Statistical Thermodynamics

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This is work in progress. The script will be updated on a weekly basis. If you find an error, send me an email: bettina.keller@fu-berlin.de

1 Introduction

1.1 What is statistical thermodynamics?

In your curriculum you have learnt so far

- how macroscopic systems behave when the external conditions (pressure, temperature, concentrationd) are altered ⇒ classical thermodynamics
- how to calculate the properties of individual microscopic particles, such as a single atom or a single molecule ⇒ Atombau und Chemische Bindung, Theoretische Chemie

You also know that macroscopic systems are an assembly of microscopic particles. Hence, it stands to reason that the behaviour of macroscopic systems is determined by the properties of the microscopic particles it consists of. **Statistical thermodynamics** provides a quantitative link between the properties of the microscopic particles and the behaviour of the bulk material.

Classical thermodynamics is a heuristic theory. It allows for quantitative prediction but does not explain why the systems behave the way they do. For example:

- Ideal gas law: $PV = nRT$. Found experimentally by investigating the behaviour of gas when the pressure, the volume and the temperature is changed.
- Phase diagrams. The state of matter of a substance is recorded at different temperatures and pressures.

It relies on quantities such as C_v, ΔH, ΔS, ΔG ... which must be measured experimentally. Statistical thermodynamics aims at predicting these parameters from the properties of the microscopic particles.

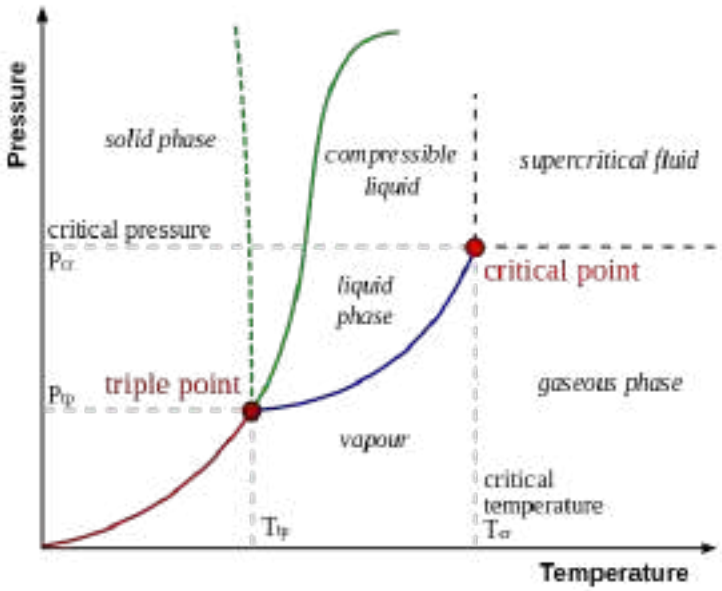


Figure 1: Typical phase diagram. Source: https://en.wikipedia.org/wiki/Phase_diagram

1.2 Classical thermodynamics is sufficient for most practical matters. Why bother studying statistical thermodynamics?

Statistical thermodynamics provides a deeper understanding for otherwise somewhat opaque concepts such as

- thermodynamic equilibrium
- free energy
- entropy
- the laws of thermodynamics

and the role temperature play in all of these. Also, you will understand how measurements of macroscopic matter can reveal information on the properties of the microscopic constituents. For example, the energy of a molecule consists of its

- translational energy
- rotational energy
- vibrational energy
- electronic energy.

In any experiment you will find mixture of molecules in different translational, rotational, vibrational, and electronic states. Thus, to interpret an experimental spectrum, we need to know the distribution of the molecules across these different energy states. Moreover, the thermodynamic quantities of a complex molecule can only be derived from experimental data (ΔH, ΔS) by applying statistical thermodynamics.

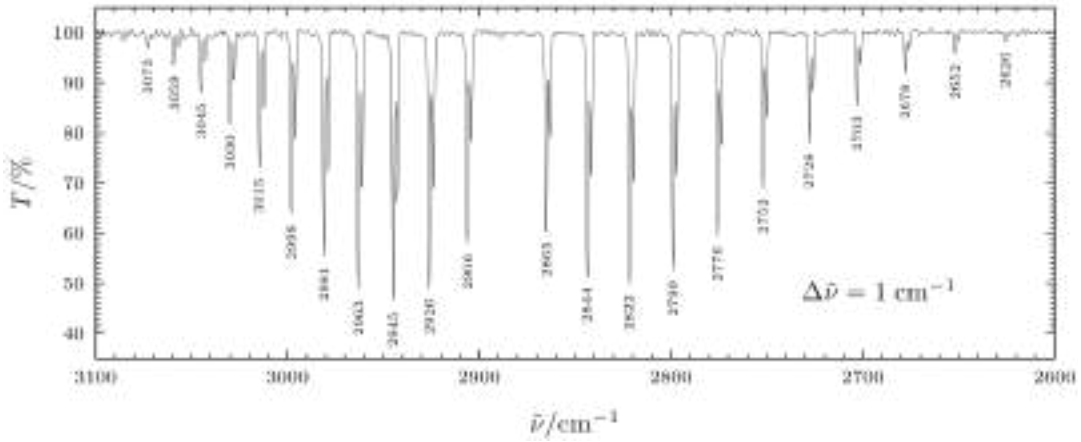


Figure 2: Infrared rotational-vibration spectrum of hydrochloric acid gas at room temperature. The dubletts in the IR absorption intensities are caused by the isotopes present in the sample: 1H-35Cl 1H-37Cl

1.3 Why is it a statistical theory?

Suppose you wanted to calculate the behaviour of 1 cm^3 of a gas. You would need to know the exact position of 10^9 particles and would have to calculate form these the desired properties. This is impractical. Hence one uses statistics and works with distributions of position and momenta. Because there are so many particles in the system, statistic quantities such as expectation values have very little variance. Thus, for a large number of particles statistical thermodynamics is an extremely precise theory.

Note: The explicit caclulation can be done using molecular dynamics simulations, albeit with typical box sizes of $5 \times 5 \times 5$ nm^3.

1.4 Classification of statistical thermodynamics

1. Equilibrium thermodynamics of non-interacting particles
   - Simple equations for which relate microscopic properties ot thermodynamic quantities
   - Examples: ideal gas, ideal crystal, black body radiation
2. Equilibrium thermodynamics of interacting particles
   - intermolecular interaction dominate the behaviour of the system
   - complex equation $\Rightarrow$ solved using approximations or simulations
   - expamples: real gases, liquids, polymers
3. Non-equilibrium thermodynamics
   - descibes the shift from one equilibrium state to another
   - involves the calculation of time-correlation functions
   - is not covered in this lecture
   - is an active field of research.

1.5 Quantum states

The quantum state (eigenstate) $\psi_s(\mathbf{x_k})$ of a single particle (atom or molecule) k is given by the time-independent Schrödinger equation

$$\epsilon_s \psi_s(\mathbf{x_k}) \quad = \quad \hat{h}_k \, \psi_s(\mathbf{x_k}) = -\frac{\hbar^2}{2m_k} \nabla_k^2 \, \psi_s(\mathbf{x_k}) + V_k(\mathbf{x}_k) \, \psi_s(\mathbf{x_k}) \tag{1.1}$$

where ϵ_s is the associated energy eigenvalue. If a system consists of N such particles which do not interact with each other, the time-independent Schrödinger equation of the system is given as

$$E_j \, \Psi_j(\mathbf{x}_1, \ldots \mathbf{x}_N) \quad = \quad \hat{H} \, \Psi_j(\mathbf{x}_1, \ldots \mathbf{x}_N) = \sum_{k=1}^{N} \hat{h}_k \, \Psi_j(\mathbf{x}_1, \ldots \mathbf{x}_N) \tag{1.2}$$

The possible quantum state of the system are [1]

$$\Psi_j(\mathbf{x}_1, \ldots \mathbf{x}_N) \quad = \quad \psi_{s(1)}(\mathbf{x}_1) \otimes \psi_{s(2)}(\mathbf{x}_2) \cdots \otimes \psi_{s(N)}(\mathbf{x}_N) \tag{1.3}$$

where each state j corresponds to a specific placement of the individual particles on the energy levels of the single-particle system, i.e. to a specific permutation

$$j \quad \leftrightarrow \quad \{s(1), s(2) \ldots s(N)\}_j \tag{1.4}$$

The associated energy level of the system is

$$E_j \quad = \quad \sum_{k=1}^{N} \epsilon_{s(k)} \tag{1.5}$$

[1] The wave function needs to be anti-symmetrized if the particles are fermions.

2 Microstates, macrostates, ensembles

2.1 Definitions

- A **particle** is a single molecule or a single atom which can occupy energy levels ϵ_0, ϵ_1, ϵ_2,.... . The energy levels are the eigenvalues of the Hamilton operator which desribes the single-particle system.
- A (thermodynamic) **system** is a collection of N particles. The particles do not need to be identical. A system can have different values of (total) energy E_1, E_2, ...
- An **ensemble** consists of an infinite (or: very large) number of copies of a particular systems.

Part of the difficulties with statistical mechanics arise because the definitions as well as the notations change when moving from quantum mechanics to a statistial mechanics. For example, in quantum mechanics a single particle is usually called a "system" and its energy levels are often denoted as E_n. When reading a text on statistical mechanics (including this script), make sure you understand what the authors mean by "system", "energy of the system" and similar terms.

In thermodynamics, the world is always divided into a **system** and its **surroundings**. The behaviour of the system depends on how the system can interact with its surroundings: Can it exchange heat or other forms of energy? Can it exchange particles with the surroundings? To come up with equations for the systems' behaviour, it will be useful to introduce the concept of an **ensemble of systems**.

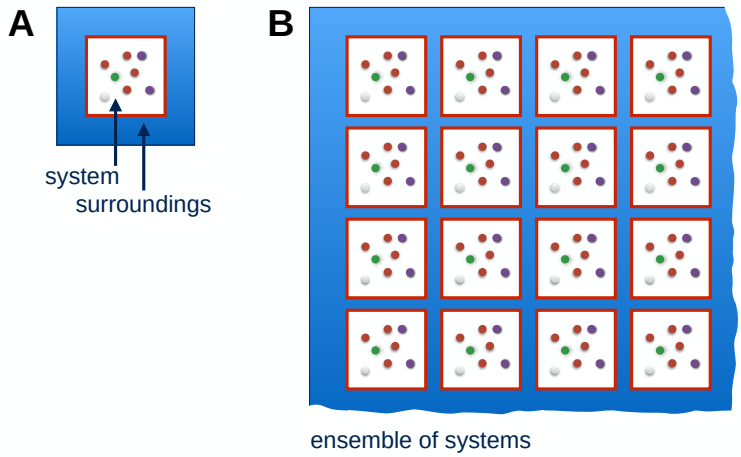


Figure 3: (**A**) a system with its surroundings; (**B**) an ensemble of systems.

2.2 Classification of ensembles

The system in an ensemble are typically not all in the same microstate or macrostate, but all of them interact in the same way with their surroundings. Therefore, ensembles can be classified by the way their systems interacts with their surroundings.

- An isolated system can neither exchange particles nor energy with its surroundings. The energy E, the volume and the number of particles N are constant in these systems $\rightarrow$ **microcanonical ensemble**.
- A closed system cannot exchange particles with its surroundings, but it can exchange energy (in form of heat or work). If the energy exchange occurs via heat but not work, the following parameters are constant: temperature T, volume V and the number of particles N $\rightarrow$ **canonical ensemble**
- In a closed system which exchanges energy with its surrounding via heat and work the following parameters are constant: temperature T, volume p and the number of particles N $\rightarrow$ **isothermal-isobaric ensemble**

- An open system exchanges particles and heat with its surroundings. The following parameters are constant temperature T, volume V and chemical potential $\mu \rightarrow$ **grand canonical ensemble**

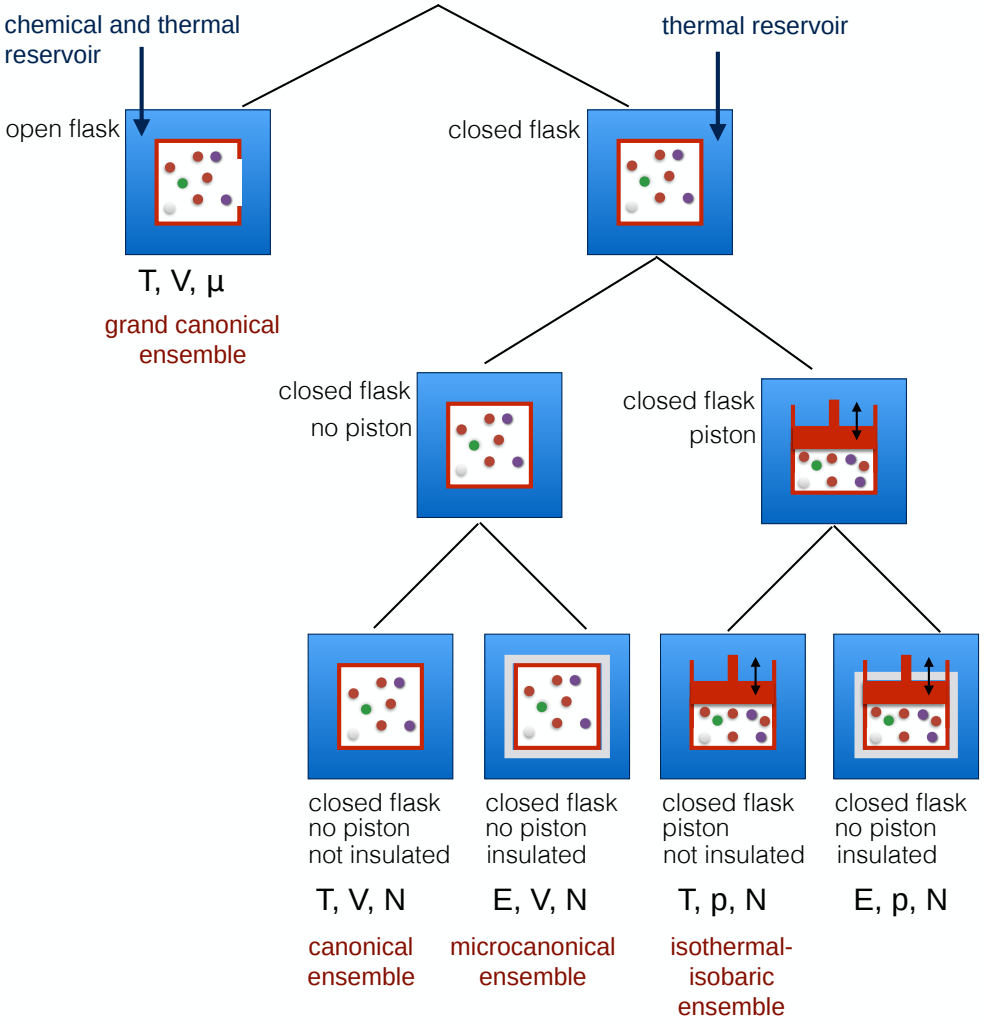


Figure 4: Classification of thermodynamic ensembles.

2.3 Illustration: Ising model

Consider a particle with two energy levels ϵ_0 and ϵ_1. [2] A physical realization of such a particle could be a particle with spin $s = \frac{1}{2}$ in an external magnetic fields. The system can be in quantum states $m_s = -1$ and $m_s = +1$ and the associated energies are

$$\begin{aligned} \epsilon_0 = \mu_B B_z m_s &= -\mu_B B_z \\ \epsilon_1 = \mu_B B_z m_s &= +\mu_B B_z \,. \end{aligned} \tag{2.1}$$

where μ_B is the Bohr magneton and B_z is the external magnetic field. Now consider N of these particles arranged in a line (one-dimensional Ising model). The possible permutations for $N = 5$ particles are shown in Fig. 2.3. In general 2^N permutations are possible for an Ising model of N particles. In statistical thermodynamics such a permutation is called **microstate**.

[2] Caution: such a particle is usually called *two-level system* - with the quantum mechanical meaning of the term "system".

↑↑↑↑↑	↑↑↑↑↓	↑↑↑↓↑	↑↑↑↓↓	↑↑↓↑↑	↑↑↓↑↓	↑↑↓↓↑	↑↑↓↓↓
5↑, 0↓ | 5	4↑, 1↓ | 3	4↑, 1↓ | 3	3↑, 2↓ | 1	4↑, 1↓ | 3	3↑, 2↓ | 1	3↑, 2↓ | 1	2↑, 3↓ | -1
↑↓↑↑↑	↑↓↑↑↓	↑↓↑↓↑	↑↓↑↓↓	↑↓↓↑↑	↑↓↓↑↓	↑↓↓↓↑	↑↓↓↓↓
4↑, 1↓ | 3	3↑, 2↓ | 1	3↑, 2↓ | 1	2↑, 3↓ | -1	3↑, 2↓ | 1	2↑, 3↓ | -1	2↑, 3↓ | 1	1↑, 4↓ | -3
↓↑↑↑↑	↓↑↑↑↓	↓↑↑↓↑	↓↑↑↓↓	↓↑↓↑↑	↓↑↓↑↓	↓↑↓↓↑	↓↑↓↓↓
4↑, 1↓ | -3	3↑, 2↓ | 1	3↑, 2↓ | 1	2↑, 3↓ | -1	3↑, 2↓ | 1	2↑, 3↓ | -1	2↑, 3↓ | -1	1↑, 4↓ | -3
↓↓↑↑↑	↓↓↑↑↓	↓↓↑↓↑	↓↓↑↓↓	↓↓↓↑↑	↓↓↓↑↓	↓↓↓↓↑	↓↓↓↓↓
3↑, 2↓ | 1	2↑, 3↓ | -1	2↑, 3↓ | -1	1↑, 4↓ | -3	2↑, 3↓ | -1	1↑, 4↓ | -3	1↑, 4↓ | -3	0↑, 5↓ | -5

	↓↑↑↓↓	permutation / microstate
combination / configuration	2↑, 3↓ | -1	macrostate $m_{\text{tot}} = \sum_{k=1}^{5} m_{s(k)}$

Figure 5: Microstates of a system with five spins, the corresponding configurations and macrostates.

Let us assume that the particles do not interact with each other, i.e the energy of a particular spin does not depend on the orientiation of the neighboring spins. The energy of the system is then given as the sum of the energies of the individual particles.

$$E_j = \sum_{k=1}^{N} \mu_B B_z m_{s(k)} = \mu_B B_z \sum_{k=1}^{N} m_{s(k)} \tag{2.2}$$

where k is the index of the particles, $m_{s(k)}$ is the spin quantum state of the kth particle, and the E_j is the energy of the system. A (non-interacting) spin system with five spins, can assume six different energy values: $E_1 = -5\mu_B B_z$, $E_2 = -3\mu_B B_z$, $E_3 = -1\mu_B B_z$, $E_4 = 1\mu_B B_z$, $E_5 = 3\mu_B B_z$, and $E_6 = 5\mu_B B_z$ (Fig. 2.3). The energy E_j together with the number of spins N in the system define the macrostate of the system. Thus, the system has 6 macrostates. Note that most macrostates can be realized by more than one microstate.

Relation to probability theory. An system of N non-interacting spins can be thought of N mutually independent random experiments, where each experiment has the two possible outcomes: $\Omega_1 = \{\uparrow, \downarrow\}$. If the N experiments are combined, the samples space of the combined experiments has $n(\Omega_N) = 2^N$ outcomes. The outcomes for $N = 5$ are shown in Fig. 2.3. That is, the microstates are the possible outcomes of this (combined) random experiment. In probability theory, this corresponds to an *ordered sample* or *permutation*. The microstates can be classified according to occupation numbers for the different energy levels, e.g. $(\uparrow\downarrow\downarrow\uparrow\downarrow) \rightarrow (2\uparrow, 3\downarrow)$ This is often called the configuration of the system. In probability theory, this corresponds to an *unordered sample* or *combination*. Finally, the system can be classified by any macroscopically measurable quantity, such as its total energy in a magnetic field. This means that all configurations (and associated microstates) have the same energy are grouped into a joint macrostate.

