# IChO'21 - Statistical Thermodynamics (prep. problem 5)

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## 1   Introduction to Statistical Thermodynamics

From the usual thermodynamics we know such properties such as entropy, internal energy and pressure. However, a lot of these properties are only observed in larger systems, *e.g.* how do we define the melting point of a single molecule? Hence, we observe that we can divide thermodynamical properties roughly in two groups - firstly, properties in bulk materials, and secondly, molecular properties. Moreover, the bulk properties certainly must be connected to the properties of the individual molecules that form the bulk material. Therefore, we must have a way to link together these different properties together - which is what the broad field of statistical thermodynamics achieves.

Give an example of molecular property determining some bulk property:

**Bulk (macroscale) properties** - pressure, enthalpy, entropy, temperature, conductivity, melting and boiling point, ...

**Molecular (microscale) properties** - molecular energy levels, vibration frequencies, molecular mass, dipole, ...

## 2   Why *statistical*?

To explain why the field is called *statistical* thermodynamics let's start by considering an example. Let's consider and ideal isolated system with fixed internal energy (U), volume (V), and number of particles (N), where these parameters define all thermodynamical parameters of the bulk system. We call state with these fixed values as a ***macrostate***.

However, as stated earlier, the bulk parameters by itself does not contain any information of how atoms or molecules behave on microscopical level. From quantum mechanics (finer details are beyond the scope) we can state that each molecule has it's associated energy levels, and it is possible for molecules to be arranged in the energy levels in many different ways. Any specific arrangement of the particles in the energy levels is called ***microstate***.

Now we can dive in to the world of *statistics* and consider a miniature toy system. In this case we consider that we have a set of energy levels with energies 0, 1, 2, 3, ... in arbitrary units. Also, let's say we have 2 distinguishable particles (A and B), and the total energy of system is fixed at 2 energy units.
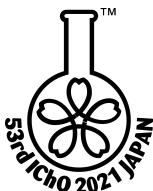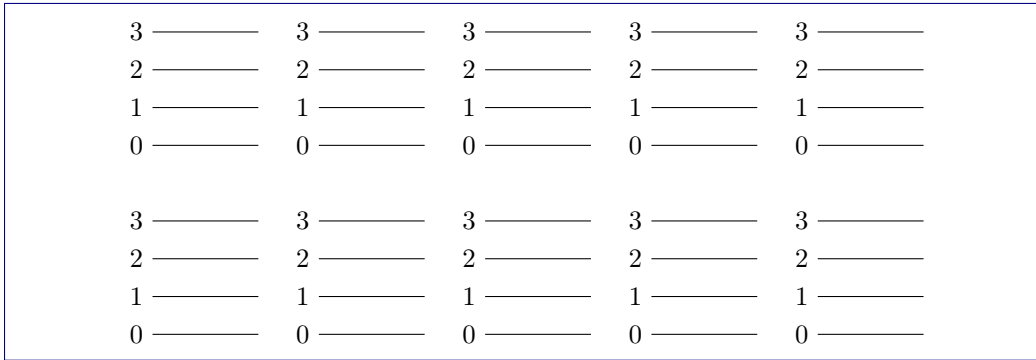Under such conditions we obtain following microstates:

**Macrostate** - bulk state with fixed properties.

**Microstate** - molecular or atomic arrangement in states.

*Fixing energy levels fixes volume, hence with given conditions we also define a macrostate, which has multiple microstates*

Now consider the case of 3 particles A, B and C with fixed energy of 3 units:

```
3 ——————    3 ——————    3 ——————    3 ——————    3 ——————
2 ——————    2 ——————    2 ——————    2 ——————    2 ——————
1 ——————    1 ——————    1 ——————    1 ——————    1 ——————
0 ——————    0 ——————    0 ——————    0 ——————    0 ——————


3 ——————    3 ——————    3 ——————    3 ——————    3 ——————
2 ——————    2 ——————    2 ——————    2 ——————    2 ——————
1 ——————    1 ——————    1 ——————    1 ——————    1 ——————
0 ——————    0 ——————    0 ——————    0 ——————    0 ——————
```

*Do not confuse these levels with molecular orbitals, we can fit more than two particles in each level!*

Consider a set of levels with energies 0, 1, 2, 3, 4, 5 and 6 units. Show that for 4 distinguishable particles with total energy of 6 units, the number of microstates $W$ is 84. What is the number of microstates if we double the spacing of energy levels (0, 2, 4...)?

