

Introduction to Statistical Mechanics

Based on the video presentations by Leonard Susskind

by

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Introduction

Statistical mechanics is used when describing systems with a large number of degrees of freedom. In this situation it is impossible to use other methods. Moreover the laws of nature may be unknown and as a consequence only statistical methods can be used.

The ensemble

In this section an ensemble of systems is considered. The ensemble consists of a large number M of identical closed systems, i.e. systems being in their own universe, all being in thermal equilibrium with a very large heat bath of temperature T .

Each system is, at any time, in a certain state with energy E_i and the state is changing randomly. No assumption is made about the probability density functions p_i for the states. In fact this is what we are trying to figure out. Since the systems are identical, each system have the same number of states N . N is assumed to be very large, and M is assumed to be much larger than N . The states are ordered according to their energy. The first state having the lowest energy and the last state having the highest energy, i.e. if $i > j$ then $E_i > E_j$. It is assumed that no two states have the same energy. This assumption and the assumption that N is finite is only made in order to simplify the description in the following, the results derived are valid anyway

Figure 1 shows four examples of state distributions, where $M = 9$ and $N = 3$ at four different instances of time. In Figure 2 the number of systems n_i being in state E_i is shown for each instance of time. Looking at a row in Figure 2, the values corresponds to a set of possible arrangements of the states over the systems.

Figure 3 shows 4 examples of such arrangements all giving the same state counts. The number of arrangements is given by:

$$N_A = \binom{M}{n_1} \binom{M - n_1}{n_2} \binom{M - n_1 - n_2}{n_3} = \frac{M!}{\prod_{i=1}^N n_i!}, \quad \text{where} \quad \sum_{i=1}^N n_i = M$$

Using Stirlings formula, $\log N! \approx N \log N - N$, we have:

$$\log N_A = M \log M - M - \sum_{i=1}^N (n_i \log n_i - n_i) \tag{1}$$

$$= M \log M - \sum_{i=1}^N n_i \log n_i \tag{2}$$

$$= M \log M - \sum_{i=1}^N M p_i \log M p_i \tag{3}$$

$$= -M \sum_{i=1}^N p_i \log p_i \tag{4}$$

$$= MS \tag{5}$$

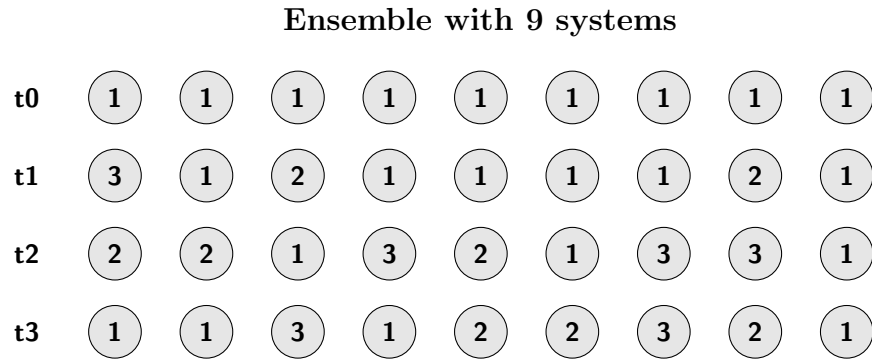


Figure 1: State distribution in the ensemble

State count for each state

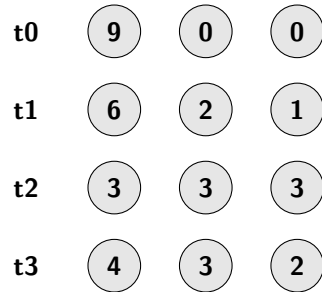


Figure 2: Number of state counts

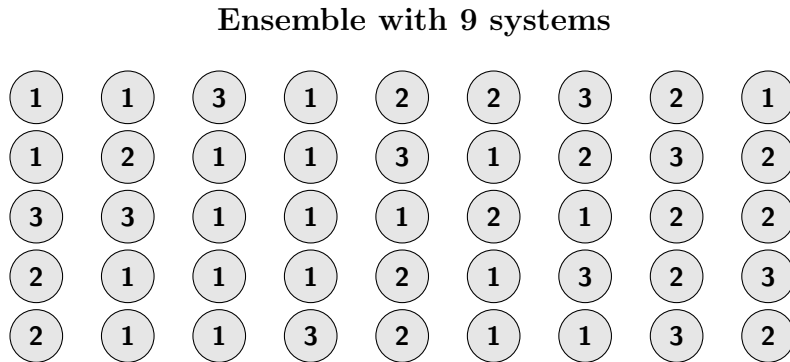


Figure 3: State distributions for state counts 4, 3, 2

where S is the entropy of the distribution p_i . The distribution p_i can now be found by maximizing N_A , since this will give the most likely distribution. This is the same as maximizing the entropy. Without any other constraints this gives $p_i = \frac{1}{N}$. As this solution leads to an infinite large value of the average energy, one more constraint must be added. The total energy of the all the systems in the ensemble is obviously proportional to M :

$$E_{tot} = ME$$

This means that the average energy $E = \frac{E_{tot}}{M}$, being the same for each system, is finite and a second constraint must be:

$$\sum_{i=1}^N E_i p_i = E$$

where E_i is the energy of the state s_i .