Note: In the Ising model, there is a one-to-one match between configuration and macrostate. This is however not the case for systems with more than two energy levels. For example, in a system with $M = 3$ equidistant energy levels and N particles, the set of occupation numbers $\mathbf{n} = \left(\frac{N}{2}, 0, \frac{N}{2}\right)$ yields the same system energy (macrostate) as $\mathbf{n} = (0, N, 0)$. Thus in the treatment of more complex systems, the microstates are first combined into occupation number which are then further combined into macrostates.

ordered sample	$\leftrightarrow$ permutation	$\leftrightarrow$ microstate
unordered sample	$\leftrightarrow$ combination	$\leftrightarrow$ configuration

3 Mathematical basics: probability theory

3.1 Random experiment

Probability theory is the mathematical theory for predicting the outcome of a *random experiment*. An experiment is called *random* if it has several possible outcomes. (An experiment which has only one possible outcome is called *deterministic*). Additionally, the set of outcomes needs to well-defined, he outcomes need to be mutually exclusive, and the experiments can be infinitely repeated. Often several outcomes are equivalent in some sense. One therefore groups them together into events. The formal definitions of a random experiment has three ingredients

- the *sample space* Ω. This is the set of all possible outcomes of an experiment.
- a set of events X. An event is a subset of all possible outcomes.
- the probability p of each event.

Note that in the following we will consider discrete outcomes (discrete random variables). The theory can however be extended to continuous variables.

Example 1: Pips when throwing a fair die

- Sample space $\Omega = \{1, 2, 3, 4, 5, 6\}$
- Events $X = \{1, 2, 3, 4, 5, 6\}$
- Probability $p_X = \{\frac{1}{6}, \frac{1}{6}, \frac{1}{6}, \frac{1}{6}, \frac{1}{6}, \frac{1}{6}\}$

Example 2: Even number of pips when throwing a fair die

- Sample space $\Omega = \{1, 2, 3, 4, 5, 6\}$
- Events $X = \{\text{even number of pips}, \text{odd number of pips}\} = \{\{2, 4, 6\}, \{1, 3, 5\}\}$
- Probability $p_X = \{\frac{1}{2}, \frac{1}{2}\}$

Example 3: Six pips when throwing an unfair die fair die. The six is twice as likely as the other faces of the die.

- Sample space $\Omega = \{1, 2, 3, 4, 5, 6\}$
- Events $X = \{\text{six pips}, \text{not six pips}\} = \{\{6\}, \{1, 2, 3, 4, 5\}\}$
- Probability of the individual outcomes $p_\Omega = \{\frac{1}{7}, \frac{1}{7}, \frac{1}{7}, \frac{1}{7}, \frac{1}{7}, \frac{2}{7}\}$. Probability of the set of events $p_X = \{\frac{2}{7}, \frac{5}{7}\}$

3.2 Combining random events

Consider the following two random events when throwing a fair die

- random event $A =$ an even number of pips
- random event $B =$ the number of pips is large than 3.

These two events occur within the same sample space. But they overlap, i.e the outcomes 3 pips and 6 pips are elements of both events. Therefore, events A and B cannot be simultaneously be part of the same random experiment. There are two ways to combine A and B into a new event C.

- *Union:* $C = A \cup B$. Either A or B occurs, i.e. the outcome of the experiment is a member of A or of B. In the example $C = \{2, 4, 5, 6\}$.
- *Intersection:* $C = A \cap B$. The outcome is a member of A and at the same time a member of B. In the example $C = \{4, 6\}$.

3.3 Mutually independent random experiments

To caclulate the probability of a particular sequence of a events obtained by a series of random experiments, one needs to establish whether the experiments are mutually independent or mutually dependent. Two random experiments are mutually independent, if the sample space Ω, the event definition X, the probability p_X of one experiment does not depend on the outcome of the other experiment. In this case the probability of a sequence of events $\{x_1, x_2\}$ is given by the production of the probabilities of each individual element

$$p(\{x_1, x_2\}) = p(x_1)p(x_2) \tag{3.1}$$

For mutually dependent experiments one needs to work with conditional probabilities.

Examples: mutually independent

- The probability of first throwing 6 pips and then 3 pips when throwing a fair die twice $p(\{6,3\}) = p(6)p(3) = \frac{1}{36}$.
- The probability of first throwing 6 pips and more than 3 pips when throwing a fair die twice $p(6, \{4,5,6\}) = p(6)p(\{4,5,6\}) = \frac{1}{12}$.
- The probability of first throwing 6 pips with a fair die and then head with a fair coin $p(6, \text{head}) = p(6)p(\text{head}) = \frac{1}{12}$. (Note: the experiments are not necessarily identical.)

3.4 Permutations and combinations

To correctly group outcocmes into events, you need to understand permutations and combinations of. Consider a set of N distinguishable objects (you can think of them as numbered). Arranging N distinguishable objects into a sequence is called a **permutation**, and the number of possible permutations is as

$$P(N,N) \quad = \quad N \cdot (N-1) \cdot (N-2) ... \cdot 1 = N! \tag{3.2}$$

where $N!$ is called the factorial of N and is defined as

$$\begin{aligned} N! &= \prod_{i=1}^{N} i \qquad \forall N \in \mathbb{N} \\ 0! &= 1\,. \end{aligned} \tag{3.3}$$

The number of ways in which k objects taken from the set of N objects can be arranged in a sequence (i.e. the number of k-permutations of N) is given as

$$P(N,k) \quad = \quad N \cdot (N-1) \cdot (N-2) ... \cdot (N-k+1) = \frac{N!}{(N-k) \cdot (N-k-1) ... \cdot 1} = \frac{N!}{(N-k)!} \tag{3.4}$$

with $N, k \in \mathbb{N}^0$ and $k \leq N$. Note that

$$\frac{N!}{(N-k)!} \quad = \quad \prod_{i=N-k+1}^{N} i\,. \tag{3.5}$$

Splitting a set of N objectso into two subset of size k and $N-k$. Consider a set of N numbered objects which is to be split into two subset of size k_0 and $k_1 = N - k_0$. An example would be n spins of which k_0 are "up", and $k_1 = N - k_0$ are "down". The configuration is denoted $\mathbf{k} = (k_0, k_1)$. How many possible ways are there to realize the configuration $\mathbf{k}$?

We start from the list of possible permutations of all N objects $P(N,N) = N!$. Then we split each of these permutations between position k and $k+1$ into two subsequences of size k and $N-k$. Each possible set of k numbers on the left side of the dividing line can be arranged into $k!$ sequences. Likewise

each possible set of $N-k$ numbers on the right side can be arranged into $(N-k)!$ sequences. Thus, the number of possible ways to distribute N objects over these two sets is

$$W(\mathbf{k}) = \frac{N!}{(N-k)!k!} \tag{3.6}$$

where

$$\binom{N}{k} = \frac{N!}{(N-k)!k!} \tag{3.7}$$

is called the **binomial coefficient**.

The last example can be generalized. Consider a set of N objects which will be split into m subsets of sizes $k_0, ...k_{m-1}$ with $\sum_{i=0}^{m-1} k_i = N$. There are

$$W(\mathbf{k}) = \binom{N}{k_0, ...k_{m-1}} = \frac{N!}{k_0!...k_{m-1}!} \tag{3.8}$$

ways to do this. Eq. 3.8 is called the **multinomial coefficient**.

Example: Choosing three out of five. We want to know the possible subsets of size three ($k=3$) within a set of five objects ($n=5$), i.e the number of combinations $W(\mathbf{k}=(3,2))$. There are $P(5,3) = 5 \cdot 4 \cdot 3 = 60$ possible sequences of length three which can be drawn from this set. For example, one can draw the ordered sequence #1, #2, #3 which corresponds to the (unordered) subset $\{\#1, \#2, \#3\}$. However, one could also draw the ordered sequence #2, #1, #3 which corresponds to the same (unordered) subset $\{\#1, \#2, \#3\}$. In total there are $3 \cdot 2 \cdot 1 = 3! = 6$ way to arrange the numbers $\{\#1, \#2, \#3\}$ into a sequence. Therefore, the subset $\{\#1, \#2, \#3\}$ appears six times in the list of permutations. The same is true for all other subsets of size three. The number of subsets (i.e. the number of combinations) is therefore $W(\mathbf{k}=(3,2)) = P(5,3)/6 = 60/6 = 10$.

Example: Flipping three out of five spins. The framework of permutations and combinations can be also applied to slightly different type of thought experiment. Consider sequence of five non-interacting spins ($n=5$), all of which are in the "up" quantum state. Such a spin model is called an Ising model (see also section 2). We (one by one) flip three out of these five spins ($k=3$) into the "down" quantum state. How many configurations exist which have two spins "up" and three spins "down"? There are $P(5,3) = 5 \cdot 4 \cdot 3 = 60$ sequences in which one can flip the three spins. Each configuration (e.g. $\downarrow\downarrow\uparrow\downarrow\uparrow$) can be generated by $3 \cdot 2 \cdot 1 = 3! = 6$ different sequences. Thus the number of configurations is $W(\mathbf{k}=(3,2)) = P(5,3)/6 = 10$.

3.5 Binomial probability distribution

The binomial probability distribution models a sequence of N repetitions of an experiments with two possible outcomes e.g. orientation of a spin $\Omega = \{\uparrow, \downarrow\}$. The probabilities of the two possible outcomes in an individual experiment is given are $p_\uparrow$ and $p_\downarrow = 1 - p_\uparrow$ There are 2^N possible sequences. Thus, the combined experiment has possible 2^N outcomes. Since the experiments in the sequence are mutually independent, the probabilities of the outcome of each experiments can be multplied to obtain the probability of the corresponding outcome of the combined experiment. E.g.

$$p(\uparrow\uparrow\downarrow) = p_\uparrow \cdot p_\uparrow \cdot p_\downarrow = p_\uparrow^2 \cdot p_\downarrow \tag{3.9}$$

Note that $p_\uparrow$ and $p_\downarrow$ are not necessarily equal and hence the probability of the outcomes of the combined experiments are not uniform. However, all outcomes which belong to the same combination of spin $\uparrow$ and spin $\downarrow$ have the same probability

$$p(\uparrow\uparrow\downarrow) = p(\uparrow\downarrow\uparrow) = p(\downarrow\uparrow\uparrow) = p_\uparrow^2 \cdot p_\downarrow \,. \tag{3.10}$$

(See also Fig. 3.5). In general terms, the probability of a particular sequence in which k spins are $\uparrow$ and $N-k$ spins are $\downarrow$ is

$$p_\uparrow^k p_\downarrow^{N-k} \quad = \quad p_\uparrow^k (1-p_\uparrow)^{N-k} \,. \tag{3.11}$$

Often one is not interested in the probability of each individual sequence but in the probability that in N experiments k spins are $\uparrow$ and $n-k$ spins are $\downarrow$, i.e. one combines a several sequences (outcomes) into an event. The number of sequences in which a particular combination of $k_0 = k$ spins $\uparrow$ and $k_1 = N-k$ spins $\downarrow$ can be generated is given by the binomial coefficient (eq. 3.7). Thus, the probability of event $X = \{k\uparrow, N-k\downarrow\}$ is equal to the probability of the configuration $\mathbf{k} = (k_0 = k, k_1 = N-k)$

$$p_X = p(\mathbf{k}) \quad = \quad \binom{N}{k} p_\uparrow^k (1-p_\uparrow)^{N-k} = \frac{N!}{k!(N-k)!} p_\uparrow^k (1-p_\uparrow)^{N-k} \tag{3.12}$$

Eq. 3.12 is called the **binomial distribution**.

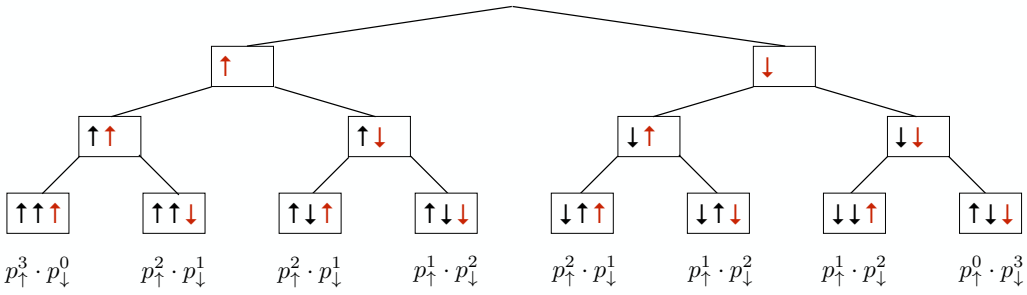


Figure 6: Possible outcomes in a sequence of three random experiments with two possible events each.

3.6 Multinomial probability distribution

The **multinomial probability distribution** is the generalization of the binomial probability distribution to the scenario in which you have a sequence of N repetitions of an experiment with m possible outcomes. For example, you could draw balls from a urn which contains balls with three different colors (red, blue, yellow). Every time you draw a ball, you note the color and put the ball back into the urn (drawing with replacement). The frequencies with which each color occurs determines the probability with which you draw ball of this color (p_{red}, p_{blue}, p_{yellow}). The probability of a particular sequence is given as the product of the outcome probabilities of the individual experiments, e.g

$$p(\text{red}, \text{red}, \text{blue}) \quad = \quad p_{\text{red}} \cdot p_{\text{red}} \cdot p_{\text{blue}} \tag{3.13}$$

and all permutations of a sequence have the same probability

$$p(\text{red}, \text{red}, \text{blue}) = p(\text{red}, \text{blue}, \text{red}) = p(\text{blue}, \text{red}, \text{red}) \quad = \quad p_{\text{red}}^2 \cdot p_{\text{blue}} \,. \tag{3.14}$$

In general, the probability of a sequence which contains k_{red} red balls, k_{blue} blue balls, and k_{yellow} yellow balls (with $k_{\text{red}} + k_{\text{blue}} + k_{\text{yellow}} = N$) is $p_{\text{red}}^{k_{\text{red}}} \cdot p_{\text{blue}}^{k_{\text{blue}}} \cdot p_{\text{yellow}}^{k_{\text{yellow}}}$. There are

$$\binom{N}{k_{\text{red}}, k_{\text{blue}}, k_{\text{yellow}}} = \frac{N!}{k_{\text{red}}! k_{\text{blue}}! k_{\text{yellow}}!} \tag{3.15}$$

possible sequences with this combination of balls. The probability of drawing such a combination is

$$p(k_{\text{red}}, k_{\text{blue}}, k_{\text{yellow}}) \quad = \quad \frac{N!}{k_{\text{red}}! k_{\text{blue}}! k_{\text{yellow}}!} p_{\text{red}}^{k_{\text{red}}} \cdot p_{\text{blue}}^{k_{\text{blue}}} \cdot p_{\text{yellow}}^{k_{\text{yellow}}} \,. \tag{3.16}$$

Generalizing to m possible outcomes with probabilities $p = \{p_0, ...p_{m-1}\}$ yields the multinomial probability distribution

$$p_X = p(\mathbf{k}) \quad = \quad \frac{N!}{k_0! \cdot ...k_{m-1}!} p_0^{k_0} \cdot ...p_{m-1}^{k_{m-1}} \,. \tag{3.17}$$

This distribution represents the probability of the event that in N trials the results are distributed as $X = \mathbf{k} = (k_0, ...k_{m-1})$ (with $\sum_{i=0}^{m-1} k_i = N$).

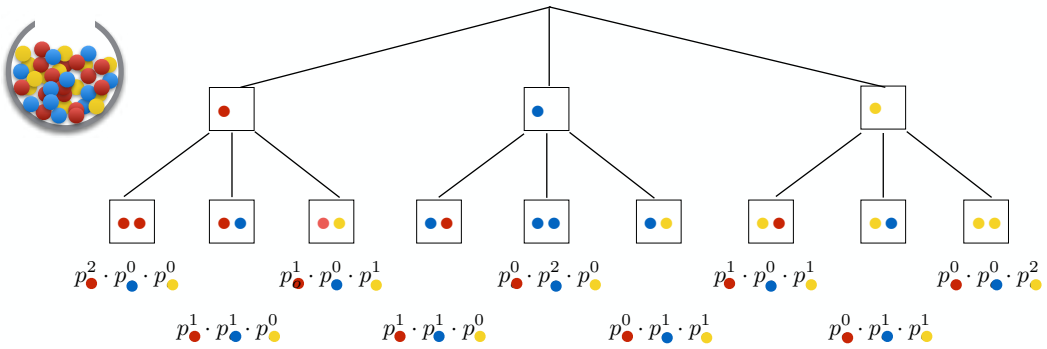


Figure 7: Drawing balls from a urn with replacment. Possible outcomes in a sequence of two random experiments with three possible events each.

3.7 Relation to Statistical Thermodynamics

Probability Theory	**Statistical Thermodynamics**
m outcomes in the single random experiment	$(\epsilon_0, ...\epsilon_{m-1})$ energy levels of the single particle
(ordered) sequence of n outcomes / outcome of the combined random experiment	microstate of a system with n particles
combination $\mathbf{k} = (k_0, k_1, ...k_{m-1})$, i.e. k_i single random experiments yielded the outcome i	configuration of the system $\mathbf{k} = (k_0, k_1, ...k_{m-1})$, i.e. number of particles k_i in energy leven ϵ_i
probability of a particular ordered sequence $p_0^{k_0} \cdot p_1^{k_1} \cdots p_{m-1}^{k_{m-1}}$	probability of a microsate $p_0^{k_0} \cdot p_1^{k_1} \cdots p_{m-1}^{k_{m-1}}$
number of sequences with a particular combination $\mathbf{k}$ $W(\mathbf{k}) = \frac{n!}{k_0! \cdot ...k_{m-1}!}$	weight of a particular configuration $\mathbf{k}$ $W(\mathbf{k}) = \frac{n!}{k_0! \cdot ...k_{m-1}!}$
probability of a particular combination $\mathbf{k}$ $p(\mathbf{k}) = \frac{n!}{k_0! \cdot ...k_{m-1}!} p_0^{k_0} \cdot ...p_{m-1}^{k_{m-1}}$	probability of a particular configuration $\mathbf{k}$ $p(\mathbf{k}) = \frac{n!}{k_0! \cdot ...k_{m-1}!} p_0^{k_0} \cdot ...p_{m-1}^{k_{m-1}}$

Comments:

- This comparison is true for distinguishable particles. For indistinguishable particles, the equations need to be modified. In particular, the distinction between fermions and bosones becomes important.
- To characterize the possible states of the system, one would need to evaluate all possible configurations $\mathbf{k}$ which quickly becomes intractable for large numbers of energy levels m and large number of particles N. Two approximations drastically simplify the equations:
  - the Stirling approximation for factorials for large N
  - the dominance of the most likely configuration $\mathbf{k}^*$ at large N

3.8 Stirling's formula

Stirling's formula

$$N! \approx \frac{N^N}{e^N}\sqrt{2\pi N} \tag{3.18}$$

holds very well for large values of N. Taking the logarithm yields

$$\ln N! \approx N\ln N - N + \frac{1}{2}\ln(2\pi N) \tag{3.19}$$

For large N, the first and second term is much bigger than the third, and one can further approximate

$$\ln N! \approx N\ln N - N\,. \tag{3.20}$$

3.9 Most likely configuration in the binomial distribution

Consider an experiment with two possible outcomes 0 and 1 (equivalently: a single particle with two energy levels ϵ_0 and ϵ_1). The outcomes are equally likely, i.e. $p_0 = p_1 = 0.5$. The experiment is repeated N times (equivalently: the system contains non-interacting N particles). The probability that the outcome 0 is obtained k times and the outcome 1 is obtained $N-k$ times (equivalently: the probability that the system is in the configuration $\mathbf{k} = (k_0 = k, k_1 = n-k)$) is

$$p(\mathbf{k}) = \frac{N!}{k!(N-k)!}\cdot p_0^k(1-p_1)^{N-k} = \frac{N!}{k!(N-k)!}\cdot 0.5^N \tag{3.21}$$

Thus, if the outcomes have equal probabilities, the probability of a configuration $\mathbf{k}$ is determined by the number of (ordered) sequences $W(\mathbf{k})$ with which this configuration can be realized (equivalently: by the number of microstates which give rise to this configuration). $W(\mathbf{k})$ is also called the weight of a configuration. The most likely configuration $\mathbf{k}^*$ is the one with the heighest weight. Thus solve

$$0 = \frac{\mathrm{d}}{\mathrm{d}k}W(\mathbf{k}) \tag{3.22}$$

Mathematically equivalent but easier is

$$\begin{aligned} 0 &= \frac{\mathrm{d}}{\mathrm{d}k}\ln W(\mathbf{k}) = \frac{\mathrm{d}}{\mathrm{d}k}\ln\frac{N!}{k!(N-k)!} = \frac{\mathrm{d}}{\mathrm{d}k}\left[\ln N! - \ln k! - \ln(N-k)!\right] \\ &= -\frac{\mathrm{d}}{\mathrm{d}k}\ln k! - \frac{\mathrm{d}}{\mathrm{d}k}\ln(N-k)!\,. \end{aligned} \tag{3.23}$$

Use Stirling's formula (eq. 3.20)

$$\begin{aligned} 0 &= -\frac{\mathrm{d}}{\mathrm{d}k}\left[k\ln k - k\right] - \frac{\mathrm{d}}{\mathrm{d}k}\left[(N-k)\ln(N-k) - (N-k)\right] = -\ln k + \ln(N-k) \\ &\Updownarrow \\ 0 &= \ln\frac{N-k}{k} \\ e^0 &= \frac{N-k}{k} \\ &\Updownarrow \\ k &= \frac{N}{2} \end{aligned} \tag{3.24}$$

The most likely configuration is $\mathbf{k}^* = (\frac{N}{2}, \frac{N}{2})$.