*Drawing all the energy levels explicitly might not be the best idea now...*
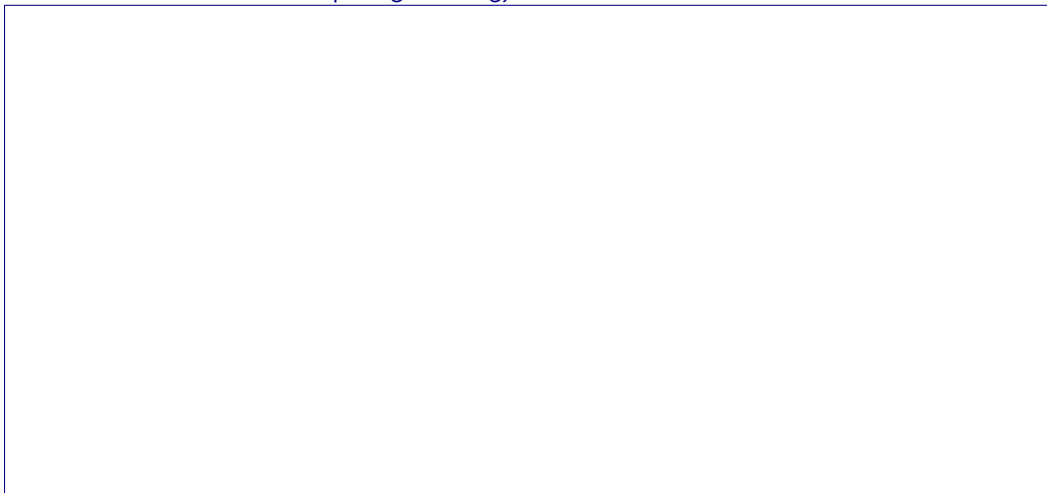
Drawing the levels and filling with particles seems fun and all, but now let's consider why we do that and what interesting results does that yield.

# 3    Postulates of Statistical Thermodynamics

1. Probability of observing specific microstate is $1/W$, where $W$ is the total number of microstates.

2. Entropy of isolated system is given by $S = k_\mathrm{B} \ln W$.

Now let's explain what the postulates imply in the case of the last exercise.

Let's consider an ideal gas. In such case the available energy levels are due to the translation of gas molecules. As a good approximation we can consider the particle energy levels with *particle in a box model*. Therefore, the we can write energy as $E_n = \frac{n^2 h^2}{8ma^2}$ with $n = 1, 2, 3, ...$, which yields us discrete energy levels as shown in previous diagrams. What this gives us is that increasing the box size, decreases the spacings of energy levels ($a$ increases, respective $E_n$ decreases). Hence if we now consider an ideal gas in a box, and now we increase the volume of the box, from thermodynamics we clearly expect the gas to expand and fill the whole box. This is an irreversible process. How can we rationalise this from statistical thermodynamics point of view?

Let's say before box expansion we have $W_i$ microstates available to the system, and after the expansion we have $W_f$ microstates. From previous exercise we saw that the number of microstates is related to the spacing of energy levels, in a way that the closer the spacings there are, the more microstates there are. Combining this with our knowledge, that increasing box size, we decrease the spacing between energy levels, we can state that $W_f > W_i$. Since the first postulate states, that each microstate is equally probable, the system will spend more time in final system's microstates (that is, it is conceivable that the ideal gas will at some point will come back to inital state, but it is very unlikely). In general this means that systems evolve into state with maximum number of accessible microstates, and hence the existence of irreversible processes are explicable using first postulate of statistical thermodynamics.
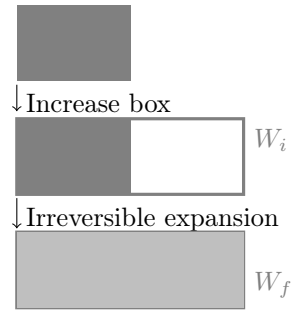
Now using second postulate we can introduce numerical values to aid the understanding. Again consider a system that has $W_i$ inital microstates and $W_f$ microstates after the process. From first postulate we can note that the probability of finding system in initial state $P_i$ is proportional to $W_i$, and similarly, $P_f \propto W_f$. From second postulate we can express $W_i$ and $W_f$ in terms of entropy, t.i. $W_i = \exp(S_i/k_{\mathrm{B}})$ and $W_f = \exp(S_f/k_{\mathrm{B}})$. And so we can now calculate the probability of finding system in initial state, as opposed to final state:

$$\frac{P_i}{P_f} = \frac{W_i}{W_f} = \frac{\exp(S_i/k_{\mathrm{B}})}{\exp(S_f/k_{\mathrm{B}})} = \exp(-\Delta S/k_{\mathrm{B}})$$

Mole of ideal gas was expanded to twice of the initial volume, calculate the probability of finding the system in initial states

↓Increase box

$W_i$

↓Irreversible expansion

$W_f$

*Entropy change due ideal gas expansion is given by* $nR\ln\left(V_f/V_i\right)$

# 4 Preparatory problem 5

Now having established postulates of statistical thermodynamics and arising results, we can move on to discuss preparatory problem.

