

## 5.1: Classical Monatomic Ideal Gases

We have already found the Helmholtz free energy of the classical monatomic ideal gas (section 4.3). I think you will agree that the canonical calculation is considerably easier than the corresponding microcanonical calculation. Here we will review the calculation, then go back and investigate just what caused the solution to be so much easier, and this investigation will lead to an important theorem.

### 5.1.1 Solving the problem

The energy

$$H(\Gamma) = \frac{1}{2m} (p_{x,1}^2 + p_{y,1}^2 + p_{z,1}^2 + p_{x,2}^2 + \cdots + p_{z,N}^2) + U(\mathbf{x}_1) + U(\mathbf{x}_2) + \cdots + U(\mathbf{x}_N) \quad (5.1.1)$$

is a sum of terms, each involving different variables, so the Boltzmann factor

$$e^{-\beta H(\Gamma)} = e^{-\beta(p_{x,1}^2/2m)} e^{-\beta(p_{y,1}^2/2m)} \times \cdots \times e^{-\beta(p_{z,N}^2/2m)} e^{-\beta U(\mathbf{x}_1)} e^{-\beta U(\mathbf{x}_2)} \times \cdots \times e^{-\beta U(\mathbf{x}_N)} \quad (5.1.2)$$

is a product of factors, each involving different variables. Thus the partition function, which in general is an integral in a  $6N$ -dimensional space, factors into 3- and 1-dimensional integrals

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

This doesn't happen in the microcanonical calculation!

Moreover, we found it easy to evaluate the  $N$  three-dimensional position integrals and the  $3N$  one-dimensional momentum integrals. The result was

$$Z(T, V, N) = \frac{V^N}{N! h^{3N}} [\sqrt{2\pi m k_B T}]^{3N}. \quad (5.1.3)$$

The result above is correct, but it is not the most convenient form for the partition function. There are lots of variables and constants floating around, many of them with hard-to-remember dimensions. The quantity  $Z$  is in fact dimensionless, but that's not obvious from the expression. For this reason is customary to define the quantity

$$\lambda(T) = \frac{h}{\sqrt{2\pi m k_B T}}, \quad (5.1.4)$$

called the "thermal de Broglie wavelength". Like any wavelength, it has the dimensions of length, and the notation  $\lambda(T)$  suggests this. It is, of course, an intensive quantity. In terms of the thermal de Broglie wavelength, the partition function for the classical monatomic ideal gas is

$$Z(T, V, N) = \frac{1}{N!} \left( \frac{V}{\lambda^3(T)} \right)^N. \quad (5.1.5)$$

If a particle of mass  $m$  has kinetic energy  $k_B T$ , then it has momentum  $\sqrt{2mk_B T}$  and thus a quantum-mechanical de Broglie wavelength of

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mk_B T}}. \quad (5.1.6)$$

The definition (5.4) above slips in an extra dimensionless factor of  $\sqrt{\pi} = 1.77$  just to make the result (5.5) easier to remember and to work with. Physically, the thermal de Broglie wavelength represents the quantal smearing of each individual point particle. Thus if the mean separation between atoms is much greater than  $\lambda(T)$ , we expect that the classical approximation will be a good one. If the mean separation is less than or about equal to  $\lambda(T)$ , we expect that a quantal treatment will be required.

After doing any calculation is it useful to perform a “debriefing” to figure out why—in general rather than technical terms—the calculation went the way it did. Almost everyone agrees that this canonical calculation is a lot easier than the corresponding microcanonical calculation to find  $\Omega(E, V, N)$  for the classical monatomic ideal gas. But what was the particular feature that made it so much easier? Surely it was the factorization of the Boltzmann factor and the subsequent factorization of the partition function. This enabled us to perform one- and three-dimensional integrals rather than the  $3N$ -dimensional integral required (see appendix D) for the microcanonical calculation. Is there anything that can be said more generally about this feature?

### 5.1.2 Theorem on decoupling Hamiltonians

Indeed there is. Suppose a Hamiltonian is a sum of two pieces

$$H(\Gamma) = H_1(\Gamma_1) + H_2(\Gamma_2), \quad (5.1.7)$$

where  $\Gamma_1$  and  $\Gamma_2$  are exclusive. (That is, the phase space variables in the list  $\Gamma_1$  and the phase space variables in the list  $\Gamma_2$  together make up the whole list  $\Gamma$ , and no variable appears in both lists.) The Hamiltonian  $H(\Gamma)$  is then said to “decouple” into the two parts  $H_1(\Gamma_1)$  and  $H_2(\Gamma_2)$ .<sup>1</sup> Then it is easy to see that the partition function will factor into two parts:

$$Z(T, V, N) = \frac{1}{N!h^{3N}} \int d\Gamma e^{-\beta H(\Gamma)} = \frac{1}{N!h^{3N}} \int d\Gamma_1 e^{-\beta H_1(\Gamma_1)} \int d\Gamma_2 e^{-\beta H_2(\Gamma_2)}. \quad (5.1.8)$$

If the Hamiltonian decouples into three parts, then this reasoning can be used to show that the partition function breaks into three factors. And so forth.

For example, the Hamiltonian of the classical monatomic ideal gas that we have just investigated decouples into  $4N$  pieces,

$$H(\Gamma) = \frac{p_{x,1}^2}{2m} + \frac{p_{y,1}^2}{2m} + \cdots + \frac{p_{z,N}^2}{2m} + U(\mathbf{x}_1) + U(\mathbf{x}_2) + \cdots + U(\mathbf{x}_N). \quad (5.1.9)$$

Each term of the form  $p^2/2m$  in the Hamiltonian leads to a factor of  $h/\lambda(T)$  in the partition function. . . each term of the form  $U(\mathbf{x})$  leads to a factor of  $V$ . Thus our theorem on decoupling Hamiltonians shows that the partition function is

$$Z(T, V, N) = \frac{1}{N!h^{3N}} \left( \frac{h}{\lambda(T)} \right)^{3N} V^N. \quad (5.1.10)$$

If the particles *do* interact, then the potential energy part of the Hamiltonian does not break up into exclusive pieces, but the kinetic energy part still does. Thus for an interacting gas with potential energy of interaction

$$U_N(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \quad (5.1.11)$$

the partition function is

$$Z(T, V, N) = \frac{1}{N!\lambda^{3N}(T)} \int_{-\infty}^{+\infty} dx_1 \cdots \int_{-\infty}^{+\infty} dz_N e^{-\beta U_N}. \quad (5.1.12)$$

Although the potential energy part of the problem is now excruciatingly difficult, our theorem on decoupling Hamiltonians assures us that the kinetic energy part is just as easy to handle for an interacting as for a non-interacting gas.

#### 5.1 Gas with pair interactions

For a pure classical monatomic gas that interacts only through pair interactions (i.e. for which there are no three-body or higher interactions) the Hamiltonian is

$$H(\Gamma) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + \sum_{i=1}^N U_A(\mathbf{x}_i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^N U_B(\mathbf{x}_i, \mathbf{x}_j), \quad (5.1.13)$$

where  $U_A(\mathbf{x})$  is the potential energy due to the interaction between a particle at point  $\mathbf{x}$  and the container, and  $U_B(\mathbf{x}, \mathbf{y})$  is the potential energy due to the interaction between a particle at point  $\mathbf{x}$  and a particle at point  $\mathbf{y}$ . The potential energy thus breaks up into a sum of  $N + N(N-1)/2$  pieces. Does the decoupling theorem apply?

<sup>1</sup>Alternatively, the two parts of the Hamiltonian are called “uncoupled”. These terms derive from the ordinary English word “to couple”, meaning to join or to connect.

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