

Lecture 6: Ideal gas ensembles

1 Introduction

A simple, instructive and practical application of the equilibrium ensemble formalisms of the previous lecture concerns an ideal gas. Such a physical system is distinguished by the property that the system energy is independent of particle position since the molecules are assumed not to interact through a long range potential¹. This weak interaction assumption works reasonably well for many gases in practical applications and so they are termed ideal to a good approximation. Some brief remarks on deviations from this are made at the end of the lecture. In order to illustrate the ensemble methods developed in the previous lecture we perform calculations for the microcanonical ensemble as well as the grand canonical ensemble.

2 Microcanonical ensemble

We follow here a heuristic rather than rigorous presentation for pedagogical reasons. As should be clear from the microcanonical ensemble members lying on a submanifold of phase space, there are some important mathematical technicalities which here we avoid for clarity. Heuristically we can write the microcanonical density in phase space as proportional to

$$D = \frac{1}{h^{3N}N!} \delta\left(\frac{E_0}{E_T} - \frac{E}{E_T}\right) = \frac{1}{h^{3N}N!} E_T \delta(E_0 - E)$$

where δ is the Dirac delta function (i.e. a distribution); E_0 is the mean thermodynamical energy and E_T is a reference energy to ensure dimensional consistency. Note that E is not fixed like E_0 and E_T but depends on the phase space variables. Now in a distribution sense we have

$$\delta(x - y) = \frac{\partial}{\partial x} \theta(x - y)$$

where θ is the Heaviside step function. The microcanonical partition function Z_M is the integral over phase space of D since it is the normalization factor. We have therefore

$$Z_M = E_T \frac{\partial}{\partial E_0} \int \frac{d^N \mathbf{p} d^N \mathbf{q}}{h^{3N}N!} \theta(E_0 - E)$$

Consider now the integral

$$I_N = \int \frac{d^N \mathbf{p} d^N \mathbf{q}}{h^{3N}N!} \theta(E_0 - E).$$

¹Molecules do however collide and this affects system non-equilibrium behavior as we shall see later. In the present context we assume such collisions do not affect total energy i.e. a system in which no collisions occurs has almost the same energy as the realistic case in which collisions do occur.

For an ideal gas E depends only on the momenta \mathbf{p} of the molecules and not on their position \mathbf{q} . Note though that the gas is assumed to be confined to a particular volume so the integrals over position result in a power of the confining volume which we call V . We have therefore the simplification

$$I_N = \frac{V^N}{\hbar^{3N} N!} \int d^3\mathbf{p}_1 \dots d^3\mathbf{p}_N \theta \left(E_0 - \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} \right)$$

where we are using the expression for the kinetic energy of a free molecule of mass m . Non-dimensionalizing the momenta using E_0 as follows

$$\mathbf{x}_i = \frac{\mathbf{p}_i}{\sqrt{2mE_0}}$$

we obtain

$$I_N = \frac{V^N}{\hbar^{3N} N!} (2mE_0)^{3N/2} C_{3N}$$

$$C_d \equiv \int dx_1 \dots dx_d \theta \left(1 - \sum_{i=1}^d x_i^2 \right)$$

Now from the nature of the step function the latter integral is clearly the volume of a hypersphere of dimension d and radius 1 which can be shown to be

$$C_d = \frac{\pi^{d/2}}{\Gamma(d/2 + 1)}$$

Inserting this into our expression for I_N and differentiating this with respect to the thermodynamical energy E_0 we obtain for the microcanonical partition function

$$Z_M = \left[\frac{V (2mE_0)^{3/2}}{\hbar^3} \right]^N \frac{3NE_T}{N! 2E_0 \Gamma(3N/2 + 1)} \quad (1)$$

The entropy $S(E_0, N, V)$ is simply the logarithm of this partition function since the microcanonical density is uniform on the submanifold of constant energy. Now the objects of interest thermodynamically are those which apply in the limit that $N \rightarrow \infty$ i.e. the number of molecules becomes very large. Of course in such a limit both the energy and entropy also become infinite so we define energy, entropy and molecular densities which are simply $\epsilon = E_0/N$, $s = S/N$ and $n = N/V$. These converge in the thermodynamical limit and a straightforward computation (albeit a little tedious) gives for the entropy density (i.e. entropy per molecule)

$$s = \log \left[\frac{e^{5/2}}{n\hbar^3} \left(\frac{4\pi\epsilon}{3} \right)^{3/2} \right] \quad (2)$$

a result for ideal gases known as the Sackur-Tetrode equation. Notice that it does not involve the reference energy E_T . Furthermore that it is also the result

of taking the thermodynamical limit. The expressions for a finite number of molecules i.e. (1) and the like are by contrast complicated functions of N . Note finally that the ideal gas simplification allowed the computation to be reduced to that of computing the volume of a hypersphere. If this simplification had not occurred the calculation would have been potentially considerably more difficult.