As previously we consider a system such that both energy and particles are conserved, and the temperature is fixed. We assume that particles behaves like ideal gas. Now, however, instead of considering energy levels, we can consider distribution of molecules in a box with diving wall. In this case let's call numer of microstates $W$ with $n$ molecules in first chamber and $m$ molecules in second chamber as $W(n, m)$.
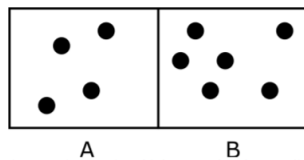
Figure 1: Example of $W(4, 6)$.

We can calculate the number of microstates in given arrangement using combinatorics, more specifically $W(n, m) = {}_{n+m}C_n = \dfrac{(n+m)!}{n!m!}$ (note that formula is symmetric with respect to $n$ and $m$)

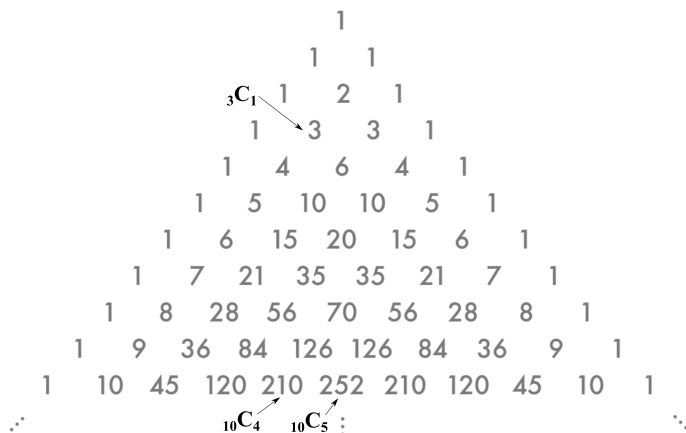*Aside* - binomial distribution and factorial approximations



Figure 2: Pascal triangle up to $N = 10$.

In general the factorials grow quite rapidly, as such if we deal with systems that have more than few molecules, it is wise to use approximations, that might reduce work with larger numbers. In this case we can approximate factorials with $n! \approx \sqrt{2\pi n}\left(\dfrac{n}{e}\right)^n$. However, whenever we use approximations, care must be taken to see whether it is appropriate to use it. From Figure 3 we observe, that the error using approximation at small values ($n < 10$) is rather large, so the approximation should not be used.

| n | n! | approx. | error / % | ln(n!) | ln(approx.) | log err. / % |
|---|---|---|---|---|---|---|
| 1 | 1 | 0.922 | 7.79 | 0 | -0.0812 | |
| 2 | 2 | 1.919 | 4.05 | 0.6931 | 0.6518 | 5.96 |
| 3 | 6 | 5.836 | 2.73 | 1.7918 | 1.7640 | 1.55 |
| 4 | 24 | 23.506 | 2.06 | 3.1781 | 3.1573 | 0.65 |
| 5 | 120 | 118.019 | 1.65 | 4.7875 | 4.7708 | 0.35 |
| 6 | 720 | 710.078 | 1.38 | 6.5793 | 6.5654 | 0.21 |
| 7 | 5040 | 4980.396 | 1.18 | 8.5252 | 8.5133 | 0.14 |
| 8 | 40320 | 39902.395 | 1.04 | 10.6046 | 10.5942 | 0.10 |
| 9 | 362880 | 359536.87 | 0.92 | 12.8018 | 12.7926 | 0.07 |
| 10 | 3628800 | 3598695.6 | 0.83 | 15.1044 | 15.0961 | 0.06 |
| ... | ... | ... | ... | ... | ... | ... |
| 98 | 9.43E+153 | 9.42E+153 | 0.09 | 354.5391 | 354.5382 | 0.00 |
| 99 | 9.33E+155 | 9.32E+155 | 0.08 | 359.1342 | 359.1334 | 0.00 |
| 100 | 9.33E+157 | 9.32E+157 | 0.08 | 363.7394 | 363.7385 | 0.00 |

Figure 3: Comparison between factorial and approximated factorial.

