Thermodynamik
Serie 10

Aufgabe 10.1 Most probable distribution method

In the lecture we derived the Maxwell-Boltzmann distribution from a kinetic point of view. We saw that f_{MB} does not depend on the particular form of the molecular interactions. Being interested only in the distribution of a gas at equilibrium, we suspect that its law of distribution can be derived without consideration of its kinematics. We perform here the derivation of f_{MB} from a statistical point of view.
We start with the idea of the Gibbs ensemble by considering a gas of N particles confined in a volume V. In chapter 10 we saw that any state of the system can be represented by a point $(p,q) = (p_1, p_2, ..., p_{3N}, q_1, ..., q_{3N})$ in its phase space Γ. The ensemble of points corresponding to the same macroscopical conditions is called the representative volume of the system. At equilibrium, we assume that the system can be found in all the states corresponding to the same macroscopic conditions with equal probability. In other words, the density function defined in (10.5) is a constant on the representative volume of the system. If we fix the energy of the system between E and $E+\Delta$ with $\Delta \ll E$, the representative volume is a compact ensemble of points bounded by the energy surfaces E and $E+\Delta$. This is the so called microcanonical ensemble (10.8).
We now proceed as follows: We define the one-particle phase space μ, in which each particle occupies one point (p,q) corresponding to its state. Thus the distribution of points in μ defines the state of the whole system. Let us divide μ into K boxes each of volume $\omega = \Delta^3 p \Delta^3 q$. The discrete distribution function f_i is given by the number of particles N_i inside the ith box:

$$f_i = \frac{N_i}{\omega} \quad .$$

Averaging over the microcanonical ensemble, we have the equilibrium distribution function

$$f_{0i} = \frac{\langle N_i \rangle}{\omega} \quad ,$$

which satisfies the following conditions:

$$\sum_i^K N_i = N \quad , \quad \sum_i^K N_i \frac{p_i^2}{2m} = E \tag{1}$$

It is clear that there exists an ensemble of points $(p,q) \in \Gamma_{E,V,N}$ which define the same distribution function f_i, e.g. exchanging two particles, one from the ith box and the other from the jth box, leaves N_i and N_j unchanged. The idea now is to find the distribution function which corresponds to the largest volume in $\Gamma_{E,V,N}$. This gives us the most probable distribution function of the system. We make the assumption that this is nothing but the equilibrium distribution function f_{0i}. Practically we are looking for the set $\{N_i\}_1^K$ which gives the largest volume $\Omega\{N_i\} \in \Gamma_{E,V,N}$ such that the conditions (eq. 1) are satisfied.

1. Show that $\Omega\{N_i\} \propto N!/N_1!N_2!...N_K!$.

2. In the following we set

$$\Omega\{N_i\} \propto \frac{N!}{N_1!N_2!...N_K!} g_1^{N_1} g_2^{N_2} ... g_K^{N_K},$$

   where $g_1, g_2, ..., g_K$ are numbers that we put equal to unity at the end the calculation. Show that f_{0i} is nothing but the Maxwell-Boltzmann distribution. *Hint:* Maximize $\log \Omega\{N_i\}$ (why log?) with respect to N_i taking into account the conditions (eq. 1). Calculate f_{0i}.

3. The average of N_i over the microcanonical ensemble is given by

$$\langle N_j \rangle = \frac{\sum_{N_i} N_j \Omega\{N_i\}}{\sum_{N_i} \Omega\{N_i\}}.$$

   Taking $\langle N_j \rangle \approx N_{0j}$, show that the mean square fluctuation is given by

$$(\Delta N_j)^2 \equiv \langle N_j^2 \rangle - \langle N_j \rangle^2 = N_{0j}.$$

   Hint: Show that for $g_i \to 1$ one has

$$\langle N_j \rangle = g_i \frac{\partial}{\partial g_i} \sum_{N_i} \Omega\{N_i\}.$$

4. The probability of any set $\{N_j\}$ to be realized is given by

$$\mathcal{P}\{N_j\} = \frac{\Omega\{N_j\}}{\sum_{N_i} \Omega\{N_i\}}.$$

   Give the schematic plot of $\mathcal{P}\{N_j\}$ as a function of N_j/N and show that the assumption $\langle N_j \rangle \approx N_{0j}$ is reasonable.

   Hint: Express $\Delta(N_j/N)$, what happens for large N?

Aufgabe 10.2 Probability of spotaneous fluctuations

We can apply the results of Task 1 to compute the probability of spontaneous fluctuations. Consider the air (gas in equilibrium) contained in a room of volume V. Compute the probability for the gas to leave a small empty space v by spontaneous fluctuations. Discuss the results.

Aufgabe 10.3 Hourglass

With this problem we want to learn how to solve a stochastic problem using a statistical approach and in particular we want to explain why a hourglass (a system that can be described by discrete non-stationary processes) can be used as a clock.
Assume that only one grain of sand at a time can pass through the hole with a probability rate η that is independent from the state of the system.
The initial contition is given by the fact that the number of sand grains n in the bottom part of the hourglass at $t = 0$ is zero:

$$P(n = 0, t = 0) = 1 \quad \text{or} \quad P(n \neq 0, t = 0) = 0 \tag{2}$$

1. Show that the time evolution $\dot{P}(n,t)$ gives a probability $P(n,t)$ that is directly proportional to t.
2. Estimate the precision of the hourglass using the fluctuations of n.