Maximizing the entropy

The problem of finding p_i can now be summarized:

Minimize:

$$-S = \sum_{i=1}^N p_i \log p_i$$

subject to the constraints:

$$\sum_{i=1}^N p_i = 1$$

and

$$\sum_{i=1}^N E_i p_i = E$$

This problem can be solved by using Lagrange multipliers:

Minimize:

$$F = -S + \alpha G_1 + \beta G_2$$

where:

$$G_1 = \sum_{i=1}^N p_i - 1$$

and

$$G_2 = \sum_{i=1}^N E_i p_i - E$$

Differentiating with respect to p_i gives:

$$\frac{\partial F}{\partial p_i} = -\frac{\partial S}{\partial p_i} + \alpha + \beta E_i \quad (6)$$

$$= N + \log p_i + \alpha + \beta E_i \quad (7)$$

$$= 0 \quad (8)$$

and

$$p_i = e^{-N} e^{-\alpha} e^{-\beta E_i}$$

Since $\sum_i p_i = 1$ we can define:

$$Z = \sum_{i=1}^N e^{-\beta E_i} = e^N e^{\alpha}$$

and we finally have:

$$p_i = \frac{1}{Z} e^{-\beta E_i}$$

This is the so called Boltzmann distribution, where Z is called the partition function. From the definition of Z we have:

$$\frac{\partial Z}{\partial \beta} = -\sum_{i=1}^N E_i e^{-\beta E_i}$$

and from the second constraint we have:

$$E = \sum_{i=1}^N E_i p_i = \sum_{i=1}^N E_i \frac{1}{Z} e^{-\beta E_i} = \frac{1}{Z} \sum_{i=1}^N E_i e^{-\beta E_i}$$

this gives:

$$E = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \log Z}{\partial \beta}$$

From the definition of the entropy S we have:

$$S = -\sum_{i=1}^N \frac{1}{Z} e^{-\beta E_i} \log \frac{1}{Z} e^{-\beta E_i} \quad (9)$$

$$= \sum_{i=1}^N \frac{1}{Z} e^{-\beta E_i} (\log Z + \beta E_i) \quad (10)$$

$$= \log Z + \beta E \quad (11)$$

giving

$$dS = \beta dE + d\beta E + \frac{\partial \log Z}{\partial \beta} d\beta = \beta dE$$

and

$$\frac{\partial E}{\partial S} = \frac{1}{\beta}$$

Ideal gas

In an ideal gas the interactions between the molecules are negligible and only kinetic energy has to be considered.

The partition function is given by;

$$Z = \sum_{i=1}^N e^{-\beta E_i} \quad (12)$$

$$= \int_x dx \int_p dp e^{-\beta \frac{p^2}{2m}} \quad (13)$$

$$= \frac{V^N}{N!} \left(\frac{2\pi m}{\beta} \right)^{\frac{3N}{2}} \quad (14)$$

$$= \left(\frac{Ve}{N} \right)^N \left(\frac{2\pi m}{\beta} \right)^{\frac{3N}{2}} \quad (15)$$

giving

$$\log Z = -\frac{3N}{2} \log \beta + \text{const}$$

or

$$E = -\frac{\partial \log Z}{\partial \beta} = \frac{3N}{2} \frac{1}{\beta}$$

It is known from experiments that heat capacity of a monatomic gas is:

$$C_V = \frac{3}{2} nR = \frac{3}{2} Nk_B$$

where

n is the number of moles

R is the gas constant

N is the number of atoms

k_B is Boltzmann's constant

Since

$$C_V = \frac{\partial E}{\partial T_K}$$

then

$$E = \frac{3}{2} Nk_B T_K = \frac{3}{2} N \frac{1}{\beta}$$

$$k_B T_K = \frac{1}{\beta}$$

and finally

$$\beta = \frac{1}{k_B T_K} = \frac{1}{T}$$

where

T_K is the temperature in Kelvin

T is the temperature in Joule

The ideal gas law

If an adiabatic change is made to a system consisting of a cylinder with a piston then:

$$dE = -Fdx = -PA dx = -PdV$$

where

F is the force applied to the piston

dx is the displacement of the piston

P is the pressure

A is the area of the cylinder

dV is the change in volume

Using the formula for $\frac{\partial E}{\partial V}|_S$ in appendix A one has:

$$\frac{\partial E}{\partial V}\Big|_S = \frac{\partial E}{\partial V}\Big|_T - \frac{\partial E}{\partial S}\Big|_V \frac{\partial S}{\partial V}\Big|_T = -P$$