4 The microcanonical ensemble

4.1 Boltzmann distribution - introducing the model

Consider a system with N particles, which is isolated from its surroundings. Thus, the number of particles N, the energy of the system E and its volume V are constant. To derivation of a statistical framework for such a system goes back to Ludwig Boltzmann (1844-1904), and is based on a number of assumptions:

1. The single particles systems are distinguishable, e.g. you can imagine them to be numbered.
2. The particles are independent of each other, i.e. they do not interact with each other.
3. Each particle occupies on of N_ϵ energy levels: $\{\epsilon_0, \epsilon_2, ...\epsilon_{N_\epsilon - 1}\}$.
4. There can be multiple particles in the same energy level. The number of particles in the ith energy level is denoted k_i.

Thus, each particles is modeled as random experiment with N_ϵ possible outcomes. The random experiment is repeated N times generating a sequence of outcomes $j = (\epsilon(1), \epsilon(2), ...\epsilon(N))$, where $\epsilon(i)$ is the energy level of the ith particle and j denotes the microstate of the system. There are N_ϵ^N possible microstates. There number of particles in energy level ϵ_s is denoted k_s, and $\mathbf{k} = (k_0, k_2, ...k_{N_{\epsilon-1}})$ with $\sum_{s=0}^{N_\epsilon - 1} k_s = N$ is called the configuration of the system.

Because the particles are independent of each other, the total energy of the system in microstate j is given as the sum of the energies of the individual particles, or equivalently as the weighted sum over all single-particle energy levels with weights according to $\mathbf{k}$

$$E_j = \sum_{i=1}^{N} \epsilon(i) = \sum_{s=0}^{N_\epsilon - 1} k_s \epsilon_s \,. \tag{4.1}$$

Note that $\epsilon(i)$ denotes the energy level of the ith particle, whereas ϵ_s the sth entry in the sequence of possible energy levels $\{\epsilon_0, \epsilon_2, ...\epsilon_{N_\epsilon - 1}\}$.

The total energy of the system is its macrostate. Given the configuration $\mathbf{k}$, one can calculate the macrostate of the system. The probability that the system is in a particular configuation $\mathbf{k}$ is given by the multinomial probability distribution

$$p(\mathbf{k}) = \frac{N!}{k_0! \cdot ...k_{N_\epsilon - 1}!} \cdot p_0^{k_0} \cdot ...p_{N_\epsilon - 1}^{k_{N_\epsilon - 1}} \,. \tag{4.2}$$

To work with this equation, we need to make an assumption on the probability p_s with which a particle occupies the energy level ϵ_s.

4.2 Postulate of equal a priori probabilities

The postulate of equal a priori probabilities states that

For an isolated system with an exactly known energy and exactly known composition, the system can be found with equal probability in any microstate consistent with that knowledge.

This is only possible if the probability p_s with which a particle occupies the energy level ϵ_s is the same for all states, i.e. $p_s = \frac{1}{N_\epsilon}$. Thus,

$$p(\mathbf{k}) = \frac{N!}{k_0! \cdot ...k_{N_\epsilon - 1}!} \cdot p_s^N \,. \tag{4.3}$$

The probability that the system is in a particular configuation $\mathbf{k}$ is then proportional to the number of microstates which give rise to the configuration, i.e. to the weight of this configuration

$$W(\mathbf{k}) = \frac{N!}{k_0! \cdot ...k_{N_\epsilon - 1}!} \,. \tag{4.4}$$

4.3 The most likely configuration $\mathbf{k}^*$

Because we work in the limit of large particle numbers N, we assume that the most likely configuration $\mathbf{k}^*$ is the dominant configuration, and that it is thus sufficient to know this configuration to determine the macrostate of the ensemble. Because of the postulate of equal a priori probabilities, this amounts to finding the configuration with the maximum weight $W(\mathbf{k})$, i.e. the configuration for which the total differential of $W(\mathbf{k})$ is zero

$$\mathrm{d}W(\mathbf{k}) \quad = \quad \sum_{s=0}^{N_\epsilon-1} \frac{\partial}{\partial k_s} W(\mathbf{k})\,\mathrm{d}k_s = 0. \tag{4.5}$$

(Interpretation of eq. 4.5: Suppose the number of particles k_s in each energy level ϵ_s is changed by a small number $\mathrm{d}k_s$, then the weight of configuration changes by $\mathrm{d}W(\mathbf{k})$. At the maximum of $W(\mathbf{k})$, the change in $W(\mathbf{k})$ upon a small change in $\mathbf{k}$ is zero.)

As in the example with binomial distribution, we solve the mathematically equivalent but easier problem

$$\mathrm{d}\ln W(\mathbf{k}) \quad = \quad \sum_{s=0}^{N_\epsilon-1} \frac{\partial}{\partial k_s} \ln W(\mathbf{k})\,\mathrm{d}k_s = 0. \tag{4.6}$$

First we rearrange

$$\begin{aligned}
\ln W(\mathbf{k}) &= \ln \frac{N!}{\prod_{i=0}^{N_\epsilon-1} k_i!} = \ln N! - \ln \prod_{i=0}^{N_\epsilon-1} k_i! = \ln N! - \sum_{i=0}^{N_\epsilon-1} \ln k_i! \\
&= N\ln N - N - \sum_{i=0}^{N_\epsilon-1} k_i \ln k_i + \underbrace{\sum_{i=0}^{N_\epsilon-1} k_i}_{N} \\
&= \underbrace{N}_{\sum k_i} \ln N - \sum_{i=0}^{N_\epsilon-1} k_i \ln k_i \\
&= -\sum_{i=0}^{N_\epsilon-0} k_i \ln \frac{k_i}{N}
\end{aligned} \tag{4.7}$$

where we have used Stirling's formula in the second line. Thus, we need to solve

$$\mathrm{d}\ln W(\mathbf{k}) \quad = \quad \sum_{s=0}^{N_\epsilon-1} \frac{\partial}{\partial k_s} \left[-\sum_{i=0}^{N_\epsilon-0} k_i \ln \frac{k_i}{N} \right] \mathrm{d}k_s = -\sum_{s=0}^{N_\epsilon-1} \left[\frac{\partial}{\partial k_s} k_s \ln \frac{k_s}{N} \right] \mathrm{d}k_s = 0 \tag{4.8}$$

Taking the derivatives yields

$$\mathrm{d}\ln W(\mathbf{k}) = -\sum_{s=0}^{N_\epsilon-1} \ln \frac{k_s}{N}\,\mathrm{d}k_s - \sum_{s=0}^{N_\epsilon-1} \mathrm{d}k_s = 0 \tag{4.9}$$

This equation has several solutions. But not all solutions are consistent with the problem we stated at the beginning. In particular, because the system is isolated from its surrounding (microcanonical ensemble), the total number of particles N needs be constant. This implies that the changes of the number of particles in each energy level $\mathrm{d}k_s$ need to add up to zero

$$\mathrm{d}N \quad = \quad \sum_{s=0}^{N_\epsilon-0} \mathrm{d}k_s = 0\,. \tag{4.10}$$

Second, the total energy stays constant, which implies that the changes in energy have to add up to zero

$$\mathrm{d}E \quad = \quad \sum_{s=0}^{N_\epsilon-1} \mathrm{d}k_s \cdot \epsilon_s = 0\,. \tag{4.11}$$

Only solutions which fulfill eq. 4.10 and eq. 4.11 are consistent with the microcanonical ensemble. We use the method of **Lagrange multipliers:** since both terms (*eq.* 4.10 and 4.11) are zero if the constraints are fulfilled, they can be substracted from *eq.* 4.9, multiplied by a factors α and β. The factors α and β are the Lagrange multipliers. One obtains

$$\begin{aligned} \mathrm{d}\ln W(\mathbf{k}) &= -\sum_{s=0}^{N_\epsilon-1} \ln\frac{k_s}{N}\,\mathrm{d}k_s - \sum_{s=0}^{N_\epsilon-1}\mathrm{d}k_s - \sum_{s=0}^{N_\epsilon-0}\mathrm{d}k_s - \beta\sum_{s=0}^{N_\epsilon-1}\mathrm{d}k_s\cdot\epsilon_s \\ &= \sum_{s=0}^{N_\epsilon-1}\left[-\ln\frac{k_s}{N} - (\alpha+1) - \beta\epsilon_s\right]\mathrm{d}k_s \\ &= 0 \end{aligned} \tag{4.12}$$

This can only be fulfilled if each individual term is zero

$$\begin{aligned} 0 &= -\ln\frac{k_s}{N} - (\alpha+1) - \beta\epsilon_s \\ &\Updownarrow \\ \frac{k_s}{N} &= e^{-(\alpha+1)}\,e^{-\beta\epsilon_s}\,. \end{aligned} \tag{4.13}$$

Requiring that $\sum \frac{k_s}{N} = 1$, we can determine $e^{-(\alpha+1)}$

$$\sum_{s=0}^{N_\epsilon-1}\frac{k_s}{N} = e^{-(\alpha+1)}\sum_{s=0}^{N_\epsilon-1}e^{-\beta\epsilon_s} = 1 \quad\Leftrightarrow\quad e^{-(\alpha+1)} = \frac{1}{\sum_{s=0}^{N_\epsilon-1}e^{-\beta\epsilon_s}} = \frac{1}{Q}\,. \tag{4.14}$$

q is the **partition function of a single particle**

$$q = \sum_{s=0}^{N_\epsilon-1} e^{-\beta\epsilon_s}\,. \tag{4.15}$$

In summary, the microstate which has the highest probability is the one for which the energy level occupancies are given as

$$\mathbf{k}^*:\quad \frac{k_s}{N} = \frac{1}{q}e^{-\beta\epsilon_s}\,. \tag{4.16}$$

If one interprets the relative populations as probabilties, one obtains the **Boltzmann distribution**

$$p_s = \frac{1}{q}e^{-\beta\epsilon_s} = \frac{e^{-\beta\epsilon_s}}{\sum_{s=0}^{N_\epsilon-1}e^{-\beta\epsilon_s}}\,. \tag{4.17}$$

From the Boltzmann distribution, any ensemble property can be calculated as

$$\langle A\rangle = \frac{1}{q}\sum_{s=0}^{N_\epsilon-1} e^{-\beta\epsilon_s}a_s\,. \tag{4.18}$$

To link the microscopic properties of particles to the macroscopic observables, one needs to know the Boltzmann distribution.

4.4 Lagrange multiplier β

Without derivation:

$$\beta = \frac{1}{k_B T}\,, \tag{4.19}$$

where $k_B = 1.381\cdot 10^{-23}$ J/K is the Boltzmann constant, and T is the absolute temperature.

5 The Boltzmann entropy and Boltzmann distribution

5.1 Boltzmann entropy

5.2 Physical reason for the logarithm in the Boltzmann entropy.

Consider two independent systems of identical particles, e.g. ideal gases, which are in microstates with statistical weights W_1 and W_2. Associated to the occupation number distributions are the entropies S_1 and S_2. If these two systems are (isothermally) combined into single system, the statistical weight is a product of the original weights.

$$W_{1.2} \quad = \quad W_1 \cdot W_2. \tag{5.1}$$

However, from classical thermodynamics we expect that the total entropy is given as a sum of the original entropies

$$S_{1,2} \quad = \quad S_1 + S_2 \tag{5.2}$$

Therefore, the entropy has to be a function of W which fulfill the following equality

$$f(W_{1,2}) = f(W_1 \cdot W_2) \quad = \quad f(W_1) + f(W_2)\,. \tag{5.3}$$

This is only possible if f is the logarithm of W. Thus, the Boltzamnn equation for the entropy is

$$S = k_B \ln W \tag{5.4}$$

where $k_B = 1.381 \cdot 10^{-23}$ J/K is the Boltzmann constant.

The Boltzman entropy increases with the number of particles N; it is an **extensive property**.

5.3 A simple explanation for the second law of thermodynamics.

Second law of thermodynamics as formulated by M. Planck: "Every process occurring in nature proceeds in the sense in which the sum of the entropies of all bodies taking part in the process is increased."

Consider to occupation number distributions (ensemble microstates) $\mathbf{n}_1$ and $\mathbf{n}_2$, which are accessible to a system with N particles. The entropy difference between these occupation number distributions can be related to the ratio of the statistical weights of these states

$$\begin{aligned} \Delta S = S_2 - S_1 \quad &= \quad k_B \ln W_2 - k_B \ln W_1 = k_B \ln \frac{W_2}{W_1} \\ &\Updownarrow \\ \frac{W_2}{W_1} \quad &= \quad \exp\left(\frac{\Delta S}{k_B}\right) \end{aligned} \tag{5.5}$$

Note that $k_B = 1.381 \cdot 10^{-23}$ is a very small number. Suppose, the ensemble of particles can be in two microstates 1 and 2 which have the same energy, but which differ by $1.381 \cdot 10^{-10} J/K$ in entropy. Then, according to eq. 5.5, the ratio of the statistical weights is given as

$$\frac{W_2}{W_1} \quad = \quad \exp\left(\frac{\Delta S}{k_B}\right) = \exp(10^{13})\,. \tag{5.6}$$

Even a small entropy difference leads to an enormous difference in the statistical weights. Hence, once the system is in the states with the higher weight (entropy) it is extremely unlikely that it will visit the microstate with the lower statistical weight again.

5.4 The dominance of the Boltzmann distribution

The Boltzmann distribution represents one out of many microstates. Yet, it is relevant because for large number of particles N this is (virtually) the only microstates that is realized.

To illustrate this consider a system with equidistant energy levels $\{\epsilon_1, \epsilon_2, ...\epsilon_{N_\epsilon}\}$ (e.g. vibrational states of a diatomic molecule). Let the Boltzmann distribution yield occupancy numbers $\{n_1, n_2, ...n_{N_\epsilon}\}$. The microstate of the Boltzmann distribution is compared to a microstate in which ν particles have been moved from state $i-1$ to state i, and ν particles have been moved to from state $i+1$ to state i. Let ν be small in comparison to the occupancy numbers, e.g.

$$\nu = n_{j+1} \cdot 10^{-3} \tag{5.7}$$

(The occupancy of the state $j+1$ is changed by 0.1%.) Since, the energy levels are equidistant the two occupation number distributions have the same total energy. According to eq. **??**, the associated change in entropy is given as

$$\Delta S = -k_B \sum_{j=i}^{N_\epsilon} \nu_j \ln \frac{n_j}{N} + k_B \sum_{j=i}^{N_\epsilon} \nu_j \tag{5.8}$$

Because the total number in the system has not been changed, the last term is zero, and we obtain

$$\begin{aligned} \Delta S &= -k_B \left[-\nu \ln \frac{n_{j-1}}{N} + 2\nu \ln \frac{n_j}{N} - \nu \ln \frac{n_{j+1}}{N} \right] \\ &= k_B \nu \left[\ln \frac{n_{j-1}}{N} - 2 \ln \frac{n_j}{N} + \ln \frac{n_{j+1}}{N} \right] \\ &= k_B \nu \ln \left[\frac{n_{j-1} n_{j+1}}{n_j^2} \right] . \end{aligned} \tag{5.9}$$

This entropy difference gives rise to the following ratio of statistical weights of the occupation number distributions (eq. 5.5)

$$\begin{aligned} \frac{W_2}{W_1} &= \exp\left(\frac{\Delta S}{k_B}\right) = \exp\left(\frac{1}{k_B} k_B \nu \ln \left[\frac{n_{j-1} n_{j+1}}{n_j^2} \right]\right) \\ &= \left(\frac{n_{j-1} n_{j+1}}{n_j^2} \right)^\nu \end{aligned} \tag{5.10}$$

Consider that $\nu = n_{j+1} \cdot 10^{-3}$, i.e. if the occupancy numbers are in the order of 1 mol $(6.022 \cdot 10^{23})$, Boltzmann distribution is approximately 10^{20} more likely than the new occupation number distribution. Although, the occupation number distribution cannot be determined unambiguously from the macrostate, for large numbers, the ambiguity is reduced so drastically, that we effectively have a one-to-one relation from macrostate to Boltzmann distribution.

5.5 The vastness of conformational space

If we interpret the energy levels as conformational states, then the Boltzmann distribution is a function of the potential energy of the conformational states plus the kinetic energy. In a classical MD simulation, the potential energy surface is determined by the force field, and the kinetic energy is given by the velocity which are distributed according to the Maxwell distribution. Thus, in principle, one could evaluate the Boltzmann weight of a particular part of the conformational space by simply integrating the Boltzmann distribution over this space - no need to simulate.

This approach does not work because of the enormous size of the conformational space. Let's approximate the conformational space of an amino acid residue in a protein chain by the space spanned by the ϕ- and ψ-backbone angles of this residues (Fig. 5.5.a). Roughly, 65% of this space is visited at room

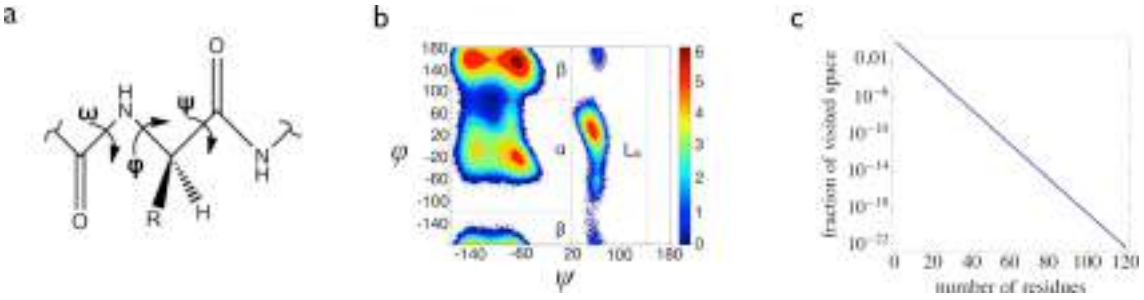


Figure 8: (a) Definition of the backbone torsion angles. (b) Ramachandran plot of an alanine residue. (c) Estimate of the fraction of the conformational space, which is visited, as a function of the peptide chain length.

temperature (i.e. the fraction of the conformational space, which is visited is f=0.65)(Fig. 5.5.b). For the remaining 35% of the conformations the potential energy is so high (due to steric clashes) that they are inaccessible at room temperature. For a chain with n residues, the visited conformational space, which is visited, can be estimated as

$$f(n) \quad = \quad 0.65^n \tag{5.11}$$

Hence, the fraction of the conformational space which is accessible at room temperature decreases exponentially with the number of residues in a peptide chain (Fig. 5.5.c).

Due to the vastness of the conformational space, the Boltzmann entropy cannot be evaluated directly from the potential energy function. Instead, a sampling algorithm is needed which samples the relevant regions of the conformational space with high probability ($\rightarrow$ importance sampling).

