Statistical Mechanics

Worksheet 7

June 1st, 2023

1 The Meaning of *Never*

It has been said[1] that *six monkeys, set to strum unintelligently on typewriters for millions of years, would be bound in time to write all the books in the British Museum.* This statement is nonsense, for it gives a misleading conclusion about very, very large numbers. Could all the monkeys in the world have typed out a single specified book in the age of the universe?

Suppose that 10^{10} monkeys have been seated at typewriters throughout the age of the universe, 10^{18}s. This number of monkeys is about three times greater than the present human population of the earth. We suppose that a monkey can hit 10 typewriter keys per second. A typewriter may have 44 keys; we accept lowercase letters in place of capital letters. Assuming that Shakespeare's *Hamlet* has 10^5 characters, will the monkeys hit upon *Hamlet*?

1. Show that the probability that any given sequence of 10^5 characters typed at random will come out in the correct sequence (the sequence of *Hamlet*) is of the order of

$$\left(\frac{1}{44}\right)^{100000} = 10^{-164345}$$

   where we have used $\log_{10} 44 = 1.64345$

2. Show that the probability that a *monkey-Hamlet* will be typed in the age of the universe is approximately $10^{-164316}$. The probability of *Hamlet* is therefore zero in any operational sense of an event, so that the original statement at the beginning of this problem is nonsense: one book, much less a library, will never occur in the total literary production of the monkeys.

2 Time for a large fluctuation

We quoted Boltzmann to the effect that two gases in a 0.1 liter container will unmix only in a time enormously long compared to $10^{(10^{10})}$ years. We shall investigate a related problem: we let a gas of atoms of ^{4}He occupy a container of volume of 0.1 liter at 300 K and a pressure of 1 atm, and we ask how long it will be before the atoms assume a configuration in which all are in one-half of the container.

[1] J. Janes, *Mysterious universe*, Cambridge University Press, 1930, p.4. The statement is attributed to Huxley

1. Estimate the number of states accessible to the system in this initial condition.

2. The gas is compressed isothermally to a volume of 0.05 liter. How many states are accessible now?

3. For the system in the 0.1 liter container, estimate the value of the ratio

$$\frac{\text{number of states for which all atoms are in one-half of the volume}}{\text{number of states for which the atoms are anywhere in the volume}}.$$

4. If the collision rate of an atom is $\approx 10^{10}$ s^{-1}, what is the total number of collisions of all atoms in the system in a year? We use this as a crude estimate of the frequency with which the state of the system changes.

5. Estimate the number of years you would expect to wait before all atoms are in one-half of the volume, starting from the equilibrium configuration.

3 Ideal Gas in the Canonical ensemble

Consider an ideal gas in the canonical ensemble characterised by a macrostate $M \equiv (T, V, N)$. The probability of having the ideal gas being in a microstate $\mu \equiv \{\vec{p}_i, \vec{q}_i\}$ is

$$p(\{\vec{p}_i, \vec{q}_i\}) = \frac{1}{Z} \exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m}\right] \cdot \begin{cases} 1 & \text{for } \{\vec{q}_i\} \in \text{ Box} \\ 0 & \text{otherwise} \end{cases}. \tag{1}$$

Where Z is the Canonical partition function.

1. Write the partition function Z of the system.

   Hint: The spatial part is easily integrable as every particle contributes with a volume. The part of the momentum is also explicitly integrable as it is a $3N$ dimensional Gaussian integral.

   Hint: Use $\lambda(T) = \frac{h}{\sqrt{2\pi m k_B T}}$, as the characteristic length associated with the action h (The minimum resolution on the phase space).

2. Use the partition function to compute the Free Energy.

3. Use the Free energy to compute the chemical potential, the pressure and the entropy. From the entropy get the internal energy and comment your results.

4 Ideal Gas in the Isobaric Ensemble

The isobaric ensemble is described by constant pressure instead of constant volume compared to the canonical ensemble, $M \equiv (N, T, P)$. A microstate $\mu \equiv \{\vec{p}_i, \vec{q}_i\}$ with a volume V, occurs with the probability

$$p(\{\vec{p}_i, \vec{q}_i\}) = \frac{1}{\mathcal{Z}} \exp\left[-\beta \sum_{i=1}^{N} \frac{p_i^2}{2m} - \beta P V\right] \cdot \begin{cases} 1 & \text{for } \{\vec{q}_i\} \in \text{ Box} \\ 0 & \text{otherwise} \end{cases}. \tag{2}$$

Where $\mathcal{Z}$ is the isobaric partition function.

1. Write the partition function $\mathcal{Z}$ of the system.

   Hint: For the spatial part, use the gamma function $\Gamma(z) = \int_0^\infty t^{z-1}e^t dt$, so that for a positive integer $\Gamma(n) = (N-1)!$. The part of the momentum is the same as before.

2. Use the partition function to compute the Gibbs Free Energy.

3. Use the Gibbs free energy to compute the volume V, the enthalpy as $H = -\frac{\partial \ln \mathcal{Z}}{\partial \beta}$ and the specific heat $C_P = dH/dT$

5 Ideal Gas in the Grand Canonical Ensemble

Consider an ideal gas in the grand canonical ensemble characterised by a macrostate $M \equiv (T, \mu, V)$, the corresponding microstates $\{\vec{p}_1, \vec{q}_1, \vec{p}_2, \vec{q}_2, \cdots\}$ have indefinite particle number.

1. Write the partition function Ξ of the system.

   Hint: Write the partition function as the sum of canonical partition functions. Use the expansion $\exp(x) = \sum_{n=0}^{\infty} x^n/n!$

2. Use the partition function Ξ to compute the grand potential.

3. Use the grand potential to compute the gas pressure, the particle number, equation of state and chemical potential.

6 Grand Partition Function of a two level system

Consider a system that may be unoccupied with energy zero or occupied by one particle in either of two states, one of energy zero and one of energy ϵ.

1. Show that the partition function for this system is

$$\Xi = 1 + \lambda + \lambda \exp(-\beta\epsilon) \tag{3}$$

   where $\lambda = \exp(\beta\mu)$ is the fugacity of the system. Our assumption excludes the possibility of one particle in each state at the same time. Notice that we include in the sum a term for $N = 0$ as a particular state of a system of a variable number of particles.

2. Show that the thermal average occupancy of the system is

$$\langle N \rangle = \frac{\lambda + \lambda \exp(-\beta\epsilon)}{\Xi} \tag{4}$$

3. Show that the thermal average occupancy of the state at energy ϵ is

$$\langle N(\epsilon) \rangle = \frac{\lambda \exp(-\beta\epsilon)}{\Xi} \tag{5}$$

4. Find an expression for the thermal average energy of the system.

5. Allow the possibility that the orbital at O and at ϵ may be occupied each by one particle at the same time; show that

$$\Xi = 1 + \lambda + \lambda \exp(-\beta\epsilon) + \lambda^2 \exp(-\beta\epsilon) = (1+\lambda)\left[1 + \exp(-\beta\epsilon)\right] \tag{6}$$

   Because Ξ can be factored as shown, we have in effect two independent systems.