

The Statistical Interpretation of Entropy

Physical meaning of entropy

Microstates and macrostates

Statistical interpretation of entropy and Boltzmann equation

Configurational entropy and thermal entropy

Calculation of the equilibrium vacancy concentration

Reading: Chapter 4 of Gaskell

Optional reading: Chapter 1.5.8 of Porter and Easterling

“Any method involving the notion of entropy, the very existence of which depends on the second law of thermodynamics, will doubtless seem to many far-fetched, and may repel beginners as obscure and difficult of comprehension.”

Willard Gibbs

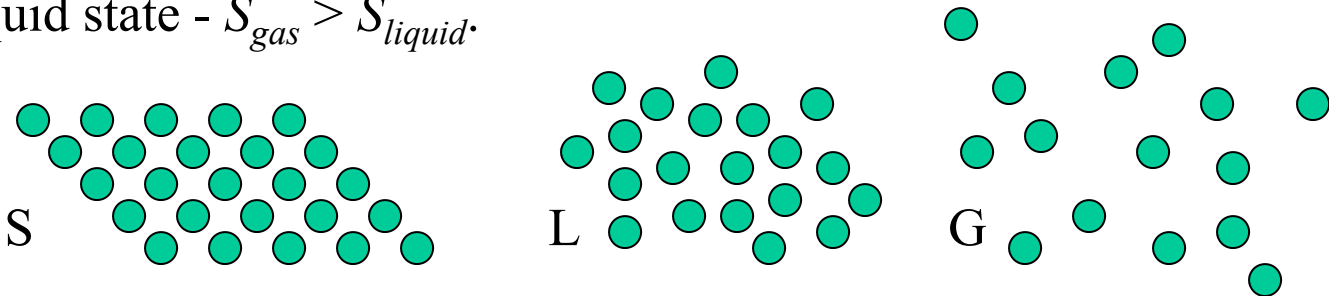
What is the physical meaning of entropy?

Entropy is introduced in phenomenological thermodynamics based on the analysis of possible and impossible processes. We know that heat flows from a hot region to a cold region of a system and that work can be irreversibly transferred into heat. To describe the observations, the entropy, and the 2nd law stating that entropy is increasing in an isolated system, have been introduced. The problem with phenomenological thermodynamics is that it only tells us **how** to describe the empirical observations, but does not tell us **why** the 2nd law works and what is the physical interpretation of entropy.

In statistical thermodynamics entropy is defined as a **measure of randomness or disorder**.

Intuitive consideration:

In a crystal atoms are vibrating about their regularly arranged lattice sites, in a liquid atomic arrangement is more random – $S_{liquid} > S_{solid}$. Atomic disorder in gaseous state is greater than in a liquid state - $S_{gas} > S_{liquid}$.



Does this agree with phenomenological thermodynamics?

Melting at constant pressure requires absorption of the latent heat of melting, $q = \Delta H_m$, therefore $\Delta S_m = \Delta H_m / T_m$

- **the increase in the entropy upon melting correlates with the increase in disorder.**

How to quantify “disorder”? Microstates and Macrostates

A **macroscopic state** of a system can be described in terms of a few macroscopic parameters, e.g. P , T , V . The system can be also described in terms of **microstates**, e.g. for a system of N particles we can specify coordinates and velocities of all atoms.

The 2nd law can be stated as follows: **The equilibrium state of an isolated system is the one in which the number of possible microscopic states is the largest.**

Example for making it intuitive (rolling dice)



Macrostate – the average of the dice.

Each die have 6 microstates, the system of 2 dices has $6 \times 6 = 36$ microstates, a system of N dice has 6^N microstates.

For two dice there are 6 ways/microstates to get macrostate $7/2 = 3.5$, but only one microstate that correspond to $2/2 = 1$ or $12/2 = 6$. The most likely macrostate is 3.5. For a big number N of dice, the macrostate for which the number of possible microstates is a maximum is also 3.5 and the larger is N , the higher is the probability to get very close to 3.5.

If you shake a large bag of dice and roll them it is likely that you get the total close to $3.5 \times N$ for which the number of ways to make it from individual dice is maximum.

