

4.3: Classical Monatomic Ideal Gas

I've told you that it's easier to do calculations in the canonical ensemble than in the microcanonical ensemble. Today I'm going to demonstrate the truth of this assertion.

Remember how we found the entropy $S(E, V, N)$ for a classical monatomic ideal gas? The hard part involved finding the volume of a shell in $3N$ -dimensional space. It took us three or four hours to derive the Sackur-Tetrode formula (equation (2.32)), namely

$$S(E, V, N) = k_B N \left[\frac{3}{2} \ln \left(\frac{4\pi m E V^{2/3}}{3h_0^2 N^{5/3}} \right) + \frac{5}{2} \right]. \quad (4.3.1)$$

It took us another hour or so to show that the energy of this system is (equation (2.57))

$$E = \frac{3}{2} N k_B T \quad (4.3.2)$$

whence

$$S(T, V, N) = k_B N \left[\frac{3}{2} \ln \left(\frac{2\pi m k_B T V^{2/3}}{h_0^2 N^{5/3}} \right) + \frac{5}{2} \right]. \quad (4.3.3)$$

In this section, we'll derive this same equation using the canonical ensemble. While the derivation is no stroll in the park, most people find it considerably easier than the microcanonical derivation.

Our strategy will be: (1) Integrate the Boltzmann factor over all phase space to find the partition function $Z(T, V, N)$. (2) Find the Helmholtz free energy using

$$F(T, V, N) = -k_B T \ln(Z(T, V, N)). \quad (4.3.4)$$

And finally (3) use the thermodynamic result

$$S(T, V, N) = -\left(\frac{\partial F}{\partial T}\right)_{V, N} \quad (4.3.5)$$

to find the entropy.

The Hamiltonian for this model system is

$$H(\Gamma) = \frac{1}{2m} (p_{x,1}^2 + p_{y,1}^2 + p_{z,1}^2 + p_{x,2}^2 + \cdots + p_{z,N}^2) + U(\mathbf{x}_1) + U(\mathbf{x}_2) + \cdots + U(\mathbf{x}_N), \quad (4.3.6)$$

where the potential energy function for each individual atom as a function of its location \mathbf{x} is

$$U(\mathbf{x}) = \begin{cases} 0 & \text{if } \mathbf{x} \text{ is inside the container} \\ \infty & \text{if outside} \end{cases} \quad (4.3.7)$$

This has been background. Now we're ready to roll up our sleeves and plunge into the work. Any questions? Okay, let's go.

The canonical partition function is

$$\begin{aligned} Z(T, V, N) &= \frac{1}{N! h_0^{3N}} \int d\Gamma e^{-\beta H(\Gamma)} \\ &= \frac{1}{N! h_0^{3N}} \int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dy_1 \int_{-\infty}^{+\infty} dz_1 \cdots \int_{-\infty}^{+\infty} dx_N \int_{-\infty}^{+\infty} dy_N \int_{-\infty}^{+\infty} dz_N \\ &\quad \times \int_{-\infty}^{+\infty} dp_{x,1} \int_{-\infty}^{+\infty} dp_{y,1} \int_{-\infty}^{+\infty} dp_{z,1} \cdots \int_{-\infty}^{+\infty} dp_{x,N} \int_{-\infty}^{+\infty} dp_{y,N} \int_{-\infty}^{+\infty} dp_{z,N} e^{-\beta H(\Gamma)} \end{aligned}$$

There are N triplets of integrals over positions and N triplets of integrals over momenta. . . in total, a $6N$ -dimensional integral. Because the Hamiltonian consists of a sum of terms, the Boltzmann factor consists of a product of quantities:

$$e^{-\beta H(\Gamma)} = e^{-\beta(p_{x,1}^2/2m)} e^{-\beta(p_{y,1}^2/2m)} \times \cdots \times e^{-\beta(p_{z,N}^2/2m)} e^{-\beta U(\mathbf{x}_1)} e^{-\beta U(\mathbf{x}_2)} \times \cdots \times e^{-\beta U(\mathbf{x}_N)}. \quad (4.3.8)$$

More importantly, however, each of these quantities depends on a different set of variables. Therefore the partition function also breaks up into a product of quantities:

$$Z(T, V, N) = \frac{1}{N!h_0^{3N}} \left[\int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dy_1 \int_{-\infty}^{+\infty} dz_1 e^{-\beta U(\mathbf{x}_1)} \right] \times \cdots \times \left[\int_{-\infty}^{+\infty} dx_N \int_{-\infty}^{+\infty} dy_N \int_{-\infty}^{+\infty} dz_N e^{-\beta U(\mathbf{x}_N)} \right] \\ \times \left[\int_{-\infty}^{+\infty} dp_{x,1} e^{-\beta(p_{x,1}^2/2m)} \right] \times \cdots \times \left[\int_{-\infty}^{+\infty} dp_{z,N} e^{-\beta(p_{z,N}^2/2m)} \right]$$

The partition function, which in general is a $6N$ -dimensional integral, has been reduced in this case to a product of N three-dimensional integrals over position and $3N$ one-dimensional integrals over momentum. (This near-miraculous simplification comes about because all of the limits of integration are constants. . . if the limits of integration of $p_{y,1}$ were functions of $p_{x,1}$ —as they are in the microcanonical ensemble—then it wouldn't happen.)

