**Statistical Physics** Summer 2019

# Canonical distribution in statistical physics — 25.03, 2019

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## 1 Overview

In the last lecture we talked about **functions of state in thermodynamics** and started **canonical distribution**.

In this lecture we covered **canonical distribution in-depth**.

## 2 Canonical distribution

We want to describe systems of many particles. Those particles will be interacting with each other. Thermodynamics is the underlying scheme, but it works in macro scale. We want to go smaller. Atom-size small.

Let's have a small system (eg. piece of chalk) in contact with environment. This system can exchange energy with the environment. We assume temperature to be constant and $T_{env} = T_{sys}$. This system can be in various energy states $r = 1, 2, ...$ Those states can be discrete or continuous. Each state has energy $\epsilon_1, \epsilon_2, ...$

**Question** What is the probability $p_r$ that the system is in state $r_x$?

Given $p_r$, average energy of the system can be explained as

$$< \epsilon >= \sum_r \epsilon_r p_r \tag{1}$$

### 2.1 Isolated system

Let's assume an isolated environment with total energy E and N systems which can exchange energy. Some systems are in state 1, some in state 2, some in state 5, etc.
States: $r = 1, 2, ...$
Energy: $\epsilon_1, \epsilon_2, ...$
Number of systems in state r: $a_r$
Conditions: $\sum_r a_r = N *$ $\quad \sum_r \epsilon_r a_r = E **$
Number of realizations of partition $(a_1, a_2, ...)$

$$P(a_1, ...) = \frac{N!}{a_1! * a_2! * ...} \tag{2}$$

We require $max(P)$. This is called a method of maximal probability, which is equivalent to $max(lnP)$, accounting for conditions * and **.

## 2.2 Maths comment

For function $f(x, y) = x + y$ let's find max, on condition $x^2 + y^2 = 1$.

Behind Lagrange: $L(x, y) = x + y + \lambda(x^2 + y^2 - 1)^1$.
Now we calculate partial derivatives and see when they are equal to 0.
$\frac{\partial L}{\partial x} = 0 \implies 1 + 2\lambda x = 0 \implies x = -\frac{1}{2\lambda} \implies x = \pm\frac{\sqrt{2}}{2}$
$\frac{\partial L}{\partial y} = 0 \implies 1 + 2\lambda y = 0 \implies y = -\frac{1}{2\lambda} \implies y = \pm\frac{\sqrt{2}}{2}$
$\frac{\partial L}{\partial \lambda} = 0 \implies x^2 + y^2 = 1 \implies \frac{1}{4\lambda^2} + \frac{1}{4\lambda^2} = 1 \implies \lambda = \pm\frac{1}{\sqrt{2}}$

## 2.3 Back to canonical distribution

$L = lnP - \lambda \sum_r a_r - \mu \sum_r \epsilon_r a_r$
$lnP = lnN! - \sum_r ln(a_r!)$
Assume $a_r >> 1$
$lnP = lnN! - \sum_r a_r(lna_r - 1)$
$\frac{\partial lnP}{\partial a_l} = -\frac{\partial}{\partial a_l}(a_l(lna_l - 1)) = -(lna_l - 1 + a_l\frac{1}{a_l}) = -lna_l$
$\frac{\partial L}{\partial a_l} = -lna_l - \lambda - \mu\epsilon_l = 0$
$lna_l = -\lambda - \mu\epsilon_l$
$e^{lna_l} = e^{-\lambda} * e^{-\mu\epsilon_l}$
Then $a_l$:

$$a_l = e^{-\lambda} * e^{-\mu\epsilon} \tag{3}$$

Let us now remove $\lambda$ which is a parameter. $\sum_r a_r = N = \sum_r e^{-\lambda} * e^{-\mu\epsilon}$
Now, $N = e^{-\lambda} \sum_r e^{-\mu\epsilon} \implies e^{-\lambda} = \frac{N}{\sum e^{-\mu\epsilon}}$
Using previous equations: $a_l = \frac{N}{\sum_r e^{-\mu\epsilon_r}} e^{-\mu\epsilon_l}$; $\quad \frac{a_l}{N} = p_l$, so

$$p_r = \frac{e^{-\mu\epsilon_r}}{\sum_l e^{-\mu\epsilon_l}} \tag{4}$$

Parameter $\mu$ is

$$\mu = \frac{1}{k_B T} = \beta \tag{5}$$

Finally

$$p_r = \frac{e^{-\beta\epsilon_r}}{\sum_l e^{-\beta\epsilon_l}} \tag{6}$$

$$z = \sum_l e^{\beta\epsilon_l} \tag{7}$$

This is the partition function.
If energy states depend on continuous degrees of freedom $\epsilon(x, p)$ where $x = \{x_1, ..., x_N\}$, $p = \{p_1, ..., p_N\}$.

$$z = \frac{1}{N!h^{3N}} \int dx_1...dx_n dp_1...dp_n e^{-\beta\epsilon(\{x_i\},\{p_i\})} \tag{8}$$

[1]-1 being a constant. Can be omitted and will be omitted in second example

## 3 Relation to thermodynamics

Average internal energy is

$$U = \frac{E}{N} \tag{9}$$

where E is previously defined as total energy of a system and N is number of systems. Then, after substituting, $U = \frac{\sum_r \epsilon_r a_r}{\sum_r a_r} = \frac{\sum_r \epsilon_r e^{-\beta \epsilon_r}}{\sum_r e^{-\beta \epsilon_r}}$.

Then, after counting partial derivative of $lnZ$ in terms of $\beta$ we get

$$U = -\frac{\partial}{\partial \beta} lnZ \tag{10}$$