3 Grand canonical ensemble

The computation in the previous section is a little cumbersome as it involves “hypergeometry” and the result for the partition function (1) is a rather complex function of N the number of molecules and requires the thermodynamical limit to interpret clearly. Canonical ensembles are usually easier to work with. We show here the grand canonical calculation beginning with a calculation of Z_G the partition function. In the last lecture we computed

$$\begin{aligned} Z_G(\lambda_1, \lambda_2) &\equiv \sum_{N=0}^{\infty} \int_{R^{2N}} \exp(-T^{-1}E + \mu T^{-1}N) dV \\ dV &= \frac{d^N \mathbf{p} d^N \mathbf{q}}{\hbar^{3N} N!} \\ \lambda_1 &= -T^{-1} \\ \lambda_2 &= \mu T^{-1} \end{aligned} \quad (3)$$

The integral over phase space can be carried out rather easily for an ideal gas since it is simply

$$E = \sum_{i=1}^N \frac{p_i^2}{2m} \quad (4)$$

Thus it does not depend on the position of molecules and the dependency with respect to momentum results in a Gaussian function which is trivially integrated. The position integration results in a factor of V^N while the momentum integration of the Gaussian gives a factor of $(2\pi mT)^{3N/2}$ hence

$$Z_G = \sum_{N=0}^{\infty} \frac{1}{N!} \left[\frac{V e^{\mu T^{-1}} (2\pi mT)^{3/2}}{\hbar^3} \right]^N$$

which is a McLaurin series for an exponential function:

$$Z_G = \exp\left(\frac{V e^{\mu T^{-1}}}{l^3}\right) \quad (5)$$

where the length scale l is the quantum wavelength of a molecule of energy T and is called the thermal wavelength:

$$l \equiv \hbar \sqrt{\frac{2\pi}{mT}} = \hbar \sqrt{\frac{2\pi}{m}} \sqrt{-\lambda_1}$$

The expression (5) is very simple and presages simple thermodynamical relations for an ideal gas. From equation (3) it is easy to derive that

$$\begin{aligned}\bar{N} &= \frac{\partial \{\log Z_G\}}{\partial \lambda_2} \\ E_0 &= \frac{\partial \{\log Z_G\}}{\partial \lambda_1}\end{aligned}\quad (6)$$

and hence using (5) that

$$\bar{N} = \frac{V e^{\mu T^{-1}}}{l^3}$$

and hence that the particle density $n = \frac{\bar{N}}{V}$ is

$$n = \frac{e^{\mu T^{-1}}}{l^3}\quad (7)$$

Likewise the thermodynamical energy can be derived from (6)

$$\begin{aligned}E_0 &= V e^{\lambda_2} \frac{\partial}{\partial \lambda_1} (l^{-3}) \\ &= V e^{\mu T^{-1}} \frac{3}{2} T l^{-3} = \frac{3}{2} \bar{N} T\end{aligned}$$

and so the energy per particle ϵ is simply

$$\epsilon = \frac{E_0}{\bar{N}} = \frac{3}{2} T\quad (8)$$

a very well known result from elementary thermodynamics of an ideal gas.

Now the entropy for the grand canonical ensemble may be derived in the same way we did in the last lecture for the canonical ensemble obtaining the modified relation

$$S = T^{-1} E_0 - \mu T^{-1} \bar{N} + \log Z_G\quad (9)$$

Furthermore from Lecture 3 we know that

$$\frac{p}{T} = \frac{\partial S}{\partial V} = \frac{\partial}{\partial V} (\log Z_G)$$

Hence using (5) and (7) we obtain

$$p = nT\quad (10)$$

another well known ideal gas equation sometimes called the equation of state. Now from (9) and (8) we can derive an entropy density equation

$$s = \frac{S}{\bar{N}} = \frac{5}{2} - \frac{\mu}{T}\quad (11)$$

We can also obtain the chemical potential μ from (7) and (8):

$$\mu = \frac{2}{3}\epsilon \log (nl^3)$$

Substituting into (11) we obtain

$$s = \log \frac{e^{5/2}}{nl^3}$$

when the definition of l is used we can see that this is the same equation we derived above using the microcanonical ensemble i.e. the Sackur-Tetrode equation (2). Notice how the grand canonical ensemble calculations were able to rather rapidly access much of the thermodynamics of the ideal gas. This is in contrast to the rather cumbersome and limited microcanonical calculation. Note though that they coincide in the thermodynamical limit.

4 Non-ideal behavior

The ideal gas assumption ignores the energetics of molecular interactions. Under certain circumstances collisions between molecules can become significant. This is dealt with by introducing a potential function which varies with the distance between any two particles (multiple collisions are extremely rare). This potential function modifies the energy equation (4) by the introduction of a function depending on molecular positions. The exponential of this function must then be integrated over with respect to any two molecules. In the ideal case the molecular position integrals simply resulted in a factor of V^N . With the potential function this is modified in such a way that depends on the gas temperature T and this additional effect modifies the usual ideal gas equations (8) and (10).

An excellent introduction to these effects may be found in Landau and Lifschitz Chapter VII.