An isolated thermodynamic system is similar – **thermal fluctuations** do the shaking, the macrostate corresponds to **the largest number of microstates**. Actually, the system of dice is closer to a quantum system with discrete states. In the classical case the states form a continuum and we have to replace the sum over states by integrals over phase space.

Statistical interpretation of entropy

If we combine two systems, the number of microstates multiply (remember $6 \times 6 = 36$ for two dice). At the same time we know that entropy is an extensive quantity, $S_{A+B} = S_A + S_B$, and if we want to relate entropy to the number of microstates, we have to make sure that this equation is satisfied.

If we take logarithm of the number of microstates, the logarithms adds when we put systems together. The quantity maximized by the second law can be defined then by equation written on Ludwig Boltzmann's tombstone in Vienna:



$$S = k_B \ln \Omega$$

where Ω is the number of microstates, k_B is the Boltzmann constant (it is the same constant that relates kinetic energy to temperature, but it was first introduced in this equation), and S is the entropy.

The 2nd law can be restated again: **An isolated system tends toward an equilibrium macrostate with maximum entropy, because then the number of microstates is the largest and this state is statistically most probable.**

The entropy is related to the number of ways the microstate can rearrange itself without affecting the macrostate.

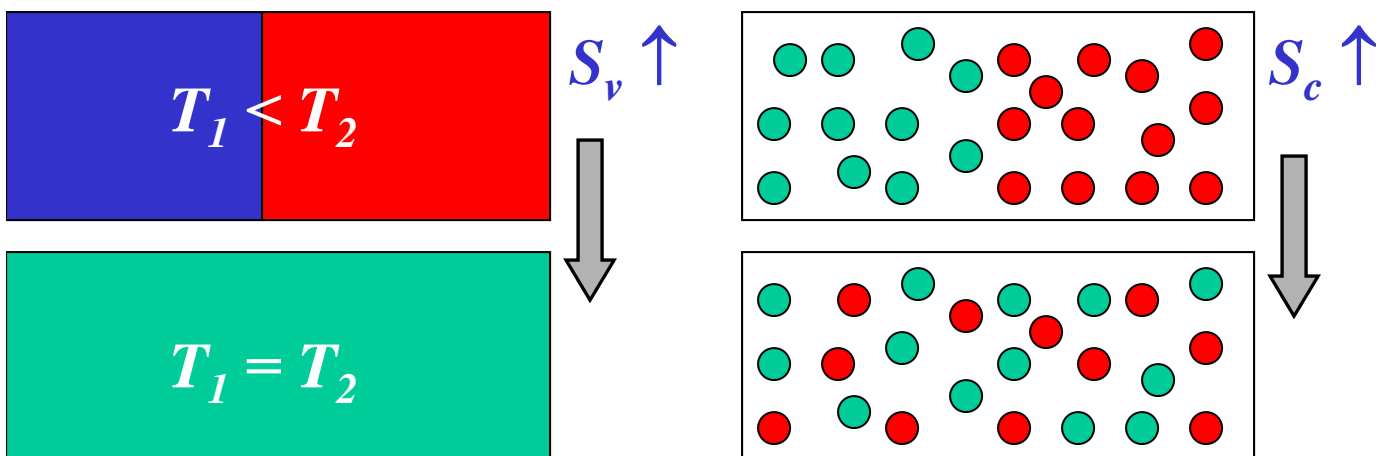
Configurational entropy and vibrational entropy

Vibrational (or thermal) entropy S_v : Entropy associated with atomic vibrations (the number of microstates Ω can be thought as the number of ways in which the thermal energy can be divided between the atoms).

The vibrational entropy of a material increases as the temperature increases and decreases as the cohesive energy increases.

The vibrational entropy plays important role in many polymorphic transitions. With increasing T , the polymorphic transition is from a phase with lower S_v to the one higher S_v .

Configurational entropy S_c : Entropy can be also considered in terms of the number of ways in which atoms themselves can be distributed in space. Mixing of elements in two crystals placed in physical contact or gases in two containers (mass transport) leads to the increase of S_c and is similar to the heat transfer case when S_v is increasing.