109 residues: $f(n = 109) = 4.05094 \cdot 10^{-21}$, **Surface 1 cent coin:** $2.1904 \cdot 10^{-6}\text{m}^2$, **Surface earth:** $510\,072\,000\text{km}^2$, **Ratio:** $4.29429 \cdot 10^{-21}$

6 The canonical ensemble

6.1 The most likely ensemble configuration $\mathbf{n}^*$

A system in a canonical ensemble

- cannot exchange particles with its surroundings $\rightarrow$ constant N
- has constant volume V
- exchanges energy in the form of heat with a surrounding thermal reservoir $\rightarrow$ constant T, but not constant E

Challenge: Find the most likely configuration $\mathbf{k}^*$ which is consistent with constant N and T. But: how does one introduce "constant T" as a constraint into the equation?

Thought experiment: Consider a large set N_{ensemble} of identical systems with N particles and volume V. Each of the systems is in contact with the same thermal reservoir at temperature T, but the set of systems as whole is isolated from the surroundings. Thus the energy of the ensemble E_{ensemble} is constant This setting is called a *canonical ensemble*.

Each system is in a quantum state $\Psi_j(\mathbf{x}_1, \dots \mathbf{x}_N)$, where x_k are the are the coordinates of the kth particle within the system. The system quantum state is associated to an system energy via

$$E_j \, \Psi_j(\mathbf{x}_1, \dots \mathbf{x}_N) \quad = \quad \hat{H} \, \Psi_j(\mathbf{x}_1, \dots \mathbf{x}_N) = \sum_{k=1}^{N} \hat{h}_k \, \Psi_j(\mathbf{x}_1, \dots \mathbf{x}_N) \tag{6.1}$$

where $\hat{H}$ is the Hamiltonian of the system, $\hat{h}_k$ are the Hamiltonians of the individual particles. Thus, within the ensemble, each system plays the role of a "super-particle", and we can treat the ensemble as a system of "super-particles" at constant N_{ensemble} and E_{ensemble}. In analogy to section 4, we have the following assumptions

1. The systems are distinguishable, e.g. you can imagine them to be numbered.
2. The systems are independent of each other, i.e. they do not interact with each other.
3. Each system occupies on of N_E energy levels: $\{E_0, E_2, ...E_{N_E-1}\}$.
4. There can be multiple systems in the same energy level. The number of particles in the jth energy level is denoted n_j.

The configuration of the ensemble is given by the number of systems in each energy level $\mathbf{n} = (n_0, n_1, \dots n_{N_E-1})$. Each configuration can be generated by several ensemble microstates (ordered sequence of systems distributed according to $\mathbf{n}$). We again assume that the a priori probabilities p_j of the energy states E_j are equal. Then the probability of finding the ensemble in a configuration $\mathbf{n}$ is given as

$$p(\mathbf{n}) \quad = \quad \frac{N_{\text{ensemble}}!}{n_0! \cdot ... n_{N_E-1}!} \cdot p_j^{N_{\text{ensemble}}} \, . \tag{6.2}$$

The probability that the ensemble is in a particular configuation $\mathbf{n}$ is then proportional to the number of ensemble microstates which give rise to the configuration, i.e. to the weight of this configuration

$$W(\mathbf{n}) \quad = \quad \frac{N_{\text{ensemble}}!}{n_0! \cdot ... n_{N_E-1}!} \, . \tag{6.3}$$

The most likely confiuration $\mathbf{n}^*$ is obtained by setting the total derivative of the weight to zero

$$\mathrm{d} \ln W(\mathbf{n}) = - \sum_{j=0}^{N_E-1} \ln \frac{n_j}{N_{\text{ensemble}}} \, \mathrm{d}n_j - \sum_{j=0}^{N_E-1} \mathrm{d}n_j = 0 \tag{6.4}$$

and solving the equation under the constraints that the number of systems in the ensemble is constant

$$\mathrm{d}N_{\text{ensemble}} \quad = \quad \sum_{j=0}^{N_E-1} \mathrm{d}n_j = 0 \, , \tag{6.5}$$

and that the total energy of the ensemble is constant

$$\mathrm{d}E_{\text{ensemble}} = \sum_{j=0}^{N_E-1} \mathrm{d}n_j \cdot E_j = 0\,. \tag{6.6}$$

This yields the Boltzmann probability distribution of finding the system in an energy state E_j

$$p_j = \frac{1}{Q} e^{-\beta E_j} = \frac{e^{-\beta E_j}}{\sum_{j=0}^{N_E-1} e^{-\beta E_j}}\,. \tag{6.7}$$

where

$$Q = \sum_{j=0}^{N_E-1} e^{-\beta E_j}\,. \tag{6.8}$$

is the **partition function of the system** and $\beta = \frac{1}{k_b T}$.

6.2 Ergodicity

With eq. 6.7, we can make statements about the entire ensemble. For example, we can calculate the average energy $\langle E \rangle$ of the systems in the ensemble as

$$\langle E \rangle_{\text{ensemble}} = \sum_{j=0}^{N_E-1} p_j \cdot E_j = \frac{1}{N_{\text{ensemble}}} \sum_{j=0}^{N_E-1} n_j \cdot E_j \tag{6.9}$$

But how does this help us to characterize the thermodynamic properties of a single system? Each system exchanges energy with the thermal reservoir and therefore continuously changes its energy state. What we could calculate for a single system is its average energy measure over a period of time T

$$\langle E \rangle_{\text{time}} = \frac{1}{N_T} \sum_{t=1}^{N_T} E(t), \tag{6.10}$$

where we assumed that the energy of the single system has been measured at regular intervals Δ. Then $T = \Delta \cdot N_T$ and $E(t)$ is the energy of the single system measured at time interval t. The **ergodic hypothesis** relates these two averages

The average time a system spends in energy state E_j is proportional to ensemble probability p_j of this state.

Thus, ensemble average and time average are equal

$$\langle E \rangle_{\text{time}} = \frac{1}{N_T} \sum_{t=1}^{N_T} E(t) = \sum_{j=0}^{N_E-1} p_j \cdot E_j = \langle E \rangle_{\text{ensemble}} \tag{6.11}$$

and we can use eq. 6.7 to characterize the time average of single system.

6.3 Relevance of the time average

A single system in a canonical ensemble fluctuates between different system energy levels E_j. Using eq. 6.7 we can calculte its average energy $\langle E \rangle$. But how representative is the average energy for the current state of the system?

The total energy of the systems is proportional to the number of particles in the system: $E \sim N$. The variance from the mean (fluctuation) is proportional to $\sqrt{N}$: $\Delta E \sim \sqrt{N}$. Thus, the relative fluctuation is

$$\frac{\Delta E}{E} = \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}}, \tag{6.12}$$

and decreases with increasing number of particles. For large number of particles, e.g $N = 10^{20}$, the fluctuation around the average energy is neglible ($\frac{\Delta E}{E} \approx 10^{-10}$), and the system can be accurately characterize by its average energy. In small systems or for phenomena which involve only few particles in a system, e.g. phase transitions, the fluctuations of the energy need to be taken into account.

7 Thermodynamic state functions

In the following, we will express thermodynamics state functions as a function of the partition sum Q. The functional dependence on Q determines whether or not a particular thermodynamics state function can be easily estimated from MD simulation data

7.1 Average and internal energy

By definition, the average energy is

$$\langle E \rangle = \sum_{i=1}^{N_E} p_i \epsilon_i = \frac{1}{Q(N,V,\beta)} \sum_{i=1}^{N_E} \epsilon_i e^{-\beta \epsilon_i} . \tag{7.1}$$

Because the numerator is essentially a derivative of the partition function

$$\sum_{i=1}^{N_E} \epsilon_i e^{-\beta \epsilon_i} = -\left(\frac{\partial}{\partial \beta} Q(N,V,\beta) \right)_{N,V} = -\left(\frac{\partial}{\partial \beta} \sum_{i=1}^{N_E} e^{-\beta \epsilon_i} \right)_{N.V} \tag{7.2}$$

we can express the average energy as a function of $Q(N,V,\beta)$ only

$$\begin{aligned} \langle E \rangle &= -\frac{1}{Q(N,V,\beta)} \left(\frac{\partial}{\partial \beta} Q(N,V,\beta) \right)_{N,V} \\ &= -\left(\frac{\partial}{\partial \beta} \ln Q(N,V,\beta) \right)_{N,V} \end{aligned} \tag{7.3}$$

One can also express eq. 7.3 as a temperature derivative, rather than a derivative with respect to β

$$\frac{\partial f}{\partial T} = \frac{\partial f}{\partial \beta} \frac{\partial \beta}{\partial T} = \left(-\frac{1}{k_B T^2} \right) \frac{\partial f}{\partial \beta} \tag{7.4}$$

where we have used $\beta = 1/(k_B T)$. With this, eq. 7.3 becomes

$$\langle E \rangle = k_B T^2 \left(\frac{\partial}{\partial T} \ln Q(N,V,T) \right)_{N,V} . \tag{7.5}$$

The average energy is related to the internal energy U by

$$U = N \cdot \langle E \rangle = -N \left(\frac{\partial}{\partial \beta} \ln Q \right)_{N,V} = N k_B T^2 \left(\frac{\partial}{\partial T} \ln Q \right)_{N,V} . \tag{7.6}$$

Often, U is reported as molar quantity in which case

$$U = \cdot \langle E \rangle = -\left(\frac{\partial}{\partial \beta} \ln Q \right)_{N,V} = k_B T^2 \left(\frac{\partial}{\partial T} \ln Q \right)_{N,V} . \tag{7.7}$$

In the following, we will use molar quantities.

7.2 Entropy

Also, the entropy can be expressed as a function of the partition function $Q(N,V,T)$. We take eq. **??** as starting point

$$\begin{aligned} S &= -k_B \sum_i p_i \ln p_i \\ &= -k_B \sum_i \frac{\exp\left(-\frac{1}{k_B T} \epsilon_i\right)}{Q} \ln \left[\frac{\exp\left(-\frac{1}{k_B T} \epsilon_i\right)}{Q} \right] \end{aligned}$$

$$
\begin{aligned}
&= -k_B \sum_i \frac{\exp\left(-\frac{1}{k_B T}\epsilon_i\right)}{Q}\left[-\frac{1}{k_B T}\epsilon_i - \ln Q\right] \\
&= \frac{1}{T}\sum_i \frac{\epsilon_i \exp\left(-\frac{1}{k_B T}\epsilon_i\right)}{Q} + k_B \sum_i \frac{\exp\left(-\frac{1}{k_B T}\epsilon_i\right)}{Q}\ln Q \\
&= \frac{U}{T} + k_B \frac{\ln Q}{Q}\sum_i \exp\left(-\frac{1}{k_B T}\epsilon_i\right) \\
&= \frac{U}{T} + k_B \ln Q
\end{aligned} \tag{7.8}
$$

Replacing U by its relation to the partition function (eq. 7.7)

$$
S = N k_B T \left(\frac{\partial}{\partial T}\ln Q\right)_{N,V} + k_B \ln Q \tag{7.9}
$$

or expressed as a derivative with respect to β

$$
S = -\frac{N}{T}\left(\frac{\partial}{\partial \beta}\ln Q\right)_{N,V} + k_B \ln Q\,. \tag{7.10}
$$

7.3 Helmholtz free energy

Since the internal energy and the entropy can be expressed as a function of the partition function Q, we can also express the Helmholtz free energy as a function of Q

$$
A = U - TS = U - T\left(\frac{U}{T} + k_B \ln Q\right) = -k_B T \ln Q\,. \tag{7.11}
$$

7.3.1 Pressure and heat capacity at constant volume

The pressure as a function of the partition function is

$$
P = -\left(\frac{\partial A}{\partial V}\right)_T = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_T\,. \tag{7.12}
$$

The heat capacity at constant volume as a function of the partition function is

$$
\begin{aligned}
C_V &= \left(\frac{\partial U}{\partial T}\right)_V \\
&= \left(\frac{\partial}{\partial T}\left(N k_B T^2 \left(\frac{\partial}{\partial T}\ln Q\right)_{N,V}\right)\right)_V \\
&= 2N k_B T \left(\frac{\partial}{\partial T}\ln Q\right)_{N,V} + N k_B T^2 \left(\frac{\partial}{\partial T^2}\ln Q\right)_{N,V}
\end{aligned} \tag{7.13}
$$

7.4 Enthalpy

In the isothermal-isobaric ensemble, one has to account for the change in volume. The relevant thermodynamic properties are the enthalpy H and the Gibbs free energy G. The enthalpy is defined as

$$
H = U + PV\,. \tag{7.14}
$$

Expressed as a function of Q:

$$
H = N k_B T^2 \left(\frac{\partial}{\partial T}\ln Q\right)_{N,V} + k_B T V \left(\frac{\partial \ln Q}{\partial V}\right)_T\,. \tag{7.15}
$$

7.5 Gibbs free energy

The Gibbs free energy is

$$\begin{aligned} G &= H - TS = A + PV \\ &= -k_B T \ln Q + k_B T V \left(\frac{\partial \ln Q}{\partial V} \right)_T . \end{aligned} \tag{7.16}$$

name	equation
internal energy	$U = N k_B T^2 \left(\frac{\partial}{\partial T} \ln Q \right)_{N,V}$
entropy	$S = N k_B T \left(\frac{\partial}{\partial T} \ln Q \right)_{N,V} + k_B \ln Q$
Helmholtz free energy	$A = -k_B T \ln Q$
enthalpy	$H = N k_B T^2 \left(\frac{\partial}{\partial T} \ln Q \right)_{N,V} + k_B T V \left(\frac{\partial}{\partial V} \ln Q \right)_T$
Gibbs free energy	$G = -k_B T \ln Q + k_B T V \left(\frac{\partial \ln Q}{\partial V} \right)_T$

Table 1: Thermodynamic state function.

8 Crystals

In the previous lectures, we have derived the canonical partition function and its relation to various thermodynamic state functions. Given the energy levels of a system of N particles, we can now calculate its energy, its entropy and its free energy. The difficulty with which we will deal in the coming lectures is to calculate the energy levels of a system with N particles. A very useful approximation is to assume that the particles do not interact with each other, because for **non-interacting particles** the energy of the system is simply a sum of the energies of the individual particles. This assumption often works well for gases, crystals and mixtures.

8.1 Non-interacting distinguishable particles

Consider a system of N non-interacting and distinguishable particles. Each particle can be in one of N_ϵ energy levels $\{\epsilon_1, \epsilon_2, ...\epsilon_{N_\epsilon}\}$. The single-particle Schrödinger equation is

$$\epsilon_s \psi_s(\mathbf{x}_k) \quad = \quad \hat{h}_k \, \psi_s(\mathbf{x}_k) = -\frac{\hbar^2}{2m_k} \nabla_k^2 \, \psi_s(\mathbf{x}_k) + V_k(\mathbf{x}_k) \, \psi_s(\mathbf{x}_k) \tag{8.1}$$

where ϵ_s is the associated energy eigenvalue. If a system consists of N such particles which do not interact with each other and which are distinguishable, the time-independent Schrödinger equation of the system is given as

$$E_j \, \Psi_j(\mathbf{x}_1, \dots \mathbf{x}_N) \quad = \quad \hat{H} \, \Psi_j(\mathbf{x}_1, \dots \mathbf{x}_N) = \sum_{k=1}^{N} \hat{h}_k \, \Psi_j(\mathbf{x}_1, \dots \mathbf{x}_N) \tag{8.2}$$

The possible quantum states of the system are

$$\Psi_j(\mathbf{x}_1, \dots \mathbf{x}_N) \quad = \quad \psi_{s(1)}(\mathbf{x}_1) \otimes \psi_{s(2)}(\mathbf{x}_2) \cdots \otimes \psi_{s(N)}(\mathbf{x}_N) \tag{8.3}$$

where each state j corresponds to a specific placement of the individual particles on the energy levels of the single-particle system, i.e. to a specific permutation

$$j \quad \leftrightarrow \quad \{s(1), s(2) \dots s(N)\}_j \tag{8.4}$$

The associated energy level of the system is

$$E_j \quad = \quad \sum_{k=1}^{N} \epsilon_{s(k)} \tag{8.5}$$

The single-particle partition function is given as

$$q(N=1, V, T) \quad = \quad \sum_{s=1}^{N_\epsilon} \exp(-\beta \epsilon_s) \tag{8.6}$$

There are N_ϵ^N ways to distribute the N particles over the N_ϵ energy levels. Each of the resulting configurations gives rise to a system energy

$$E_j \quad = \quad \epsilon_{s(1)} + \epsilon_{s(2)} + ...\epsilon_{s(N)} \tag{8.7}$$

where $\epsilon_{s(k)}$ is the energy level of the kth particle. The partition function of the system is

$$Q \quad = \quad \sum_j \exp(-\beta E_j) = \sum_{s(l)=1}^{N_\epsilon} \sum_{s(m)=1}^{N_\epsilon} \dots \sum_{s(z)=1}^{N_\epsilon} \exp(-\beta[\epsilon_{s(l)} + \epsilon_{s(m)} + ...\epsilon_{s(z)}]) \tag{8.8}$$

In eq. 8.8, there are as many sums as there are particles in the system, such that all possible configurations are included in the summation. Luckily eq. 8.8 can be simplified.

For illustration, consider a system with $N = 2$ particles which can be in $N_\epsilon = 3$ energy levels. The partition function of this system is

$$\begin{aligned} Q &= \sum_{l=1}^{3}\sum_{m=1}^{3} \exp(-\beta[\epsilon_{s(l)} + \epsilon_{s(m)}]) \\ &= e^{-\beta\epsilon_1}e^{-\beta\epsilon_1} + e^{-\beta\epsilon_1}e^{-\beta\epsilon_2} + e^{-\beta\epsilon_1}e^{-\beta\epsilon_3} + \\ &\quad e^{-\beta\epsilon_2}e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2}e^{-\beta\epsilon_2} + e^{-\beta\epsilon_2}e^{-\beta\epsilon_3} + \\ &\quad e^{-\beta\epsilon_3}e^{-\beta\epsilon_1} + e^{-\beta\epsilon_3}e^{-\beta\epsilon_2} + e^{-\beta\epsilon_3}e^{-\beta\epsilon_3} + \\ &= \left[e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2} + e^{-\beta\epsilon_3}\right]^2 \\ &= \left[\sum_{i=1}^{3} e^{-\beta\epsilon_i}\right]^2 \\ &= q^N \end{aligned} \tag{8.9}$$

This can be generalized to arbitrary values of N and N_ϵ. Thus, the partition function of a system of N non-interacting and distinguishable particles can be factorized as

$$Q = q^N \tag{8.10}$$

where q is the single-particle partition function.

In most realistic systems, the particles are however indistunguishable due to their quantum nature. Thus, eq. 8.10 only applies to systems in which the particles are nonthelesss distinguishable because they are fixed to specific position in space. For example, it can be applied to calculate the thermodynamic properties of ideal crystals.

8.2 Crystals: Dulong-Petit law (1819)

We discuss the heat capacity of crystals

$$C_{m,V} = \left(\frac{\partial U_m}{\partial T}\right)_V \tag{8.11}$$

A first estimate can be obtained without the full formalism of statistical mechanics. The model assumptions are:

1. Particles in the crystal are bound to fixed positions in the crystal lattice.
2. The particles oscillate around their equilibrium positions in three dimensions (three degrees of freedom per particle).
3. The oscillations in each dimension are independent from the oscillations in the other diimensions and independent from the oscillations of other particles in the crystal.
4. The oscillations can be modelled by a harmonic oscillator.

