = \left(\frac{\partial S}{\partial U} \right)_{V,N}^{-1}, \quad (142)$$

and other thermodynamic variables can be found by similar means. The probability of finding the system in a macrostate is

$$\mathcal{P}_{\text{macrostate}} = \frac{\Omega_{\text{macrostate}}}{\Omega_{\text{tot}}}. \quad (143)$$

- Partition function/free energy: The system is in thermal contact with a reservoir that fixes T . The free energy is given by

$$F = -kT \ln Z = U - TS = F(T, V, N). \quad (144)$$

The entropy can be obtained from the free energy by differentiation:

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V, N}, \quad (145)$$

and other thermodynamic variables can be found by similar means. The probability of finding the system in a microstate is

$$\mathcal{P}_{\text{microstate}} = \frac{e^{-\beta E_n}}{Z}, \quad (146)$$

where $\beta = 1/kT$.

While it is formally true that these approaches apply to distinct physical situations, it is often possible to use either for the same system. The energy of a large system in thermal contact with a reservoir fluctuates very little about the thermal average dictated by the temperature of the reservoir, so a suitable choice of T would permit the use of the new formalism to mimic very closely the thermodynamics of an isolated system having energy precisely fixed at the average value $F + TS$. We saw an example of this when we recovered the Sackur-Tetrode expression for the entropy of an ideal gas in the last exercise.

[EOC, Wed. 4/5/2006, #34; End of material for Exam II]