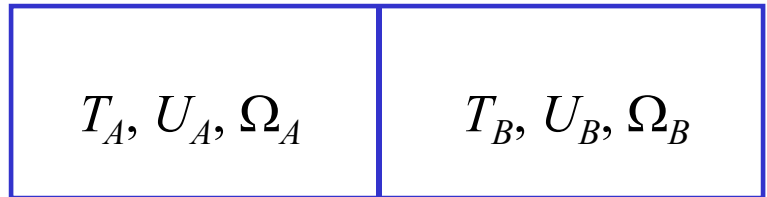
Heat flow and production of entropy

Phenomenological thermodynamics: transfer of energy from hot to cold is an irreversible process that leads to the production of entropy.

Consideration of probabilities of microstates can lead to the same conclusion.

$$U_{tot} = U_A + U_B$$

$$\Omega_{tot} = \Omega_A(U_A)\Omega_B(U_B)$$



When the thermal contact is made between the two systems, the number of microstates, $\Omega_{tot} = \Omega_A\Omega_B$ is not in the maximum and heat starts to flow, increasing the value of Ω_{tot} . The heat flows until the increase in Ω_A caused by the increase in U_A is greater than the decrease in Ω_B caused by the decrease in U_B . The heat flow stops when Ω_{tot} reaches its maximum value, *i.e.* $\delta \ln \Omega_A \Omega_B = 0$

If we only have a heat exchange (no work) $\delta q = \delta q_A = -\delta q_B$

$$\left. \begin{aligned} dS &= \frac{\delta q}{T} \\ S &= k_B \ln \Omega \end{aligned} \right\} \begin{aligned} d \ln \Omega_A &= \frac{\delta q_A}{k_B T_A} & d \ln \Omega_B &= \frac{\delta q_B}{k_B T_B} = -\frac{\delta q_A}{k_B T_B} \end{aligned}$$

$$d \ln \Omega_A \Omega_B = d \ln \Omega_A + d \ln \Omega_B = \frac{\delta q}{k_B} \left(\frac{1}{T_A} - \frac{1}{T_B} \right)$$

$\delta \ln \Omega_A \Omega_B = 0$ only when $T_A = T_B$ – reversible heat transfer is only possible after temperatures are equal

Configurational entropy - equilibrium vacancy concentration

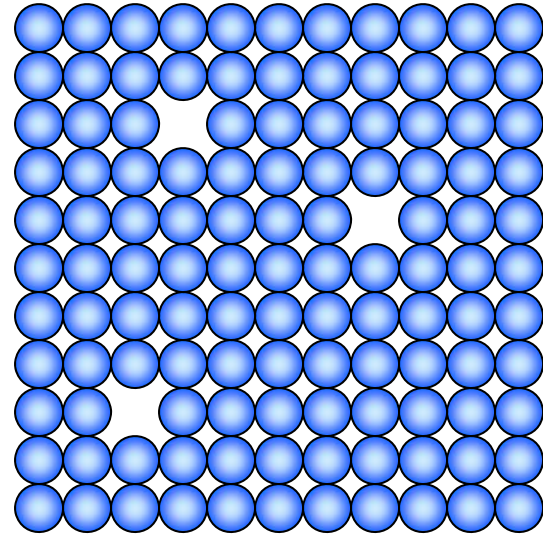
The configurational entropy of a crystal refers to the distinguishable ways the atoms can be arranged on the lattice sites. For monoatomic crystals the only origin of configurational entropy is the presence of crystal defects such as vacancies – lattice sites without atoms.

Removal of an atom from its lattice site

- breaks bonds and increases the internal energy U by ε_v^f .
- Increases the randomness of the atomic configuration, and, thus, S_c .

Let's first calculate ΔS_c for n vacancies:

$$\Delta S_c^n = S_c^n - S_c^0 \quad S_c^n = k_B \ln(\Omega_n)$$



Consider a crystal lattice with N lattice sites and assume that N is large enough so that we can neglect the surface in our consideration and assume that all lattice sites are equivalent.