Moreover, the N position integrals differ only in the dummy variable of integration: they all have the same value. The same holds for the $3N$ integrals over momentum. The partition function is nothing more than

$$Z(T, V, N) = \frac{1}{N!h_0^{3N}} \left[\int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dy \int_{-\infty}^{+\infty} dz e^{-\beta U(\mathbf{x})} \right]^N \\ \times \left[\int_{-\infty}^{+\infty} dp e^{-\beta(p^2/2m)} \right]^{3N}$$

It is not difficult to evaluate the two integrals remaining. The position integral ranges over all space, but for any point in space outside of the container, its integrand is

$$e^{-\beta U(\mathbf{x})} = e^{-\beta(\infty)} = 0. \quad (4.3.9)$$

Meanwhile, for any point in space within the container, the integrand is

$$e^{-\beta U(\mathbf{x})} = e^{-\beta(0)} = 1. \quad (4.3.10)$$

Thus

$$\int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dy \int_{-\infty}^{+\infty} dz e^{-\beta U(\mathbf{x})} = \iiint_{\text{container}} dx_1 dy_1 dz_1 1 = V. \quad (4.3.11)$$

Meanwhile, the momentum integral is a clear cousin to the Gaussian integral (equation B.5)

$$\int_{-\infty}^{+\infty} e^{-u^2} du = \sqrt{\pi}. \quad (4.3.12)$$

Use of the substitution $u = \sqrt{\beta/2m}p$ in the momentum integral gives

$$\int_{-\infty}^{+\infty} dp e^{-\beta(p^2/2m)} = \sqrt{2m/\beta} \int_{-\infty}^{+\infty} e^{-u^2} du = \sqrt{2\pi m k_B T}. \quad (4.3.13)$$

Putting all this together gives us

$$Z(T, V, N) = \frac{V^N}{N!h_0^{3N}} (\sqrt{2\pi m k_B T})^{3N} = \frac{1}{N!} \left(\frac{2\pi m k_B T V^{2/3}}{h_0^2} \right)^{3N/2}. \quad (4.3.14)$$

We've completed the first step of our three-step plan. Now we must find the free energy

$$F(T, V, N) = -k_B T \ln Z = -k_B T \ln \left[\frac{1}{N!} \left(\frac{2\pi m k_B T V^{2/3}}{h_0^2} \right)^{3N/2} \right]. \quad (4.3.15)$$

Something's a bit funny here. If we double V and N , we should double F , but this doesn't exactly happen: that factor of $N!$ is sure to mess things up. What's gone wrong? We ran into the same problem in when we used the microcanonical ensemble (at equation (2.24)) and it has the same solution: we must take the thermodynamic limit. For large values of N ,

$$\begin{aligned}
 F(T, V, N) &= -k_B T \ln \left[\frac{1}{N!} \left(\frac{2\pi m k_B T V^{2/3}}{h_0^2} \right)^{3N/2} \right] \\
 &= -k_B T \left[\ln \left(\frac{2\pi m k_B T V^{2/3}}{h_0^2} \right)^{3N/2} - \ln N! \right] \\
 &\approx -k_B T \left[\frac{3}{2} N \ln \left(\frac{2\pi m k_B T V^{2/3}}{h_0^2} \right) - N \ln N + N \right]
 \end{aligned}$$

But

$$-N \ln N = \frac{3}{2} N \left(-\frac{2}{3} \ln N \right) = \frac{3}{2} N \ln(N^{-2/3})$$

so

$$F(T, V, N) = -k_B T N \left[\frac{3}{2} \ln \left(\frac{2\pi m k_B T V^{2/3}}{h_0^2 N^{2/3}} \right) + 1 \right]. \quad (4.3.16)$$

This feels a lot healthier: If we double both V and N , then the ratio $(V^{2/3}/N^{2/3})$ is unchanged, so the free energy exactly doubles. Now the final step: Take the derivative with respect to temperature to find the entropy. To do this, recognize that within the square brackets we have

$$\left[\frac{3}{2} \ln(T) + \text{a lot of things independent of } T \right]$$

With this realization the derivative becomes straightforward:

$$S(T, V, N) = -\frac{\partial F}{\partial T} \Big|_{V, N} = k_B N \left[\frac{3}{2} \ln \left(\frac{2\pi m k_B T V^{2/3}}{h_0^2 N^{2/3}} \right) + 1 \right] + k_B T N \left[\frac{3}{2} \frac{1}{T} \right] \quad (4.3.17)$$

or

$$S(T, V, N) = k_B N \left[\frac{3}{2} \ln \left(\frac{2\pi m k_B T V^{2/3}}{h_0^2 N^{2/3}} \right) + \frac{5}{2} \right]. \quad (4.3.18)$$

Wow. This is exactly the same as expression (4.10), which came from a (considerably longer) microcanonical derivation.

We've come a long way and it is certainly appropriate to take a moment here to bask in our triumph. But while doing so, a small but troubling question might arise: Why *should* we get the same answer from a canonical and a microcanonical calculation? After all, the ensembles in question are quite distinct: In a microcanonical ensemble each system has the same energy. In a canonical ensemble the individual systems can have any energy they'd like, as reflected by states that range from crystalline to plasma. Why should we get identical entropies from such very different collections?

Loose remark: One often hears that for a gas at temperature T , the probability of an atom having energy E is proportional to the "Boltzman factor" $e^{-E/k_B T}$. This is true only for non-interacting atoms. If the atoms interact then the kinetic energy belongs to atoms but the potential energy belongs to atom pairs, so it's impossible to define "the energy of an atom". What is always true is that in the canonical ensemble at temperature T , the probability of a system having energy E is proportional to $e^{-E/k_B T}$.

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