Since

$$\frac{\partial E}{\partial S}\Big|_V = T$$

then

$$\frac{\partial E}{\partial V}\Big|_T - T \frac{\partial S}{\partial V}\Big|_T = -P$$

or

$$\frac{\partial(E - TS)}{\partial V}\Big|_T = -P$$

Inserting

$$E - TS = -T \log Z$$

one has

$$\frac{\partial(-T \log Z)}{\partial V}\Big|_T = -P$$

or

$$P = T \frac{\partial \log Z}{\partial V}\Big|_T$$

From the previous section we have:

$$Z = \left(\frac{Ve}{N}\right)^N \left(\frac{2\pi m}{\beta}\right)^{\frac{3N}{2}}$$

or

$$\log Z = N \log V + \text{terms independent of } V$$

and finally

$$P = T \frac{\partial \log Z}{\partial V}\Big|_T = \frac{N}{V} T = \frac{n}{V} k_B T_K$$

Differentials

Given a function $F(x, y)$ then:

$$dF = \frac{\partial F}{\partial x} dx + \frac{\partial F}{\partial y} dy = F_x dx + F_y dy$$

If on the other hand $F_x(x, y)$ and $F_y(x, y)$ are given then they can only be differentials of some function $F(x, y)$ if:

$$\frac{\partial^2 F}{\partial x \partial y} = \frac{\partial^2 F}{\partial y \partial x} = \frac{\partial F_y}{\partial x} = \frac{\partial F_x}{\partial y}$$

or

$$\frac{\partial F_y}{\partial x} - \frac{\partial F_x}{\partial y} = 0$$

Example given:

$$F_x(x, y) = y$$

$$F_y(x, y) = x$$

then

$$\frac{\partial F_x}{\partial y} = \frac{\partial F_y}{\partial x} = 1$$

and a solution is:

$$G(x, y) = xy$$

Now if we return to the cylinder and piston above we have:

$$dE = -PdV, \text{ if } dS = 0$$

$$dE = TdS, \text{ if } dV = 0$$

If we first keep S fixed and then V fixed we have:

$$dE = -PdV + TdS$$

$-PdV$ is the work done and $TdS = dQ$ is the applied heat. By rearranging the equation we have:

$$dQ = dE + PdV$$

Now

$$\frac{\partial Q}{\partial E} = 1$$

$$\frac{\partial Q}{\partial V} = P$$

$$\frac{\partial^2 Q}{\partial V \partial E} = 0$$

$$\frac{\partial^2 Q}{\partial E \partial V} = \left. \frac{\partial P}{\partial E} \right|_V = \frac{2}{3} \frac{1}{V}$$

This means that Q depends on the path.

The harmonic oscillator

Regarding a spring and a mass in equilibrium with a heat bath at temperature T :

Classical

$$E(p, x) = \frac{1}{2m}p^2 + \frac{\kappa}{2}x^2$$

$$Z = \int_{-\infty}^{\infty} e^{-\beta \frac{1}{2m}p^2} dp \int_{-\infty}^{\infty} e^{-\beta \frac{\kappa}{2}x^2} dx \quad (16)$$

$$= \sqrt{\frac{2\pi m}{\beta}} C1 \sqrt{\frac{2\pi}{\kappa\beta}} C1 \quad (17)$$

$$= \frac{2\pi}{\beta} \sqrt{\frac{m}{\kappa}} C1 C2 \quad (18)$$

$$E = -\frac{\partial \log Z}{\partial \beta} = \frac{1}{\beta} = T$$

Does not depend on κ

Hit it and it will start vibrating even if it is stiff

Quantum

$$Z = \sum e^{-\beta n \hbar \omega} = \sum (e^{-\beta \hbar \omega})^n \approx \frac{1}{1 - e^{-\beta \hbar \omega}}$$

$$E = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{\hbar \omega e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}}$$

Compare

High temperature, β small

$$E = \frac{1}{\beta} = T$$

Same as classical

Low temperature, β large

$$E = \hbar \omega e^{-\beta \hbar \omega}$$

Appendix A

If an adiabatic change is made then:

$$dE = \left. \frac{\partial E}{\partial V} \right|_T dV + \left. \frac{\partial E}{\partial T} \right|_V dT$$

$$\left. \frac{\partial S}{\partial V} \right|_T dV + \left. \frac{\partial S}{\partial T} \right|_V dT = dS = 0$$

$$dT = \frac{\frac{\partial S}{\partial V}|_T}{\frac{\partial S}{\partial T}|_V} dV$$

$$\frac{\partial E}{\partial V}\Big|_S = \frac{\partial E}{\partial V}\Big|_T - \frac{\partial E}{\partial T}\Big|_V \frac{\frac{\partial S}{\partial V}|_T}{\frac{\partial S}{\partial T}|_V}$$

$$\frac{\partial E}{\partial V}\Big|_S = \frac{\partial E}{\partial V}\Big|_T - \frac{\partial E}{\partial S}\Big|_V \frac{\partial S}{\partial V}\Big|_T$$