If there are no vacancies, there is only one configuration:

$$n = 0: S_c^0 = k_B \ln(1) = 0$$

If there is one vacancy, it can be located on any of the N sites – N different configurations are possible:

$$n = 1: S_c^1 = k_B \ln(N)$$

If there are two vacancies, for each location of the first vacancy we have $N-1$ locations of the second one:

$$n = 2: S_c^2 = k_B \ln[1/2 N(N-1)] \gg S_c^1$$

$1/2$ comes from the fact that vacancies are identical \rightarrow states where one vacancy is at site i and the second one at j , are identical to the state (j, i)

Equilibrium vacancy concentration (2)

$$n = 0: S_c^0 = k_B \ln(1) = 0$$

$$n = 1: S_c^1 = k_B \ln(N)$$

$$n = 2: S_c^2 = k_B \ln[1/2 N(N-1)] \gg S_c^1$$

$$n = 3: S_c^2 = k_B \ln[1/6 N(N-1)(N-2)] \gg S_c^2$$

... in general, the number of distinct configurations for n vacancies is

$$\frac{1}{n!} N(N-1)(N-2)\dots(N-n+1) = \frac{N!}{n!(N-n)!}$$

$$\Delta S_c^n = S_c^n = k_B \ln \frac{N!}{n!(N-n)!}$$

The equilibrium concentration of vacancies is the one that corresponds to the minimum of free energy: $A = U - TS$

Neglecting a small change in the vibrational entropy due to the change in the vibrational frequencies of atoms around a vacancy (formation entropy), and ignoring the vacancy-vacancy interactions, we can write:

$$\Delta U^n = n\varepsilon_v^f \quad \Delta A^n = \Delta U^n - T\Delta S_c^n = n\varepsilon_v^f - k_B T \ln \frac{N!}{n!(N-n)!}$$

If N is large enough, introduction of the first vacancy will reduce the free energy for any finite T : $\Delta A^1 = \varepsilon_v^f - k_B T \ln N < 0$

To find the equilibrium vacancy concentration: $\left. \frac{\partial \Delta A^n}{\partial n} \right|_{n=n_{eq}} = 0$

Equilibrium vacancy concentration (3)

Let's first consider $\frac{\partial S_c^n}{\partial n}$ using Stirling formula for big numbers:
 $\ln N! \approx N \ln N - N$

$$\frac{\partial S_c^n}{\partial n} = k_B \frac{\partial}{\partial n} \left\{ \ln \frac{N!}{n!(N-n)!} \right\} = k_B \frac{\partial}{\partial n} \{ \ln N! - \ln n! - \ln(N-n)! \} \approx$$

$$k_B \frac{\partial}{\partial n} \{ N \ln N - N - n \ln n + n - (N-n) \ln(N-n) + (N-n) \} =$$

$$k_B \frac{\partial}{\partial n} \{ N \ln N - n \ln n - (N-n) \ln(N-n) \} =$$

$$k_B \left\{ -\ln n - 1 + \ln(N-n) - \frac{(N-n)}{(N-n)}(-1) \right\} = k_B \ln \left(\frac{N-n}{n} \right) =$$

$$k_B \ln \left(\frac{N}{n} - 1 \right) \approx k_B \ln \left(\frac{N}{n} \right) = -k_B \ln \left(\frac{n}{N} \right)$$

For the equilibrium concentration of vacancies:

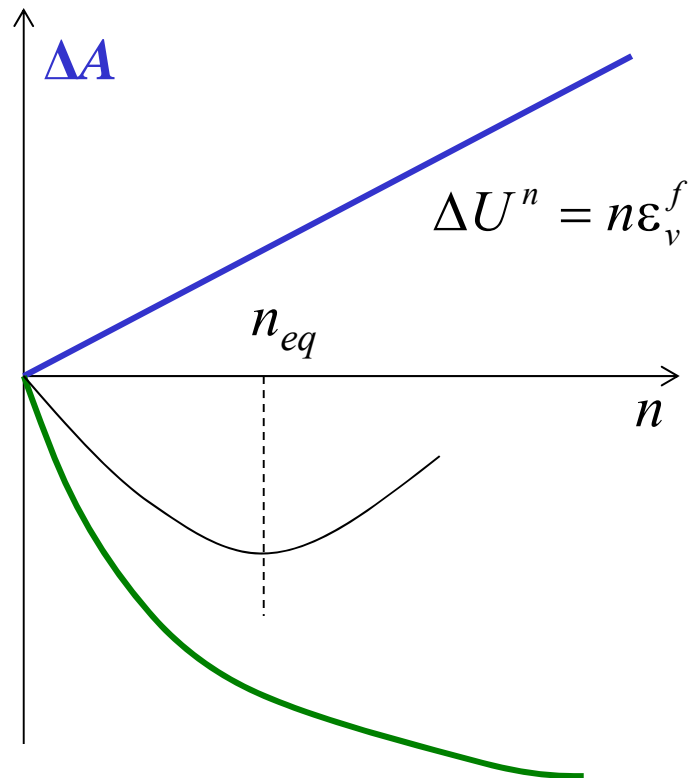
$$\left. \frac{\partial \Delta A^n}{\partial n} \right|_{n=n_{eq}} = \left. \frac{\partial}{\partial n} \{ n \varepsilon_v^f - T S_c^n \} \right|_{n=n_{eq}} = \varepsilon_v^f + k_B T \ln \left(\frac{n_{eq}}{N} \right) = 0$$

$$n_{eq} = N \exp \left(- \frac{\varepsilon_v^f}{k_B T} \right)$$

Equilibrium vacancy concentration (4)

$$\frac{n_{eq}}{N} = \exp\left(-\frac{\varepsilon_v^f}{k_B T}\right)$$

The equilibrium vacancy concentration is defined by the balance between the internal (potential) energy of vacancy formation and the increase of the configurational entropy.



$$\left. \frac{\partial(-T\Delta S_c^n)}{\partial n} \right|_{\frac{n}{N} \rightarrow 0} \approx k_B T \ln\left(\frac{n}{N}\right) \Big|_{\frac{n}{N} \rightarrow 0} \rightarrow -\infty \quad -T\Delta S_c^n = -k_B T \ln(\Omega_n)$$

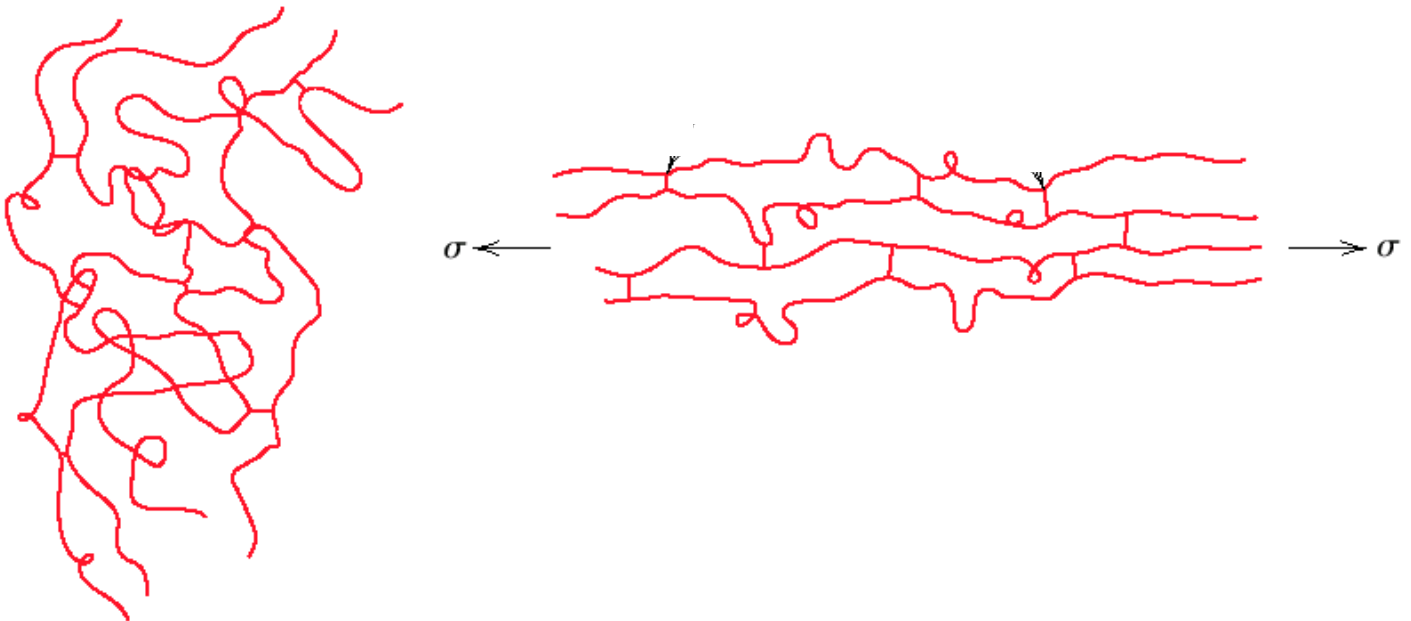
steep dependence of the entropy term at small n/N
 \rightarrow *defect-free crystals do not exist (nanoparticles?)*