Calculate $W(40, 60)$ and $W(50, 50)$ to two significant digits.

*Make sure to write down general form to calculate $W(n, m)$ with approximation, it will be useful for later.*

*Check that $W(40, 60) < W(50, 50)$, which should be expected from previous discussion.*

*Statistical Thermodynamics*
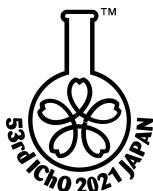
Now consider that the dividing boundary is removed, meaning that molecules are free to move in all box. From the first statistical thermodynamics postulate we expect that the time system spends in microstate is proportional to $W(n, m)$.

Calculate arrangement $(n^*, N - n^*)$ with highest probability of occurrence for $N = 10, 100$ and the corresponding probabilities to observe such state.

Calculate the probability of observing a state in which $n^*$ is in the range $n^* - 0.02N \leq n^* \leq n^* + 0.02N$ for $N = 10, 100$.
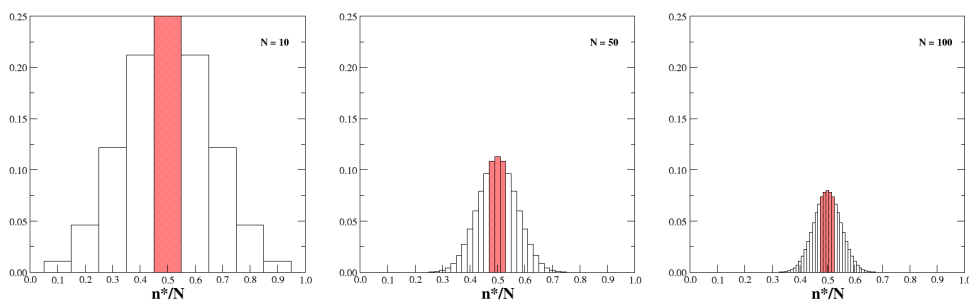


Figure 4: Probability distribution for $N = 10, 50, 100$.
Shaded area is the range $n^* - 0.02N \leq n^* \leq n^* + 0.02N$.

Note the more narrow distribution as $N$ increases.

*Statistical Thermodynamics*

Next, let's revisit the entropy of gas expansion. However, now we will assume that microstates are formed by molecules filling small subsections $\Delta V$. In this case given available volume $V_1$ the total number of microstates is given by $W_A = V_1/\Delta V$. Similarly we can write number of microstates for different volume as $W_{AB} = V_2/\Delta V$. Thus:

$$\frac{W_{AB}}{W_A} = \frac{V_2}{V_1}$$

Now let's consider chamber A filled with $n$ moles of gas molecules, while chamber B is empty (state 1). Afterwards, we remove the dividing boundary and let gas A expand spontaneously throughout the entire container (state 2) at a constant temperature.

Express the change in entropy $\Delta S = S_2 - S_1$ in terms of the gas constants R, $V_1$ and $V_2$.
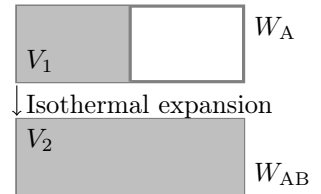
Calculate the difference in entropy for an isothermal expansion of the two-chamber system described above when the chamber A is initially filled with oxygen molecules (0.30 mol). Use $V_1 = 0.10$ m$^3$ and $V_2 = 0.40$ m$^3$.

Now instead we can consider mixing of two different gases in the same volume as shown in margin.

Calculate the difference in entropy associated with the mixing process.
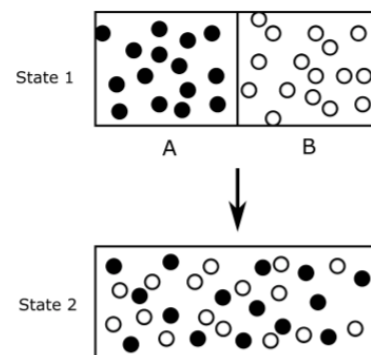
State 1

A        B
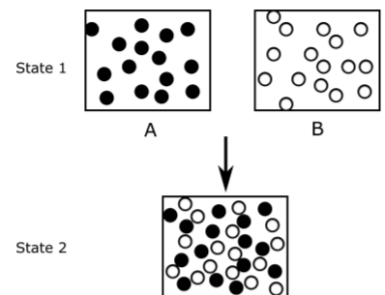
State 2

*Does the answer make sense? Consider the count of microstates before and after.*
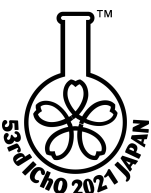
Next we can consider mixing of two kinds of gas molecules, $\alpha$ ($n_\alpha$ moles) and $\beta$ ($n_\beta$ moles), which are separately filled into chambers A (volume $V_A$ and B (volume $V_B$, respectively, at a temperature $T$ and a pressure $P$ (State 1). Let State 2 reperesent the complete mixture of the gas molecules after removing the boundary wall. See margin for ilustration.