According to the equipartition theorem, every degree of freedom has an average kinetic energy of

$$E_{\text{kin}} = \frac{1}{2}k_B T\,. \tag{8.12}$$

The average potential energy is equal to the average kinetic enegy $E_{\text{pot}} = E_{\text{kin}}$. Thus, the average total energy per degree of freedom is

$$E_{\text{tot}} = E_{\text{kin}} + E_{\text{pot}} = 2 \cdot \frac{1}{2}k_B T = k_B T\,. \tag{8.13}$$

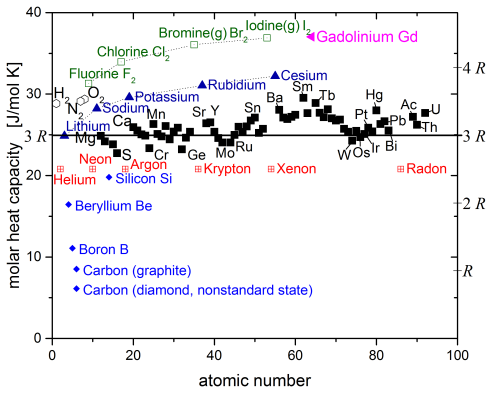
There are $3N$ degrees of freedom. The internal energy for 1 Mol particles is then

$$U = E_{\text{tot}} = 3 \cdot N_A \cdot k_B \cdot T = 3 \cdot R \cdot T \tag{8.14}$$

Thus, the estimate for the heat capacity is

$$C_{m,V} = \left(\frac{\partial U_m}{\partial T}\right)_V = \left(\frac{3 \cdot R \cdot}{\partial T}\right)_V = 3 \cdot R \tag{8.15}$$

This is the **Dulong-Petit law**. Is is a good approximation for many substances at room temperature, but fails at low and high temperatures.



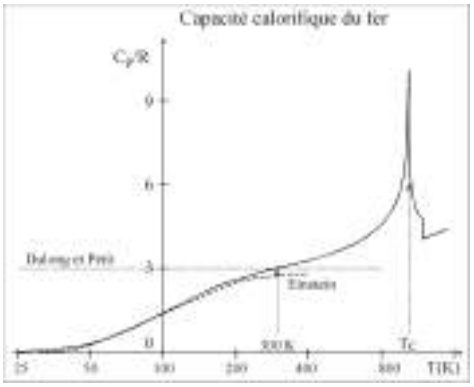


Figure 9: Heat capacity. https://commons.wikimedia.org/wiki/File:Cp_Fe.gif https://commons.wikimedia.org/wiki/File:GraphHeatCapacityOfTheElements.png

8.3 Crystals: Einstein model (1907)

The model of the temperature of the heat capacity at temperatures below 300 K can be drastically improved by the formalism of the statistical mechanics. The same model apply as for the Dulon-Petit law. However, in point 4 we use the quantum mechanical harmonic oscillator, and the internal energy is estimated via the partition function Q.

The energy levels of the Schrödinger equation for the harmonic oscillator (with potential $V(x) = \frac{1}{2}\kappa x^2$ where κ is the force constant) are

$$\epsilon_{\text{vib},\nu} = h\nu_0 \left(\nu + \frac{1}{2}\right) \tag{8.16}$$

with quantum numbers $\nu = 0, 1, 2, ...$ All energy levels are non-degenerate, i.e. $g_\nu = 1$ for all ν. Thus the partition function is given as

$$q_{\text{vib}} = \sum_{\nu=0}^{\infty} \exp\left[-\frac{1}{k_B T}\left(h\nu_0\left(\nu + \frac{1}{2}\right)\right)\right] = \exp\left[-\frac{h\nu_0}{k_B}\frac{1}{2T}\right] \cdot \sum_{\nu=0}^{\infty} \exp\left[-\frac{h\nu_0}{k_B}\frac{\nu}{T}\right] \tag{8.17}$$

We combine the constants into a new constant, the *characteristic temperature* or *Einstein temperature* Θ_{vib}

$$\Theta_{\text{vib}} = \frac{h\nu_0}{k_B} \tag{8.18}$$

and can rearrange eq. 11.12

$$q_{\text{vib}} = \exp\left[-\Theta_{\text{vib}}\frac{1}{2T}\right] \cdot \sum_{\nu=0}^{\infty} \exp\left[-\Theta_{\text{vib}}\frac{\nu}{T}\right] = \sum_{\nu=0}^{\infty} \left(\exp\left[-\Theta_{\text{vib}}\frac{1}{T}\right]\right)^{\nu}$$

$$= \frac{\exp\left[-\Theta_{\text{vib}}\frac{1}{2T}\right]}{1-\exp\left[-\frac{\Theta_{\text{vib}}}{T}\right]}. \tag{8.19}$$

We have used that vibrational partition function has the form of a geometric series, which converges

$$\sum_{\nu=0}^{\infty} q^{\nu} = \frac{1}{1-q} \tag{8.20}$$

with $q = \exp\left[-\frac{\Theta_{\text{vib}}}{T}\right]$. Note that

$$\nu_0 = \frac{\omega}{2\pi} = \frac{1}{2\pi}\sqrt{\frac{\kappa}{m}} \tag{8.21}$$

where m is the mass of the particle. Thus, the characteristic temperature Θ_{vib} on the force constant of the potential and the mass of the particle.

The partition function of a crystal with N particles is

$$Q = q_{\text{vib}}^{3N} = \left[\frac{\exp\left[-\Theta_{\text{vib}}\frac{1}{2T}\right]}{1-\exp\left[-\frac{\Theta_{\text{vib}}}{T}\right]}\right]^{3N}. \tag{8.22}$$

The internal energy is

$$\begin{aligned}
& U \\
= \; & k_B T^2 \left(\frac{\partial}{\partial T}\ln Q\right)_{N,V} \\
= \; & k_B T^2 \left(\frac{\partial}{\partial T}\ln\left[\frac{\exp\left[-\Theta_{\text{vib}}\frac{1}{2T}\right]}{1-\exp\left[-\frac{\Theta_{\text{vib}}}{T}\right]}\right]^{3N}\right)_{N,V} \\
= \; & k_B T^2 \left(\frac{\partial}{\partial T} 3N \ln\left[\frac{\exp\left[-\Theta_{\text{vib}}\frac{1}{2T}\right]}{1-\exp\left[-\frac{\Theta_{\text{vib}}}{T}\right]}\right]\right)_{N,V} \\
= \; & k_B T^2 \left(\frac{\partial}{\partial T} 3N \ln\left[\exp\left[-\Theta_{\text{vib}}\frac{1}{2T}\right]\right]\right)_{N,V} - k_B T^2 \left(\frac{\partial}{\partial T} 3N \ln\left[1-\exp\left[-\frac{\Theta_{\text{vib}}}{T}\right]\right]\right)_{N,V} \\
= \; & k_B T^2 \left(\frac{\partial}{\partial T}\left[-\Theta_{\text{vib}}\frac{3N}{2T}\right]\right)_{N,V} - k_B T^2 \cdot 3N \cdot \left[1-\exp\left[-\frac{\Theta_{\text{vib}}}{T}\right]\right]^{-1} \cdot \left(\frac{\partial}{\partial T}\left[1-\exp\left[-\frac{\Theta_{\text{vib}}}{T}\right]\right]\right)_{N,V} \\
= \; & k_B T^2 \left[\Theta_{\text{vib}}\frac{3N}{2T^2}\right] - k_B T^2 \cdot 3N \cdot \left[1-\exp\left[-\frac{\Theta_{\text{vib}}}{T}\right]\right]^{-1} \cdot \left(-\exp\left[-\frac{\Theta_{\text{vib}}}{T}\right]\right) \cdot \left(\frac{\Theta_{\text{vib}}}{T^2}\right) \\
= \; & \frac{3}{2}Nk_B\Theta_{\text{vib}} + k_B \cdot 3N \cdot \Theta_{\text{vib}} \cdot \frac{\exp\left[-\frac{\Theta_{\text{vib}}}{T}\right]}{1-\exp\left[-\frac{\Theta_{\text{vib}}}{T}\right]} \\
= \; & \frac{3}{2}Nk_B\Theta_{\text{vib}} + k_B \cdot 3N \cdot \Theta_{\text{vib}} \cdot \frac{1}{\exp\left[\frac{\Theta_{\text{vib}}}{T}\right]-1}
\end{aligned} \tag{8.23}$$

and the molar internal energy is

$$U = \frac{3}{2}NR\Theta_{\text{vib}} + R \cdot 3N \cdot \Theta_{\text{vib}} \cdot \frac{1}{\exp\left[\frac{\Theta_{\text{vib}}}{T}\right]-1}. \tag{8.24}$$

For the heat capacity, we obtain

$$C_{m,V} = \left(\frac{\partial U_m}{\partial T}\right)_V$$

$$= R \cdot 3N \cdot \left(\frac{\Theta_{\text{vib}}}{T}\right)^2 \cdot \frac{\exp\left[\frac{\Theta_{\text{vib}}}{T}\right]}{\left(\exp\left[\frac{\Theta_{\text{vib}}}{T}\right]-1\right)^2} \tag{8.25}$$

For high temperatures $T \gg \Theta_{\text{vib}}$ or $\frac{\Theta_{\text{vib}}}{T} << 1$, the Taylor expansion of $\exp\left[\frac{\Theta_{\text{vib}}}{T}\right]$ can be truncated after the linear term, and the equation approach the Dulong-Petit law

$$\begin{aligned} C_{m,V} &= R \cdot 3N \cdot \left(\frac{\Theta_{\text{vib}}}{T}\right)^2 \cdot \frac{1+\frac{\Theta_{\text{vib}}}{T}+\ldots}{\left(1+\frac{\Theta_{\text{vib}}}{T}+\cdots-1\right)^2} \\ &= R \cdot 3N \cdot \left(1+\frac{\Theta_{\text{vib}}}{T}+\ldots\right) \\ &\approx R \cdot 3N \end{aligned} \tag{8.26}$$

- In the Einstein model, the heat capacity depends on single substance dependent parameter: Θ_{vib}.
- The model can be further by accounting for coupled vibrations in the crystal (Debye theory) and for magnetic effects.

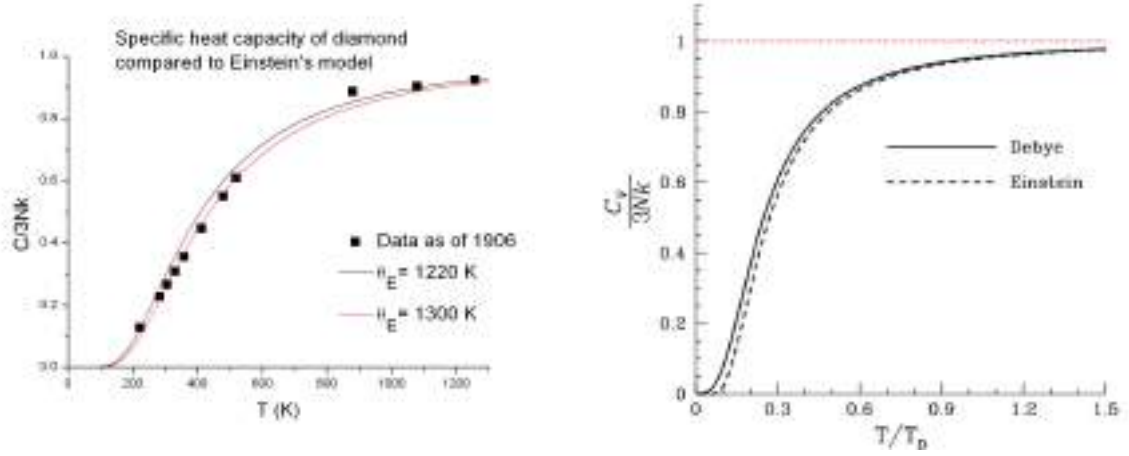


Figure 10: Heat capacity. http://www.hep.manchester.ac.uk/u/forshaw/BoseFermi/main.htm, https://commons.wikimedia.org/wiki/File:DebyeVSEinstein.jpg

9 Fermi-Dirac, Bose-Einstein, and Maxwell-Boltzmann statistics

9.1 Non-interacting indistinguishable particles

For a system of N non-interacting distinguishable particles, the wave functions is given as

$$\Psi_j(\mathbf{x}_1, \dots \mathbf{x}_N) \quad = \quad \psi_{s(1)}(\mathbf{x}_1) \otimes \psi_{s(2)}(\mathbf{x}_2) \cdots \otimes \psi_{s(N)}(\mathbf{x}_N) \tag{9.1}$$

where each state j corresponds to a specific placement of the individual particles on the energy levels of the single-particle system, i.e. to a specific permutation / microstate

$$j \quad \leftrightarrow \quad \{s(1), s(2) \dots s(N)\}_j \tag{9.2}$$

with an associated energy of

$$E_j \quad = \quad \sum_{k=1}^{N} \epsilon_{s(k)} \, . \tag{9.3}$$

The total number of microstates (analogous to the sample space in probability theory) is

$$\Omega = N_\epsilon^N \tag{9.4}$$

where N_ϵ is the number of energy levels in the single particle system. (The are N_ϵ choices to place the fist particle, N_ϵ choices to place the second particle etc.)

Example: Consider a system with $N = 2$ indistinguishable particles, denoted i and j. Each of the particles can occupy $N_\epsilon = 3$ energy levels. The total number of microstates is $\Omega = 3^2 = 9$. The possible configurations and their associated weights (number of microstates per configuration) are

$$\begin{aligned}
\mathbf{k}_1 = (0,0,2) \quad &\Rightarrow \quad W(\mathbf{k}_1) = \frac{2!}{0!0!2!} = 1 \\
\mathbf{k}_2 = (0,2,0) \quad &\Rightarrow \quad W(\mathbf{k}_2) = \frac{2!}{0!2!0!} = 1 \\
\mathbf{k}_3 = (2,0,0) \quad &\Rightarrow \quad W(\mathbf{k}_3) = \frac{2!}{2!0!0!} = 1 \\
\mathbf{k}_4 = (0,1,1) \quad &\Rightarrow \quad W(\mathbf{k}_4) = \frac{2!}{0!1!1!} = 2 \\
\mathbf{k}_5 = (1,0,1) \quad &\Rightarrow \quad W(\mathbf{k}_5) = \frac{2!}{1!0!1!} = 2 \\
\mathbf{k}_6 = (1,1,0) \quad &\Rightarrow \quad W(\mathbf{k}_6) = \frac{2!}{1!1!0!} = 2
\end{aligned} \tag{9.5}$$

yielding a total of 9 microstates. [3]. Represented as a table the microstates are

		j		
		ϵ_1	ϵ_2	ϵ_3
	ϵ_1	$(2,0,0)$	$(1,1,0)$	$(1,0,1)$
i	ϵ_2	$(1,1,0)$	$(0,2,0)$	$(0,1,1)$
	ϵ_3	$(1,0,1)$	$(0,1,1)$	$(0,0,2)$

Note that, by exchanging particles i and j, there are two ways the generate the configurations in the off-diagonal matrix elements, and hence $W(\mathbf{k}_4) = W(\mathbf{k}_5) = W(\mathbf{k}_6) = 2$, but there is only one way to generate the configurations in which both particles occupy the same energy level.

[3] Remember that the number of microstates per configuration $\mathbf{k}$ is given as $W(\mathbf{k}) = \frac{N!}{k_0! \dots k_{N_\epsilon - 1}!}$

9.2 Fermi-Dirac statistics

For fermions, the wave function change its sign upon the exchange of two particles k and l, but otherwise remains the same

$$\begin{aligned}\Psi_j(\mathbf{x}_1,\dots\mathbf{x}_k,\mathbf{x}_l\dots\mathbf{x}_N) &= \psi_{s(1)}(\mathbf{x}_1)\otimes\dots\psi_{s(k)}(\mathbf{x}_k)\otimes\psi_{s(l)}(\mathbf{x}_l)\otimes\dots\otimes\psi_{s(N)}(\mathbf{x}_N)\\ &= -\psi_{s(1)}(\mathbf{x}_1)\otimes\dots\psi_{s(k)}(\mathbf{x}_l)\otimes\psi_{s(l)}(\mathbf{x}_k)\otimes\dots\otimes\psi_{s(N)}(\mathbf{x}_N)\\ &= -\Psi_j(\mathbf{x}_1,\dots\mathbf{x}_l,\mathbf{x}_k\dots\mathbf{x}_N)\end{aligned} \tag{9.6}$$

This implies that there is can be at most 1 particle per spin-energy state, which further implies that $N_\epsilon > N$. In the two-particle example this means that microstates on opposited sites of the diagonal in this table are identical and only count once to the number of microstates. Thus, $W(\mathbf{k}_4) = W(\mathbf{k}_5) = W(\mathbf{k}_6) = 1$. The fact that the wave function has to change sign upon the exchange of two particles k and l implies that ther can be at most a single particle in each energy state. Proof: Consider a microstate with two particles in state $\psi_{s(k)}$

$$\begin{aligned}\Psi_j(\mathbf{x}_1,\dots\mathbf{x}_k,\mathbf{x}_l\dots\mathbf{x}_N) &= \psi_{s(1)}(\mathbf{x}_1)\otimes\dots\psi_{s(k)}(\mathbf{x}_k)\otimes\psi_{s(k)}(\mathbf{x}_l)\otimes\dots\otimes\psi_{s(N)}(\mathbf{x}_N)\\ &= \psi_{s(1)}(\mathbf{x}_1)\otimes\dots\psi_{s(k)}(\mathbf{x}_l)\otimes\psi_{s(k)}(\mathbf{x}_k)\otimes\dots\otimes\psi_{s(N)}(\mathbf{x}_N)\\ &= \Psi_j(\mathbf{x}_1,\dots\mathbf{x}_l,\mathbf{x}_k\dots\mathbf{x}_N)\\ &\neq -\Psi_j(\mathbf{x}_1,\dots\mathbf{x}_l,\mathbf{x}_k\dots\mathbf{x}_N)\,.\end{aligned} \tag{9.7}$$

In the two-particle example, this means that $W(\mathbf{k}_1) = W(\mathbf{k}_2) = W(\mathbf{k}_3) = 0$

The total number of microstates for a system of N fermoins is equal to the number of ways in which N indistinguishable particles can be places in N_ϵ single-particle quantum states, with the limitation of one particle per single-particle quantum state. The number of ways in which N distinguishable particles can be places in N_ϵ single-particle quantum states, with the limitation of one particle per single-particle quantum state is

$$N_\epsilon\cdot(N_\epsilon-1)\cdot\dots(N_\epsilon-N+1) = \frac{N_\epsilon!}{(N_\epsilon-N)!} \tag{9.8}$$

To account for the fact that the particles are indistinguishable, one has to divide by the number of permutation of the N particles and obtains

$$\Omega_{\text{fermion}} = \frac{N_\epsilon!}{(N_\epsilon-N)!N!} \tag{9.9}$$

In general, we however have an infinite number of single-particle quantum states. To account for this, we consider the density of states $D(\epsilon_i)$, i.e. the number of qunatum states g_i in an small energy interval $\epsilon_i+\delta\epsilon$

$$g_i = D(\epsilon_i)\delta\epsilon\,, \tag{9.10}$$

and the average number of particles N_i per quantum state ϵ_i

$$f(\epsilon_i) = \frac{N_i}{g_i} \tag{9.11}$$

(Fig. 11). For fermions, $f(_i) \in [0,1]$, or equivalently $N_i \leq g_i$. We assume that the particles in $\epsilon_i+\delta\epsilon$ can exchange with particles in the neighboring energy intervals. In equilibrium, the temperature T and the chemical potential μ are the same in all energy intervals.