For metals, $\varepsilon_v^f \approx 9k_B T_m$. We can estimate that at room temperature in copper there is one vacancy per 10^{15} lattice atoms, whereas just below the melting point there is one vacancy for every 10,000 atoms – very strong temperature dependence.

The formation **energy** ε_v^f in crystals, that we used in the derivation, is practically indistinguishable from the formation **enthalpy** H_v^f which has to be used if the pressure and not the volume is kept constant.

Demonstration of the effect of configurational entropy

Rapid stretching or unstretching of a wide rubber band is nearly isentropic/adiabatic process (there is almost no transfer of heat to or from the rubber band during this fast processes). The stretching decreases the configurational entropy S_{conf} (molecular structure becomes more ordered).



Since the stretching is isentropic, then the thermal/vibrational entropy S_v must increase to compensate for the decrease of S_{conf} . Since S_v is a function of T only, therefore the T should increase as a result of the stretching. Similarly, T should decrease as a result of rapid unstretching. You can carry out this experiment and measure the T by your lip.

Summary (I)

What is entropy?

Entropy is the measure of the "**probability**" of a given macrostate, or, essentially the same thing, the number of **microstates** possible for the given **macrostate**.

What is a microstate and a macrostate?

Any particular arrangement of atoms where we look only on average quantities is a **macrostate**. Any individual arrangement defining the properties (e.g. positions and velocities) of all the atoms for a given macrostate is a **microstate**. For a microstate it matters what individual particles do, for the macrostate it does not.

What is the probability of a macrostate?

The probability for a macrostate = the number of possible ways/microstates to generate the same macrostate divided by the number of all microstates (all possible combinations of the dice, which is a constant). Remember examples on playing dice and on equilibrium concentration of vacancies.

Example with vacancies: we just have to find how many ways (# of microstates) are there to arrange n vacancies (macrostate!) in a crystal of N lattice sites. After we find the probability, we can use the Boltzmann equation to calculate the entropy and we can use the equilibrium condition to select the most likely macrostate - the number of vacancies in equilibrium.

Summary (II)

Just knowing the internal energy U of a system with a constant volume and temperature is not enough to determine what the equilibrium configuration is. There could be many macrostates with the same U .

That's why just minimizing U (or H) is not good enough, we have to minimize $A = U - TS$ or $G = H - TS$ to find the equilibrium configuration of the system.

Of all the macrostates possible for a given U (or H), the one with the largest entropy at the given temperature will be the one that the system will adopt.

Equilibrium is a state in which the best possible balance between a small energy and a large entropy is achieved.

High entropies often mean high energies and vice versa - both quantities are opposed to each other. The entropy part in A or G becomes more important at high temperatures.

The entropy of a certain macrostate can be calculated by the statistical definition of the entropy S , using the Boltzmann entropy equation:

$$S = k_B \ln \Omega$$

Summary (III)

Irreversible transition takes a system from a less probable state to a more probable state. The transition in the opposite direction (decrease of the entropy of the “universe”) is considered by the statistical thermodynamics as **an improbable process**, whereas the classical thermodynamics just postulates that such transition **is impossible**.