Express the entropy change $\Delta S = S_2 - S_1$ from State 1 to State 2 in terms of $R$, $n_\alpha$ and $n_\beta$.



State 1

A       B

State 2

Instead consider a case where instead of gas $\beta$ chamber B is filled with gas $\alpha$ ($n_\beta$ moles) (State 1), before the boundary wall is removed (State 2). Calculate the entropy difference from State 1 and State 2.

Next, additionally to only considering ideal gases, we can move on to discuss entropy arising from molecular orientation in a crystal. The most prominent example of this is *residual entropy*, which can be observed in multiple crystals.

According to the third law of thermodynamics, the entropy of a pure and perfect crystal approaches zero as the absolute temperature approaches zero. However, in a real molecular crystal, the molecules may not be completely aligned at low temperatures. Thus, even when the absolute temperature approaches zero, the crystal can retain nonzero entropy value. This is called *residual entropy*, and can be detected as a difference in experimentally measured entropy calculations and statistical thermodynamics predictions.

For example, because carbon monoxide (CO) is a heterogeneous diatomic molecule, CO molecules have a definite orientation in the CO crystal. Picture in margin illustrates disordered and completely ordered CO crystal. Because CO molecules can exhibit two different orientations in the crystal, the residual entropy per mole if the molecular orientations are completly random in the crystal would be: $S = k_B \ln 2^{N_A} = R \ln 2 = 5.7 \text{ J K}^{-1}\,\text{mol}^{-1}$
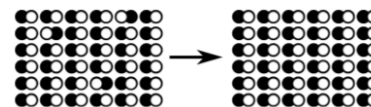


In OCS molecule residual entropy is observed to be 0, explain why that might be the case.

Every methane ($CH_4$) molecule in crystal is surrounded by four methane molecules in a tetragonal fashion. Calculate the molar residual entropy of isotopically labelled methane, $H_3CD$, when the molecules are completely randomly oriented.

More sophisticated case is when considering residual entropy of ice. Arrangement of water molecules in an ice crystal is shown in a margin. In this case we have to consider the so-called 'ice-rules':
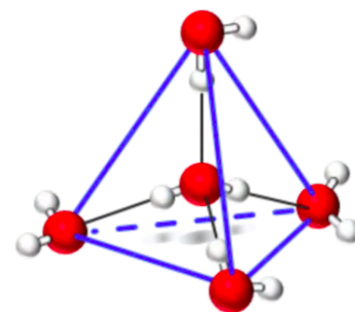
1. Each hydrogen atom must be located between two adjacent oxygen atoms.

2. Two of the four hydrogen atoms that surround each oxygen atom must be positioned closer to that oxygen than to the neighbouring oxygen atoms, while the other two hydrogens should be located closer to one of the neighbouring oxygen atoms.



Now let us estimate the molar residual entropy of ice using the following procedure.
There are two stable sites for a hydrogen atom between two adjacent oxygen atoms. Calculate the number of possible configurations of hydrogen atoms in a crystal composed of 1 mole of water ($N_A$ molecules) without any constraints of the ice rules

Calculate the number of possible configurations for four hydrogen atoms around the central oxygen atom in margin picture

Some of the configurations calculated in previous point such as $H_3O^+$, in which three protons are arranged closest to one oxygen atom, violate ice rules. List all chemical species that break the ice rules and calculate the number of configurations for each species. Then, calculate the number of configurations that satisfy the ice rules.

Based on these considerations, calculate the molar residual entropy when the orientations of water molecules is completely random in ice.

It is also possible to consider (albeit useless in practical cases) residual entropy in cases of same element's different isotopes. Let's consider chlorine gas ($Cl_2$) and assume that it consists of $^{37}Cl$ (25%) and $^{35}Cl$ (75%). What are the different isotope species in the chlorine gas and at what abundancies?

Let's now consider a crystal made out of 16 $Cl_2$ molecules. Consider how many ways there are in arranging each isotopic species in this crystal. Now consider a mole of $Cl_2$ gas, and calculate how many microstates there are in random crystal. What is the expected residual entropy?

*Statistical Thermodynamics*