Let A_i, U_i, and S_i be the free energy, the internal energy and the entropy of the subsystem, which are related by the Gibb-Helmholtz equation

$$A_i = U_i - TS_i\,. \tag{9.12}$$

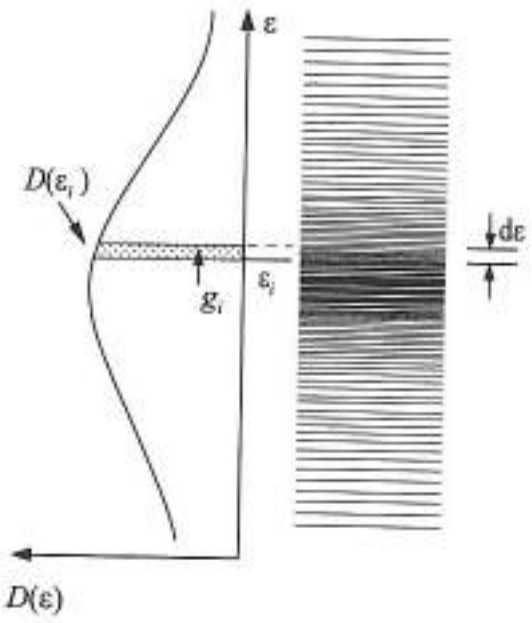


Figure 11: Density of states. W. Göpel, H.-D. Wiemhöfer, ãStatistische Thermodynamik", Spektrum Akademischer Verlag (2000)

The chemical potential is given as a the derivative of the free energy A_i with respect to the number of particles N_i in the subsystem

$$\mu = \left(\frac{\partial A_i}{\partial N_i}\right)_{T,V} = \left(\frac{\partial U_i}{\partial N_i}\right)_{T,V} - T\left(\frac{\partial S_i}{\partial N_i}\right)_{T,V} = \text{const.} \tag{9.13}$$

If $\delta\epsilon$ is very small, we have

$$U_i = N_i\epsilon_i \tag{9.14}$$

The Boltzmann entropy is

$$S_i = k_b \ln \Omega_i(N_i, g_i) \tag{9.15}$$

where Ω_i denotes the number of microstates in the energy interal $\epsilon_i + \delta\epsilon$ (extension of W - the number of microstates per configuration - which we had earlier in the course). Ω_i depends on the number of quantum states g_i and the number of particles N_i in this energy interval. Inserting eqs. 9.14 and 9.15 into eq. 9.16 yields

$$\mu = \epsilon_i - k_B T\left(\frac{\partial \ln \Omega_i}{\partial N_i}\right)_{T,V} = \text{const.} \tag{9.16}$$

For fermions, Ω_i is analogous to eq. 9.9

$$\Omega_{i,\text{fermion}} = \frac{g_i!}{(g_i - N_i)!N_i!} \tag{9.17}$$

Using the Stirling approximation, the derivative with respect to the number of particles in eq. 9.16 is

$$\left(\frac{\partial \ln \Omega_{i,\text{fermion}}}{\partial N_i}\right)_{T,V} \approx \ln\left[\frac{g_i - N_i}{N_i}\right] \tag{9.18}$$

and thus

$$\mu = \epsilon_i - k_B T \ln\left[\frac{g_i - N_i}{N_i}\right] = \text{const.} \tag{9.19}$$

The average number of particles per quantum state for a system of fermions is

$$f_{\text{fermions}}(\epsilon_i) = \frac{N_i}{g_i} = \left[\exp\left(\frac{\epsilon_i - \mu}{k_B T}\right) + 1\right]^{-1} \tag{9.20}$$

9.3 Bose-Einstein statistics

For bosones, the wave function does not change upon the exchange of two particles k and l

$$\begin{aligned} \Psi_j(\mathbf{x}_1, \ldots \mathbf{x}_k, \mathbf{x}_l \ldots \mathbf{x}_N) &= \psi_{s(1)}(\mathbf{x}_1) \otimes \ldots \psi_{s(k)}(\mathbf{x}_k) \otimes \psi_{s(l)}(\mathbf{x}_l) \otimes \cdots \otimes \psi_{s(N)}(\mathbf{x}_N) \\ &= \psi_{s(1)}(\mathbf{x}_1) \otimes \ldots \psi_{s(k)}(\mathbf{x}_l) \otimes \psi_{s(l)}(\mathbf{x}_k) \otimes \cdots \otimes \psi_{s(N)}(\mathbf{x}_N) \\ &= \Psi_j(\mathbf{x}_1, \ldots \mathbf{x}_l, \mathbf{x}_k \ldots \mathbf{x}_N) \end{aligned} \tag{9.21}$$

In the two-particle example this means that microstates on opposited sites of the diagonal in this table are identical and only count once to the number of microstates. Thus for bosones, $W(\mathbf{k}_4) = W(\mathbf{k}_5) = W(\mathbf{k}_6) = 1$. But wave functions with more than one particle per single-particle quantum state are permitted: $W(\mathbf{k}_1) = W(\mathbf{k}_2) = W(\mathbf{k}_3) = 1$.

The total number of microstates for a system with N bosones and N_ϵ single-particle quantum states is

$$\Omega_{\text{bosones}} = \frac{(N + N_\epsilon - 1)!}{(N!(N_\epsilon - 1)!} \tag{9.22}$$

(The derivation is more complicated than for fermions.) The extension to single particle quantum states is analogous the derivation for the fermions (eqs. 9.10 - 9.16). The number of microstates in the energy interval $\epsilon_i + \delta\epsilon$ for bosones is

$$\Omega_{i,\text{bosones}} = \frac{(N_i + g_i - 1)!}{(N_i!(g_i - 1)!} \tag{9.23}$$

Using the Stirling approximation, the derivative with respect to the number of particles in eq. 9.16 is

$$\left(\frac{\partial \ln \Omega_{i,\text{bosones}}}{\partial N_i}\right)_{T,V} \approx \ln\left[\frac{N_i + g_i - 1}{N_i}\right] \approx \ln\left[\frac{N_i + g_i}{N_i}\right] \tag{9.24}$$

and thus

$$\mu = \epsilon_i - k_B T \ln\left[\frac{N_i + g_i}{N_i}\right] = \text{const.} \tag{9.25}$$

The average number of particles per quantum state for a system of bosones is

$$f_{\text{bosones}}(\epsilon_i) = \frac{N_i}{g_i} = \left[\exp\left(\frac{\epsilon_i - \mu}{k_B T}\right) - 1\right]^{-1} \tag{9.26}$$

9.4 Maxwell-Boltzmann statistics

Bose-Einstein statistics and Fermi-Dirac statistics only differ by a in the sign before 1 in the numerator. If $\epsilon_i \gg \mu$, the exponential function becomes large, and the term 1 can be neglected. The resulting average number of particles per quantum state is the Maxwell-Boltzmann distribution

$$f_{\text{fermions}} \approx f_{\text{bosones}} \approx f_{\text{Maxwell-Boltzmann}} = \left[\exp\left(\frac{\epsilon_i - \mu}{k_B T}\right)\right]^{-1} \tag{9.27}$$

In all three types of statistic the average number of particles per quantum state is determined by the chemical potential within the energy scale μ and the temperature T. In some systems (e.g. diluted gases of atoms or molecules), the chemical potential can be much lower than the lowest single-particle energy - $\epsilon_i \gg \mu$ for all $\epsilon_i \geq \epsilon_0$ - and the Maxwell-Boltzmann statistics can be used.

The chemical potential μ can be related to the single-particle partition function q

$$\begin{aligned} N = \sum_i N &= \sum_i g_i \left[\exp\left(\frac{\epsilon_i - \mu}{k_B T} \right) \right]^{-1} \\ &= \sum_i g_i \exp\left(-\frac{\epsilon_i - \mu}{k_B T} \right) \\ &= \sum_i g_i \exp\left(-\frac{\epsilon_i}{k_B T} \right) \cdot \exp\left(\frac{\mu}{k_B T} \right) = q \cdot \exp\left(\frac{\mu}{k_B T} \right) \end{aligned} \tag{9.28}$$

and thus

$$\mu = -k_B T \ln \frac{q}{N} \,. \tag{9.29}$$

For $g_i \gg N_i$, the expressions for the chemical potential for fermions and bosones (eqs. 9.19 and 9.30) simplify

$$\mu \approx \epsilon_i - k_B T \ln \frac{g_i}{N_i} = \text{const.} \tag{9.30}$$

These two equations for μ can be combined to obtain an expression for the relative number of particles in the single-particle quantum state i

$$\frac{N_i}{g_i N} = \frac{f_{\text{Maxwell-Boltzmann}}}{N} = \frac{\exp\left(-\frac{\epsilon_i}{k_B T} \right)}{q} \tag{9.31}$$

This is the Boltzmann distribution.

10 Ideal mono-atomic gas

In a system with N indistinguishable bosones, eq. 8.10 overcounts the number of terms. One can correct this by dividing the partition function by the number of permutations for N particles

$$Q = \frac{q^N}{N!} \tag{10.1}$$

Eq. 10.1 is called **Maxwell-Boltzmann statistics**. It is an approximation to the true partition function, because q^N contains terms in which two or more particles occupy the same singl-particle energy level for which less than $N!$ permutations exist. Thus, by dividing everything by $N!$ one underestimates the partition function. The deviation from the true partition function is only significant if the number of microstates with two or more particles in the same energy level is a sizeable compared to the total number of microstates. In most physical systems, the number of single-particle energy levels is much larger than the number of particles, i.e. $N_\epsilon \gg N$, and the Maxwell-Boltzmann statistics is an excellent approximation.

10.1 Partition function

Consider a gas of N non-interacting atoms with mass m (ideal mono-atomic gas). Let us assume that the gas follows the Maxwell-Boltzmann statistics. Thus, its partition function is given as

$$Q = \frac{1}{N!} q^N \,. \tag{10.2}$$

where q is the single-particle partition function. The gas is confined to a container of volume

$$V = L_x \cdot L_y \cdot L_z \tag{10.3}$$

where L_x, L_y, andd L_z are the length of the container in x, y, and z direction. Since the gas of atoms the only contributions to its energy are the translational energy and the electronic energy. We neglect the contributions by the electronic energy, i.e we assume that all atoms are in the electronic ground state. The translational energy is given by the quantum mechanical treatment of a particle in a box (see exercise 2)

$$\epsilon_{\text{trans}} = \epsilon_x + \epsilon_y + \epsilon_z = \frac{h^2}{8m}\left[\left(\frac{n_x}{L_x}\right)^2 + \left(\frac{n_y}{L_y}\right)^2 + \left(\frac{n_z}{L_z}\right)^2\right] \tag{10.4}$$

where n_x, n_y, $n_z \in \mathbb{N}_{>0}$ are the quantum numbers. The single-particle partition function is hence given as

$$\begin{aligned} q_{\text{trans}} &= \sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} \exp\left[-\frac{\epsilon_x+\epsilon_y+\epsilon_z}{k_B T}\right] \\ &= \sum_{n_x=1}^{\infty} \exp\left[-\frac{h^2 n_x^2}{k_B T 8 m L_x^2}\right] \cdot \sum_{n_y=1}^{\infty} \exp\left[-\frac{h^2 n_y^2}{k_B T 8 m L_y^2}\right] \cdot \sum_{n_z=1}^{\infty} \exp\left[-\frac{h^2 n_z^2}{k_B T 8 m L_z^2}\right] . \end{aligned} \tag{10.5}$$

At room temperature, the energy level are so closely spaced that we can assume an energy continuum (half-classical approximation)

$$\sum_{n_x=1}^{\infty} \exp\left[-\frac{h^2 n_x^2}{k_B T 8 m L_x^2}\right] \approx \int_0^{\infty} \exp\left[-\frac{h^2 n_x^2}{k_B T 8 m L_x^2}\right] dn_x \,. \tag{10.6}$$

This integral is analogous to an integral over a Gauß function

$$\int_0^{\infty} \exp(-qx^2) dx = \frac{1}{2}\sqrt{\frac{\pi}{q}} \,. \tag{10.7}$$

Hence, we can write the single-particle partition function in a closed form

q_{trans}

$$
\begin{aligned}
&= \int_0^\infty \exp\left[-\frac{h^2}{k_B T 8 m L_x^2} n_x^2\right] dn_x \cdot \int_0^\infty \exp\left[-\frac{h^2}{k_B T 8 m L_y^2} n_y^2\right] dn_y \cdot \int_0^\infty \exp\left[-\frac{h^2}{k_B T 8 m L_z^2} n_z^2\right] dn_z \\
&= \frac{1}{2}\sqrt{\pi \frac{k_B T 8 m L_x^2}{h^2}} \cdot \frac{1}{2}\sqrt{\pi \frac{k_B T 8 m L_y^2}{h^2}} \cdot \frac{1}{2}\sqrt{\pi \frac{k_B T 8 m L_z^2}{h^2}} \\
&= \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \cdot V \qquad (10.8)
\end{aligned}
$$

where we have used eq. 10.3. The translational single-particle partition function depends on V, T, and m as

$$
\begin{aligned}
q_{\text{trans}} &\sim V \\
q_{\text{trans}} &\sim T^{3/2} \\
q_{\text{trans}} &\sim m^{3/2}\,. \qquad (10.9)
\end{aligned}
$$

Let us abbreviate eq. 10.8 as

$$
q_{\text{trans}} = \frac{V}{\lambda^3} \qquad (10.10)
$$

with

$$
\lambda = \left(\frac{h^2}{2\pi m k_B T}\right)^{1/2}. \qquad (10.11)
$$

The partition function for the system of N particles is given as

$$
Q = \frac{1}{N!} q_{\text{trans}}^N = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N \qquad (10.12)
$$

Thermal de Broglie wavelength. The factor λ has units of meters and can be interpreted as the wave length of the particle. It is also called the thermal de Boglie wavelength can be used to estimate at which particle densities the half-classical approximation breaks down and quantum effects start playing a role

$$
\left(\frac{V}{N}\right)^{\frac{1}{3}} \leq \lambda\,. \qquad (10.13)
$$

That is, if the volume per particle is smaller than λ^3, the approximation is not valid.

Using the definition of the de Broglie wave length, we obtain

$$
\begin{aligned}
\lambda &= \frac{h}{p} = \left(\frac{h^2}{2\pi m k_B T}\right)^{1/2} \\
&\Updownarrow \\
p &= \sqrt{2\pi m k_B T} \qquad (10.14)
\end{aligned}
$$

for the momentum of a single particle. The effective kinetic energy of a single particle is then

$$
E_{kin} = \frac{p^2}{2m} = \pi k_B T\,. \qquad (10.15)
$$

This expression differs from the average kinetic energy of an ideal gas particle, which is $E_{kin} = U = {}^3\!/_2 k_B T$ and will be derived in the following section. This is because eq. 10.15 has been derived from the single-particle partition function, i.e it does not acount for the fact that there are N particles in the box and that the particles are indistinguishable. The expression in eq. 10.15 exists. I however could not find out in which situations it is useful.

10.2 Thermodynamic state functions

Most thermodynamic state functions are a function of the logarithm of the partition function. Thus,

$$\begin{aligned} \ln Q &= \ln \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N \\ &= N \ln\left[\frac{V}{\lambda^3}\right] - \ln N! \\ &\approx N \ln\left[\frac{V}{\lambda^3}\right] - N \ln[N] + N \end{aligned} \tag{10.16}$$

where we have used Stirling's approximation.

The **Helmholtz free energy** is given as

$$A = -k_B T \ln Q = -k_B T N \ln\left[\frac{V}{\lambda^3}\right] + k_B T N \left(\ln[N] - 1\right) . \tag{10.17}$$

The **ideal gas law** is obtained by deriving eq. 10.17 with respect to the volume

$$p = -\left(\frac{\partial A}{\partial V}\right)_{T,N} = \frac{k_B T N}{V} = \frac{nRT}{V} \tag{10.18}$$

where the ideal gas constant is given as $R = k_B N_A$. N_A is Avogadro's constant and $n = N/N_A$. The **molar inner energy** ($N = N_A$) is given as

$$\begin{aligned} U_m &= k_B T^2 \left(\frac{\partial \ln Q}{\partial T}\right)_{V,N} \\ &= k_B T^2 \left(\frac{\partial}{\partial T} N_A \ln \frac{1}{\lambda^3}\right)_{V,N} \\ &= k_B T^2 N_A \left(\frac{\partial}{\partial T} \ln\left(\frac{h^2}{2\pi m k_B T}\right)^{-3/2}\right)_{V,N} \\ &= k_B T^2 N_A \frac{3}{2}\left(\frac{\partial}{\partial T} \ln\left(\frac{2\pi m k_B T}{h^2}\right)\right)_{V,N} \\ &= k_B T^2 N_A \frac{3}{2}\frac{1}{T} \\ &= \frac{3}{2} k_B T N_A \\ &= \frac{3}{2} RT . \end{aligned} \tag{10.19}$$

The **molar heat capacity** is given as

$$C_{V,m} = \left(\frac{\partial U}{\partial T}\right)_{N,V} = \frac{3}{2} R . \tag{10.20}$$

The **entropy** of mono-atomic ideal gas is given as

$$\begin{aligned} S &= \frac{U - A}{T} \\ &= \frac{3}{2} k_B N + k_B N \ln\left[\frac{V}{\lambda^3}\right] - k_B N \left(\ln[N] - 1\right) \\ &= k_B N \left(\frac{3}{2} + 1 + \ln\left[\frac{V}{\lambda^3}\right] - \ln[N]\right) \\ &= k_B N \left(\frac{5}{2} - \ln\left[\lambda^3\right] + \ln\left[\frac{V}{N}\right]\right) \\ &= k_B N \left(\frac{5}{2} - \frac{3}{2}\ln\left[\frac{h^2}{2\pi m k_B T}\right] + \ln\left[\frac{V}{N}\right]\right) \end{aligned}$$

$$= k_B N \left(\frac{5}{2} + \frac{3}{2} \ln \left[\frac{2\pi m k_B}{h^2} \right] + \frac{3}{2} \ln T + \ln \left[\frac{V}{N} \right] \right) \tag{10.21}$$

This is the **Sackur-Tetrode equation**, which one also finds in the following rearrangements

$$\begin{aligned} S &= k_B N \left(\frac{5}{2} + \ln \left[\left(\frac{V}{N} \right) \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \right] \right) \\ &= k_B N \left(\frac{5}{2} + \ln \left[\left(\frac{V}{N} \right) \left(\frac{4\pi m}{3h^2} \frac{U}{N} \right)^{3/2} \right] \right) \end{aligned} \tag{10.22}$$

and

$$S = k_B N \left(\frac{5}{2} + \ln \left[\frac{V}{N\lambda^3} \right] \right) . \tag{10.23}$$

10.3 Gibbs paradoxon

From a theoretical point of view, atoms are indistinguihsable and need to be described by quantum mechanics. Thus, the factor $N!$ arises in eq. 10.2. But is this factor consistent with macroscopic observations? Let's reformulated the entropy of an ideal gas without the factor $N!$ (i.e. assuming distinguishable particles). Eq. 10.21 then becomes

$$S_1 = \frac{3}{2} k_B N + k_B N \ln \left[\frac{V}{\lambda^3} \right] \tag{10.24}$$

If we double the system (i.e. $N \to 2N$, $N \to 2V$) the entropy of a gas of distinguishable particles is

$$\begin{aligned} S_2 &= 3k_B N + k_B 2N \ln \left[\frac{2V}{\lambda^3} \right] \\ &= 3k_B N + k_B 2N \ln \left[\frac{V}{\lambda^3} \right] + k_B 2N \ln [2] \\ &= 2S_1 + k_B 2N \ln [2] \end{aligned} \tag{10.25}$$

This is in contrast to the observation in classical thermodynamics, which requires that the entropies doubles of the systems size doubles

$$S_2 = 2S_1 . \tag{10.26}$$

One the other hand, eq. 10.23, which was derived for indistinguishable particles, fulfills the observed additivity of the entropy. Hence, the factor $N!$ is necessary in the partition function of ideal gases.

11 Ideal gas with internal degrees of freedom

In this chapter we consider a gas of N molecules which do not interact with each other. Hence, the partition function Q can be factorized into the single-particle partition functions q and, assuming Maxwell-Boltzmann statistics, it is given as

$$Q = \frac{q^N}{N!}. \tag{11.1}$$

To calculate the single-particle partition function, we need to know the total energy of a single molecule. At moderate temperatures, the energy of a single molecule can be approximated by a sum over seperate energy term

$$\epsilon_{\text{molecule}} = \epsilon_0 + \epsilon_{\text{trans}} + \underbrace{\epsilon_{\text{vib}} + \epsilon_{\text{rot}} + \epsilon_e + \epsilon_n}_{\epsilon_{\text{int}}}. \tag{11.2}$$

ϵ_0 is the energy of the molecule if all contributing terms are in the ground state, i.e. the ground state energy is moved to seperate term and all other terms are zero for the lowest quantum number. ϵ_{trans} is the translational energy. The following four terms are grouped together to yield the internal energy ϵ_{int}: the vibrational energy ϵ_{vib}, the rotational energy ϵ_{rot}, the electronic energy ϵ_e, and the energy of the nuclear degrees of freedom ϵ_n. The single-particle partition function is thus given as a product

$$\begin{aligned} q_{\text{molecule}} &= q_0 \cdot q_{\text{trans}} \cdot \underbrace{q_{\text{vib}} \cdot q_{\text{rot}} \cdot q_e \cdot q_n}_{q_{\text{int}}} \cdot \\ &= q_{\text{trans}} \cdot q_{\text{int}} \cdot e^{-\epsilon_0/k_B T}. \end{aligned} \tag{11.3}$$

and the partition function of the system is given as

$$\begin{aligned} Q &= \frac{1}{N!} q_{\text{molecule}}^N \\ &= \frac{1}{N!} q_{\text{trans}}^N \cdot q_{\text{int}}^N \cdot e^{-N\epsilon_0/k_B T} \\ &= Q_{\text{trans}} \cdot Q_{\text{int}} \cdot e^{-N\epsilon_0/k_B T}, \end{aligned} \tag{11.4}$$

where we have incorporated the factor $1/N!$ into the translational partition function. In chapter 10, we have derived an expression for the translational partition function

$$Q_{\text{trans}} = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N \tag{11.5}$$

where V is the volume and λ is the

11.1 Electronic partition function

The electronic partition function is given as

$$q_e = \sum_{i=0}^{\infty} g_{e,i} \exp\left(-\frac{\epsilon_{e,i}}{k_B T}\right) \tag{11.6}$$

where $\epsilon_{e,i}$ is the energy of the ith electronic state and $g_{e,i}$ is the degeneracy of this state. The ground state electronic energy is incorporated into the term ϵ_0 in the total moleculer energy. Thus, $\epsilon_{e,0} = 0$ and the first term only contains the degeneracy of the electronic ground state

$$q_e = g_{e,0} + g_{e,1} \exp\left(-\frac{\epsilon_{e,1}}{k_B T}\right) + g_{e,2} \exp\left(-\frac{\epsilon_{e,2}}{k_B T}\right) + ... \tag{11.7}$$

For most molecules at moderate temperatures, the first excited electronic state is high compared to $k_B T$. Hence, the higher electronic states are hardly populated and can be neglected.

$$q_e = g_{e,0} \qquad \text{if } \epsilon_{e,i\geq 1} - \epsilon_{e,0} \gg k_B T \tag{11.8}$$

For most molecules, the degeneracy of the electronic ground state is $g_{e,0} = 1$ and therefore $q_e = 1$. Exceptions are molecules with an odd number of electrons, such as NO or NO_2, but also O_2.

11.2 Nuclear partition function

Similar to the electronic energy levels, typically only the nuclear ground state of an atom is populated (at moderate temperatures). Hence the nuclear partition function is given by the degeneracy of the nuclear ground state which for an atom with nuclear spin I is given as

$$z_n = g_{n,0} = 2I + 1 \tag{11.9}$$

For a molecule with N_{atom} atoms, one needs to take the degeneracy of the nuclear ground state of all atoms into account and thus

$$z_n = \prod_{i=1}^{N_{\text{atom}}} (2I_i + 1)\,. \tag{11.10}$$

Many atoms have spin $I = 0$ and contribute a factor $g_{n,0} = 1$ to the partition function. One has however to pay attention to molecules with a rotational symmetry. Atoms which are symmetry equivalent are also indistinguishable. If these atoms additionally have a spin greater than zero, the rotational partition function cannot be decoupled from the rotational partition function.

11.3 Vibrational partition function

Two-atomic molecules. For a two-atomic molecule, the molecular vibration can be modelled by a one-dimensional harmonic potential along the bond vector. The corresponding Schrödinger equation is the Schrödinger equation for the harmonic oscillator with energy levels

$$\epsilon_{\text{vib},\nu} = h\nu_0 \left(\nu + \frac{1}{2}\right) \tag{11.11}$$

with quantum numbers $\nu = 0, 1, 2, ...$ All energy levels are non-degenerate, i.e. $g_\nu = 1$ for all ν. The ground state energy $\epsilon = {}^1\!/_2 h\nu_0$ is incorporated into the ground state energy of the molecule ϵ_0. Thus the partition function is given as

$$q_{\text{vib}} = \sum_{\nu=0}^{\infty} \exp\left[-\frac{1}{k_B T}\left(\epsilon_{\text{vib},\nu} - \frac{1}{2}h\nu_0\right)\right] = \sum_{\nu=0}^{\infty} \exp\left[-\frac{1}{k_B T}\nu h\nu_0\right] \tag{11.12}$$

We combine the constants into a new constant, the *characteristic temperature* Θ_{vib}

$$\Theta_{\text{vib}} = \frac{h\nu_0}{k_B} \tag{11.13}$$

and can rearrange eq. 11.12

$$\begin{aligned} q_{\text{vib}} &= \sum_{\nu=0}^{\infty} \exp\left[-\Theta_{\text{vib}}\frac{\nu}{T}\right] = \sum_{\nu=0}^{\infty}\left(\exp\left[-\Theta_{\text{vib}}\frac{1}{T}\right]\right)^{\nu} \\ &= \frac{1}{1 - \exp\left[-\frac{\Theta_{\text{vib}}}{T}\right]}\,. \end{aligned} \tag{11.14}$$

We have used that vibrational partition function has the form of a geometric series, which converges

$$\sum_{\nu=0}^{\infty} q^\nu = \frac{1}{1-q} \tag{11.15}$$

with $q = \exp\left[-\frac{\Theta_{\text{vib}}}{T}\right]$.

Molecules with more than two atoms. Using a normal mode analysis, one can decompose the complex vibration of a molecule with more than two atoms in a superposition of harmonic oscillations. The vibration in each of these so-called normal modes can be described by an independent harmonic oscillator with a specific ground state frequency ν_0. Thus, the total vibrational energy of a molecule is given as sum of the energies of harmonic oscillators. For linear molecules, this sum has $3N_{\text{atom}} - 5$ terms and for non-linear molecules, it has $3N_{\text{atom}} - 6$ terms

$$\begin{aligned} \epsilon_{\text{vib}} &= \sum_{i=1}^{3N_{\text{atom}}-6(5)} \epsilon_{\text{vib}}(\nu_i; \nu_{0,i}) - \frac{1}{2} h\nu_{i,0} \\ &= \sum_{i=1}^{3N_{\text{atom}}-6(5)} h\nu_{i,0}\, \nu_i \,. \end{aligned} \tag{11.16}$$

where we shifted the ground state energy to zero. The single-particle vibrational partition function is the thus given as

$$\begin{aligned} q_{\text{vib}} &= \sum_{\nu_1=0}^{\infty} \sum_{\nu_2=0}^{\infty} \cdots \sum_{\nu_{3N-6(5)=0}}^{\infty} \exp\left[-\frac{1}{k_B T} \epsilon_{\text{vib}}(\nu_i)\right] \\ &= \sum_{\nu_1=0}^{\infty} \sum_{\nu_2=0}^{\infty} \cdots \sum_{\nu_{3N-6(5)=0}}^{\infty} \exp\left[\sum_{i=1}^{3N_{\text{atom}}-6(5)} -\frac{\Theta_{\text{vib},i}}{T} \nu_i\right] \\ &= \sum_{\nu_1=0}^{\infty} \sum_{\nu_2=0}^{\infty} \cdots \sum_{\nu_{3N-6(5)=0}}^{\infty} \prod_{i=1}^{3N_{\text{atom}}-6(5)} \exp\left[-\frac{\Theta_{\text{vib},i}}{T} \nu_i\right] \\ &= \prod_{i=1}^{3N_{\text{atom}}-6(5)} \sum_{\nu_i=0}^{\infty} \left(\exp\left[-\frac{\Theta_{\text{vib},i}}{T}\right]\right)^{\nu_i} \\ &= \prod_{i=1}^{3N_{\text{atom}}-6(5)} q_{\text{vib}}(\Theta_{\text{vib},i}) \end{aligned} \tag{11.17}$$

[4] The characteristic frequencies $\nu_{0,i}$ of the normal modes can be obtained by carrying out a normal mode analysis using a quantum chemistry software. Alternatively, they can be measured by IR or Raman spectroscopy Note however that this approach is only useful for relatively small molecules. For large molecules the assumption that vibrational and rotational modes are decoupled is not valid. Moreover, the normal mode analysis is only valid for a molecule close to a minimum in the potential energy surface. Should the potential energy surface have more than one minimum, i.e. should the molecule have several conformations, the normal mode analysis needs to be carried out for each minimum and the different conformations need to be accounted for in the partition function.

[4] You can exchange sum and product, e.g.

$$\begin{aligned} \sum_{x_1=1}^{3} \sum_{x_2=1}^{3} \prod_{i=1}^{2} x_i &= \sum_{x_1=1}^{3} \sum_{x_2=1}^{3} x_i \cdot x_2 = 1\cdot 1 + 1\cdot 2 + 1\cdot 3 + 2\cdot 1 + 2\cdot 2 + 2\cdot 3 + 3\cdot 1 + 3\cdot 2 + 2\cdot 3 \\ &= (1+2+3)\cdot(1+2+3) = \prod_{i=1}^{2} \sum_{x_i=1}^{3} x_i \end{aligned}$$

11.4 Rotational partition function

Molecules rotate around their axes of inertia. The moment of intertia I for a diatomic molecule is given as

$$I = m_1 r_1^2 + m_2 r_2^2 = \mu r_0^2 \tag{11.18}$$

where m_1 and m_2 are the masses of the two atoms and r_1 and r_2 are the respective distances to the center of mass. The rotation can be described by an equivalent one-particle problem, in which the particle with reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{11.19}$$

rotates around a fixed center at a radius

$$r_0 = r_1 + r_2 \,. \tag{11.20}$$

The quantum mechanical treatment of this problem is called the "quantum-mechanical rigid rotator" and yield energy levels

$$\epsilon_{\mathsf{rot},J} = J(J+1)\frac{h^2}{8\pi^2 I} \qquad \text{with } J = 0, 1, 2, ... \tag{11.21}$$

where J is the rotational quantum number. The energy levels are degenerate with a degeneracy factor

$$g_J = 2J + 1 \,. \tag{11.22}$$

(Note that the rotational ground state with $J = 0$ and $g_J = 1$ is the only rotational state which is not degenerate.) Hence we obtain for the rotational partition function

$$q_{\mathsf{rot}} = \sum_{J=0}^{\infty} (2J+1) \exp\left[-\frac{1}{k_B T} J(J+1)\frac{h^2}{8\pi^2 I}\right] . \tag{11.23}$$

Analogously to the vibrational partition function, we combine the constants in the exponent into a new constant, the *characteristic temperature* for the rotation Θ_{rot}

$$\Theta_{\mathsf{rot}} = \frac{h^2}{k_B 8\pi^2 I} \tag{11.24}$$

and rewrite the rotational partition function as

$$q_{\mathsf{rot}} = \sum_{J=0}^{\infty} (2J+1) \exp\left[-J(J+1)\frac{\Theta_{\mathsf{rot}}}{T}\right] . \tag{11.25}$$

For many common molecules, the rotational characteristic temperature is very small - in the order of 0.1 to 1 K. Molecules with a small moment of intertia can have larger characteristic temperatures, which are however still well below room temperature. Examples are H_2: $\Theta_{\mathsf{rot}} = 87.6$ K or HF: $\Theta_{\mathsf{rot}} = 30.2$ K (see https://en.wikipedia.org/wiki/Rotational_temperature)

Population of the rotational energy levels. The relative population of the rotational energy levels p_J is given as

$$p_J = \frac{N_J}{N} \sim (2J+1) \exp\left[-J(J+1)\frac{\Theta_{\mathsf{rot}}}{T}\right] . \tag{11.26}$$

where N_J is the number of particles in rotational state J (see Fig. 12). The rotational level with the highest relative population is given as

$$J_{\mathsf{max}} = \sqrt{\frac{T}{2\Theta_{\mathsf{rot}}}} - \frac{1}{2} \,. \tag{11.27}$$

This value is a measure how dense the rotational states are. Since the shape of the population distribution is the same for all diatomic molecules, J_{max} tells us how many states can be found before the maximum.

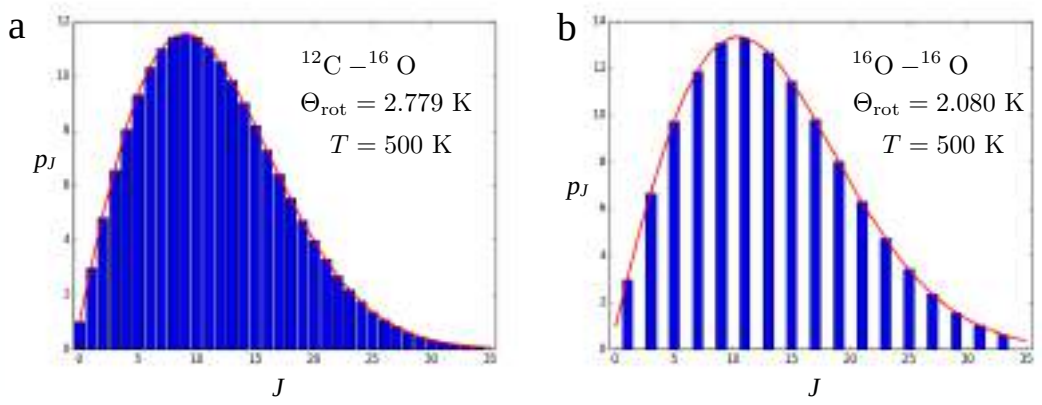


Figure 12: Population of the rotational levels for diatomic molecules. **a**: ^{12}C-^{16}O; **b**: ^{16}O-^{16}O.

High temperature approximation: diatomic unsymmetric molecules At high temperatures (i.e. $\Theta_{\rm rot} \gg T$), the energy levels of diatomic molecules are sufficiently closely spaced that we can replace the sum in eq. 11.23 by an integral.

$$\begin{aligned} q_{\rm rot} &= \sum_{J=0}^{\infty} (2J+1) \exp\left[-J(J+1)\frac{\Theta_{\rm rot}}{T}\right] \\ &\approx \int (2J+1) \exp\left[-J(J+1)\frac{\Theta_{\rm rot}}{T}\right] dJ \\ &= \int (2J+1) \exp\left[-x\frac{\Theta_{\rm rot}}{T}\right] \frac{dx}{2J+1} \\ &= \int \exp\left[-x\frac{\Theta_{\rm rot}}{T}\right] dx \\ &= -\frac{T}{\Theta_{\rm rot}} \left| \exp\left[-x\frac{\Theta_{\rm rot}}{T}\right] \right|_0^{\infty} \\ &= \frac{T}{\Theta_{\rm rot}} . \end{aligned} \tag{11.28}$$

This equation is valid for diatomic unsymmetric molecules, such as CO, NO or ^{35}Cl^{37}Cl and linear unsymmetric molecules with more than two atoms, such as OCS and HCCD.

High temperature approximation: diatomic symmetric molecules In symmetric linear molecules, such as H_2, CO_2, C_2H_2, a rotation around their symmetry axis by 180° generates a structure which is indistinguishable from the original structure. Therefore only half of the rotational wavefunctions are allowed (whether wave function with odd or even symmetry are allowed depends on the nuclear spins) (see Fig. 12.b) and the rotational partition function is reduced by the factor 2 compared to an analogous unsymmetric molecule.

$$q_{\rm rot} = \frac{1}{2}\frac{T}{\Theta_{\rm rot}} . \tag{11.29}$$

Eq. 11.28 and eq. 11.29 can be summarized as

$$q_{\rm rot} = \frac{1}{\sigma}\frac{T}{\Theta_{\rm rot}} \qquad \begin{cases} \sigma = 1 & \text{unsymmetric linear molecule} \\ \sigma = 2 & \text{symmetric linear molecule} \end{cases} \tag{11.30}$$

where σ is the symmetry number.

High temperature approximation: nonlinear molecules Linear molecules have two rotational axes A and B with identical moments of inertia $I_A = I_B$ and hence $\Theta_{\rm rot} = \Theta_{{\rm rot},A} = \Theta_{{\rm rot},B}$. Nonlinear molecules

have three rotational axes A, B, and C with different moments of inertia I_A, I_B, and I_C. Each of the axes has its own characteristic temperature $\Theta_{\mathsf{rot},A}$, $\Theta_{\mathsf{rot},B}$, and $\Theta_{\mathsf{rot},C}$. For the rotational partition function of nonlinear molecules one obtains

$$q_{\mathsf{rot}} = \frac{\pi^{1/2}}{\sigma}\left[\frac{T}{\Theta_{\mathsf{rot},A}}\cdot\frac{T}{\Theta_{\mathsf{rot},B}}\cdot\frac{T}{\Theta_{\mathsf{rot},C}}\right]^{1/2} = \left(\frac{8\pi k_B T}{h^2}\right)^{3/2}\frac{(\pi I_A I_B I_C)^{1/2}}{\sigma} \tag{11.31}$$

Again σ is the symmetry number, i.e the number of symmetry operations which yield conformation which is indistinguishable from the starting conformation. For example $\sigma(\mathsf{HCl}) = 1$, $\sigma(\mathsf{H_2}) = 2$, $\sigma(\mathsf{NH_3}) = 3$, $\sigma(\mathsf{CH_4}) = 12$, $\sigma(\mathsf{benzene}) = 12$.

Nuclear spins and rotational states: $\mathsf{O_2}$ The stable isotopes of oxygen are

- ^{16}O, abundance: 99.757%, nuclear spin: $I = 0$
- ^{17}O, abundance: 0.038%, nuclear spin: $I = \frac{5}{2}$
- ^{18}O, abundance: 0.205%, nuclear spin: $I = 0$

The molecular wave function $\mathsf{O_2}$ is

$$\Psi(\mathsf{O_2}) \approx \psi_{\mathsf{trans}}\cdot\psi_{\mathsf{rot}}\cdot\psi_{\mathsf{vib}}\cdot\psi_{\mathsf{e}}\cdot\psi_{\mathsf{n}} \tag{11.32}$$

If the $\mathsf{O_2}$ molecule consists of atomes of the same isotope, the wavefunction must obey the symmetry / anti-symmetry properties of the corresponding isotopes, i.e.

a. $\Psi(\mathsf{O_2})$ is symmetric for the exchange of the two atoms

$$+\Psi(\mathsf{O_2}) \xrightarrow{\text{exchange}} +\Psi(\mathsf{O_2})$$

if the isotopes are bosones (^{16}O or ^{18}O)

b. $\Psi(\mathsf{O_2})$ is anti-symmetric for the exchange of the two atoms

$$+\Psi(\mathsf{O_2}) \xrightarrow{\text{exchange}} -\Psi(\mathsf{O_2})$$

if the isotopes are fermions (^{17}O)

The electronic ground state of $\mathsf{O_2}$ is anti-symmetric with respect to the exchange of the two atoms. ψ_{vib} and ψ_{vib} depend on the positions of the center of mass and the distance between the two atoms and are therefore symmetric with respect to an exchange of the two atoms. Thus the product $\psi_{\mathsf{trans}}\cdot\psi_{\mathsf{vib}}\cdot\psi_{\mathsf{e}}$ is anti-symmetric for all isotopes. Whether the molecule wave function $\Psi(\mathsf{O_2})$ is symmetric or anti-symmetric depends on the symmetry of $\psi_{\mathsf{rot}}\cdot\psi_{\mathsf{n}}$.

For the two bosone isotopes (^{16}O or ^{18}O), ψ_{n} is symmetric because both nuclei can only be in one quantum state: $I = 0$. Thus for ^{16}O-^{16}O and ^{18}O-^{18}O , the rotational wave function ψ_{rot} must be antisymmetric such that the molecular wave function is symmetric. This means, that rotational states with even quantum number $J = 0, 2, 4...$ are not allowed and only rotational states with odd quantum numbers $J = 1, 3, 5, ...$ are occupied (see Fig. 12.b). By far the vast majority of the molecules in natural oxygen are ^{16}O-^{16}O. In these molecules half of the rotational are "missing". By comparison, ^{16}O-^{17}O has the full set of rotational states.

For the fermion isotope (^{17}O, $I = 5/2$), each nucleus can assume $2I + 1 = 6$ different quantum states. The nuclear wave function ψ_{n} has hence a degeneracy of

$$g_n = (2I + 1)\cdot(2I + 1) = 36\,.$$

Of these 36 degenerate states, 15 have a antisymmetric nuclear wavefunction and 21 have a symmetric nuclear wavefunction. Therefore ^{17}O-^{17}O exists in two different variants: (i) ψ_{n} anti-symmetric, and (ii) ψ_{n} symmetric. In variant i the rotational wavefunction has to be anti-symmetric such that $\Psi(\mathsf{O_2})$ is antisymmetric ($\Rightarrow$ only $J = 1, 3, 5..$ allowed), whereas in variant ii the rotational wavefunction has to be symmetric such the $\Psi(\mathsf{O_2})$ is antisymmetric ($\Rightarrow$ only $J = 0, 2, 4, ...$ allowed).

Rotational vibrational spectroscopy Let us consider the rotational vibrational spectrum of $^1H^{35}Cl$. The absorption lines in this spectrum correspond to transitions form the rotational states J of the vibrational ground state $\nu = 0$ to the rotational states J' of the first excited vibrational states $\nu' = 1$. The selection rule is $J' = J \pm 1$.

The transition $(\nu = 0, J = 0) \to (\nu' = 1, J' = 0)$ is not allowed but would occur at an energy of

$$\Delta E = h\nu_0 = \Theta_{\text{vib}} \cdot k_B = 35.463\,\text{kJ/mol} = 2964\,\text{cm}^{-1} \tag{11.33}$$

where we used $\Theta_{\text{vib}} = 4265$ K.

The transitition into higher rotational states $(\nu = 0, J) \to (\nu' = 1, J' = J+1)$ (R-branch of the spectrum) occur at energies

$$\begin{aligned} \Delta E &= 2964\,\text{cm}^{-1} + (J+1)(J+1+1)\Theta_{\text{rot}} \cdot k_B - J(J+1)\Theta_{\text{rot}} \cdot k_B \\ &= 2964\,\text{cm}^{-1} + (2J+2) \cdot \Theta_{\text{rot}} \cdot k_B \\ &= 2964\,\text{cm}^{-1} + (2J+2) \cdot 0.1249\,\text{kJ/mol} \\ &= 2964\,\text{cm}^{-1} + (2J+2) \cdot 10.44\,\text{cm}^{-1} \end{aligned} \tag{11.34}$$

where we have used $\Theta_{\text{rot}} = 15.021$ K. Likewise the transitions to lower rotational states $(\nu = 0, J) \to (\nu' = 1, J' = J-1)$ (R-branch of the spectrum) occur at energies

$$\begin{aligned} \Delta E &= 2964\,\text{cm}^{-1} + (J-1)(J-1+1)\Theta_{\text{rot}} \cdot k_B - J(J+1)\Theta_{\text{rot}} \cdot k_B \\ &= 2964\,\text{cm}^{-1} - 2J \cdot \Theta_{\text{rot}} \cdot k_B \\ &= 2964\,\text{cm}^{-1} - 2J \cdot 0.1249\,\text{kJ/mol} \\ &= 2964\,\text{cm}^{-1} - 2J \cdot 10.44\,\text{cm}^{-1} \end{aligned} \tag{11.35}$$

The relative heights of the absorption lines is given by the population of the initial state, i.e. by eq. 11.26.

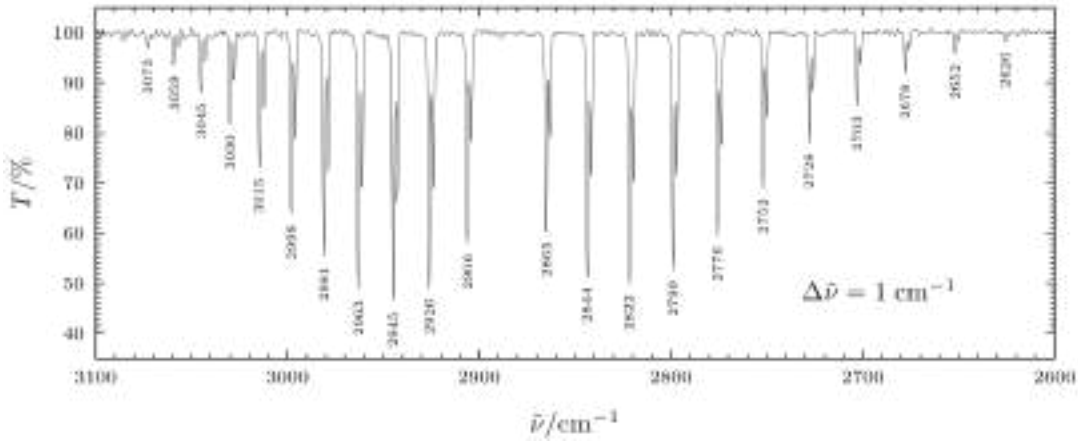


Figure 13: Infrared rotational-vibration spectrum of hydrochloric acid gas at room temperature. The dubletts in the IR absorption intensities are caused by the isotopes present in the sample: ^1H-^{35}Cl and ^1H-^{37}Cl

12 Mixtures of ideal gases

Consider a container with volume V which is subdivided by a wall into two containers with volumes V_A and V_B. Container with volume V_A contains N_A particles of an ideal gas A and container with volume V_B contains N_B particles of a different ideal gas B. The partition function for this system is

$$Q_I = Q_A(N_A, V_A, T) \cdot Q_B(N_B, V_V, T) = \frac{q_A^{N_A}(V_A, T)}{N_A!} \cdot \frac{q_B^{N_B}(V_B, T)}{N_B!} \tag{12.1}$$

If the dividing wall is removed, all particles can access the entire volume $V = V_A + V_B$, and the partition function of the system is

$$Q_{II} = \frac{q_A^{N_A}(V, T)}{N_A!} \cdot \frac{q_B^{N_B}(V, T)}{N_B!} \tag{12.2}$$

Note that since particles of type A are still distinguishable from particles of type B, one has to divide by $N_A!$ and $N_B!$ rather than by $N!$.

12.1 The change of thermodynamic state functions upon mixing

The partition functions Q_I and Q_{II} differ only in the volume. The partition function of an ideal gas particle depends on the volume only throught the translational partition function

$$q_{\text{trans}} = = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \cdot V\,. \tag{12.3}$$

Thus, we can write

$$\begin{aligned} q_A(V, T) &= \zeta_A(T) V \\ q_B(V, T) &= \zeta_B(T) V \end{aligned} \tag{12.4}$$

where ζ_A and ζ_B are functions which depend on the single-particle partition function of gas A and B. For the partition function of the two systems, we obtain

$$Q_I = \frac{\zeta_A^{N_A} V_A^{N_A}}{N_A!} \cdot \frac{\zeta_B^{N_B} V_B^{N_B}}{N_B!} \tag{12.5}$$

and

$$Q_{II} = \frac{\zeta_A^{N_A} V^{N_A}}{N_A!} \cdot \frac{\zeta_B^{N_B} V^{N_B}}{N_B!}\,. \tag{12.6}$$

The free energies of the two systems are

$$\begin{aligned} A_I &= -k_B T \ln Q_I \\ &= -k_B T \left[N_A \ln \zeta_A + N_A \ln V_A + N_B \ln \zeta_B + N_B \ln V_B - \ln N_A! - \ln N_B!\right] \end{aligned} \tag{12.7}$$

and

$$\begin{aligned} A_{II} &= -k_B T \ln Q_{II} \\ &= -k_B T \left[N_A \ln \zeta_A + N_A \ln V + N_B \ln \zeta_B + N_B \ln V - \ln N_A! - \ln N_B!\right] \end{aligned} \tag{12.8}$$

The free energy of mixing is given as the free energy difference

$$\begin{aligned} \Delta A &= A_{II} - A_I \\ &= -k_B T \left[N_A \ln V + N_B \ln V - N_A \ln V_A - N_B \ln V_B\right] \\ &= k_B T \left[N_A \ln \frac{V_A}{V} + N_B \ln \frac{V_B}{V}\right] \end{aligned}$$

$$= (N_A + N_B)k_B T \left[x_A \ln \frac{V_A}{V} + x_B \ln \frac{V_B}{V} \right] \tag{12.9}$$

where we defined the molar fractions

$$\begin{aligned} x_A &= \frac{N_A}{N_A + N_B} \\ x_B &= \frac{N_B}{N_A + N_B} \,. \end{aligned} \tag{12.10}$$

Thus for ideal gases, the free energy of mixing depends on the temperature via $k_B T$ on the relative size of the original volumes and the number of molecules in these volumes. It is independent of partition functions for the internal degrees of freedom.

For the change of entropy and the change of internal energy upon mixing, we obtain

$$\Delta S = -\left(\frac{\partial \Delta A}{\partial T} \right)_{N_A, N_B, V} = -\frac{\Delta A}{T} \tag{12.11}$$

and

$$\Delta U = \Delta A + T\Delta S = 0 \,. \tag{12.12}$$

The pressure is defined as minus the partial derivative of the free energy with respect to the volume. Thus for system II, we have

$$P_{II} = -\left(\frac{\partial A_{II}}{\partial V} \right)_{N_A, N_B, T} = k_B T \frac{N_A}{V} + k_B T \frac{N_B}{V} = P_A + P_B \tag{12.13}$$

where P_A and P_B are the partial pressures of the two components in the mixture.

For mixing two ideal gases at constant pressure, the equations for the thermodynamic state functions are more complicated. A particularly simple form however arises of the pressure in the two containers A and B is the same. Then

$$\begin{aligned} x_A &= \frac{N_A}{N} = \frac{V_A}{V} \\ x_B &= \frac{N_B}{N} = \frac{V_B}{V} \,. \end{aligned} \tag{12.14}$$

Upon removal of the barrier neither the pressure nor the volume changes and the volume work is zero

$$P\Delta V = 0 \,. \tag{12.15}$$

Hence,

$$\Delta H = \Delta U = 0 \tag{12.16}$$

$$\Delta G = \Delta A = (N_A + N_B)k_B T \left[x_A \ln x_A + x_B \ln x_B \right] \tag{12.17}$$

and

$$\Delta S = -(N_A + N_B)k_B \left[x_A \ln x_A + x_B \ln x_B \right] \,. \tag{12.18}$$

12.2 The chemical potential

Eqs. 12.7 to 12.9 suggest that the sensitivity of the free energy with respect to a change of particle numbers might be a useful property

$$\begin{aligned}
\mu_A &= \left(\frac{\partial A_{II}}{\partial N_A}\right)_{N_B,T,V} \\
&= -k_BT\left(\frac{\partial}{\partial N_A}\left[N_A\ln\zeta_A + N_A\ln V + N_B\ln\zeta_B + N_B\ln V - \ln N_A! - \ln N_B!\right]\right)_{N_B,T,V} \\
&= -k_BT\left(\frac{\partial}{\partial N_A}\left[N_A\ln\zeta_A + N_A\ln V - N_A\ln N_A + N_A\right]\right)_{N_B,T,V} \\
&= -k_BT\left[\ln\zeta_A + \ln V - \ln N_A - N_A\frac{1}{N_A} + 1\right] \\
&= -k_BT\ln\frac{\zeta_A V}{N_A} = -k_BT\ln\frac{q_A}{N_A}
\end{aligned} \tag{12.19}$$

μ_A ist the *chemical potential* of the component A in a mixture. If the mixture consists of more than one component, the chemical potential of the kth component is given as

$$\mu_k = \left(\frac{\partial A}{\partial N_k}\right)_{N_j,T,V} = -k_BT\ln\frac{q_k}{N_k} \qquad \text{with } j \neq k\,. \tag{12.20}$$

That is, one consideres the change of free energy upon a change of the particle numbers of component k while keeping the temperature, the volume and the particle numbers of all other components fixed.

In eq. 12.19, we replace

$$V = \frac{Nk_BT}{P} \tag{12.21}$$

and

$$N_A = \frac{P_AV}{k_BT} \tag{12.22}$$

(where P_A ist the partial pressure of component A in the mixture) and obtain

$$\begin{aligned}
\mu_A &= -k_BT\left[\ln\frac{\zeta_Ak_BT}{P} + \ln N - \ln\frac{P_AV}{k_BT}\right] \\
&= -k_BT\left[\ln\frac{\zeta_Ak_BT}{P} + \ln\frac{PV}{k_BT} - \ln\frac{P_AV}{k_BT}\right] \\
&= -k_BT\left[\ln\frac{\zeta_Ak_BT}{P} + \ln\frac{P}{P_A}\right] \\
&= -k_BT\ln\frac{\zeta_Ak_BT}{P} + k_BT\ln\frac{P_A}{P}
\end{aligned} \tag{12.23}$$

At standard pressure, i.e. $P = P^0 = 1$ bar:

$$\mu_A = \mu_A^0 + k_BT\ln\frac{P_A}{P^0} \tag{12.24}$$

where

$$\mu_A^0 = -k_BT\ln\frac{\zeta_Ak_BT}{P} \tag{12.25}$$

is the standard chemical potential of component A.

13 Chemical equilibrium

So far we have considered physical changes (changes in temperature, pressure, volume...) and the properties of spectra. Next, we will consider actual chemical reactions. In fact, one can calculate the equilibrium constant of a reaction from the microscopic properties of the reagents and the products. For reactions of small molecules in the gas phase this approach yields very accurate results. It is useful for reactions which occur under such extreme conditions that the equilibrium constant cannot be probed experimentally (e.g. in explosions, volcanoes etc.).

13.1 From the partition functions to equilibrium constants

The equilibrium condition for the generic chemical reaction

$$\nu_A A + \nu_B B \quad \rightleftarrows \quad \nu_C C + \nu_D D \tag{13.1}$$

is

$$\nu_A \mu_A + \nu_B \mu_B \quad = \quad \nu_C \mu_C + \nu_D \mu_D \tag{13.2}$$

where ν_k is the stoichiometric number of the kth component and μ_k is chemical potential. Let us assume the reaction takes place in the gas phase and all reactants and products behave as ideal gases. The the chemical potential is given as

$$\mu_k \quad = \quad -k_B T \ln \frac{q_k(V,T)}{N_k} \qquad k = A, B, C, D \tag{13.3}$$

Inserting in eq. 13.2 yields a simple equilibrium condition

$$\begin{aligned}
\nu_A \mu_A + \nu_B \mu_B &= \nu_C \mu_C + \nu_D \mu_D \\
\nu_A \ln \frac{q_A(V,T)}{N_A} + \nu_B \ln \frac{q_B(V,T)}{N_B} &= \nu_C \ln \frac{q_C(V,T)}{N_C} + \nu_D \ln \frac{q_D(V,T)}{N_D} \\
\ln \frac{q_C^{\nu_C} q_D^{\nu_D}}{q_A^{\nu_A} q_B^{\nu_B}} &= \ln \frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} \\
\frac{q_C^{\nu_C} q_D^{\nu_D}}{q_A^{\nu_A} q_B^{\nu_B}} &= \frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}}
\end{aligned} \tag{13.4}$$

Equilibrium constant. Using absolute particle numbers is impracticle. We therefore replace the particle numbers by dimensionless concentrations

$$c_k \quad = \quad \frac{N_k}{v} \qquad k = A, B, C, D\,. \tag{13.5}$$

with

$$v \quad = \quad \frac{V}{V^0} \tag{13.6}$$

where V^0 is the standard volume. We obtain

$$\frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} \quad = \quad \frac{c_C^{\nu_C} c_D^{\nu_D}}{c_A^{\nu_A} c_B^{\nu_B}} \cdot \frac{v^{\nu_C} v^{\nu_D}}{v^{\nu_A} v^{\nu_B}} = \frac{q_C^{\nu_C} q_D^{\nu_D}}{q_A^{\nu_A} q_B^{\nu_B}}\,. \tag{13.7}$$

We define the equilibrium constant K as

$$K \quad = \quad \frac{c_C^{\nu_C} c_D^{\nu_D}}{c_A^{\nu_A} c_B^{\nu_B}} = \frac{\left(q_C/v\right)^{\nu_C} \left(q_D/v\right)^{\nu_D}}{\left(q_A/v\right)^{\nu_A} \left(q_B/v\right)^{\nu_B}}\,. \tag{13.8}$$

In an ideal gas, the single-particle function depends linearly on the volume

$$q_k \quad = \quad V \zeta_k(T) \qquad k = A, B, C, D\,. \tag{13.9}$$

Thus the property

$$\frac{q_k}{v} = \frac{q_k}{V}V^0 = \frac{V\zeta_k(T)}{V}V^0 = V^0\zeta_k(T) \qquad k = A, B, C, D\,. \tag{13.10}$$

corresponds to the single-particle partition function in a standard volume V^0 and only depends on the temperature. Eq. 13.8 defines the equilibrium constant in a standard volume, which then only depends on the temperature.

Reference energy level. In the chapter 9 we have calculated the molecular partition function q^0 with respect to reference energy level ϵ_0, where ϵ_0 was defined as the energy of the quantum mechanical ground state. To this we shifted the energy levels

$$\epsilon_i^0 = \epsilon_i - \epsilon_0 \tag{13.11}$$

where ϵ_i is the true quantum energy and ϵ_i^0 is the energy with respect to the reference energy level The partition q is related to the shifted partition function q_k^0 by

$$\begin{aligned} q_k &= \sum_{i=0} \exp\left(-\frac{1}{k_B T}\epsilon_i\right) \\ &= \sum_{i=0} \exp\left(-\frac{1}{k_B T}(\epsilon_i^0 + \epsilon_0)\right) = \sum_{i=0} \exp\left(-\frac{\epsilon_i^0}{k_B T}\right)\exp\left(-\frac{\epsilon_0}{k_B T}\right) \\ &= q_k^0 \exp\left(-\frac{\epsilon_0}{k_B T}\right) \end{aligned} \tag{13.12}$$

The partition function q_k^0 can be calculated using the approximations discussed in chapter 9. The factor $\exp\left(-\frac{\epsilon_0}{k_B T}\right)$ corrects the partition function, such q_k applies to the true ground state energy. So far, we have never explicitly calculated the correction factor. This however becomes necessary when dealing with chemical reactions. Inserting eq. 13.12 into eq. 13.8 yields

$$K = \frac{\left(q_C^0/v\right)^{\nu_C}\left(q_D^0/v\right)^{\nu_D}}{\left(q_A^0/v\right)^{\nu_A}\left(q_B^0/v\right)^{\nu_B}} \cdot \exp\left(-\frac{\Delta\epsilon_0}{k_B T}\right) \tag{13.13}$$

with

$$\Delta\epsilon_0 = \nu_C\epsilon_{0,C} + \nu_D\epsilon_{0,D} - \nu_A\epsilon_{0,A} - \nu_B\epsilon_{0,B}\,. \tag{13.14}$$

Derivation of eq. 13.2 from eq. 13.1 The chemical reaction in eq. 13.1 takes place in mixture of N_A particles of type A, N_B particles of type B, N_C particles of type C, and N_D particles of type D. Assuming ideal particles, the partition function of this mixture is

$$Q = \frac{q_A^{N_A}}{N_A!} \cdot \frac{q_B^{N_B}}{N_B!} \cdot \frac{q_C^{N_C}}{N_C!} \cdot \frac{q_D^{N_D}}{N_D!}\,. \tag{13.15}$$

q_A, q_B, q_C, and q_D are the single-particle partition functions. The corresponding free energy is

$$\begin{aligned} A &= -k_B T \ln Q \\ &= -k_B T\left[N_A \ln q^A + N_B \ln q^B + N_C \ln q^C + N_D \ln q^D - \ln N_A! - \ln N_B! - \ln N_C! - \ln N_D!\right]\,. \end{aligned} \tag{13.16}$$

The change of free energy with respect to a change of the particle numbers of one of the substances k defines the chemical potential of this substance in this reaction

$$\mu_k = \left(\frac{\partial A}{\partial N_k}\right)_{N_j, T, V} \qquad k = A, B, C, D,\ j \neq k\,. \tag{13.17}$$

If the number of particles are change in all four substances by small amounts dN_A, dN_B, dN_C, and dN_D, the corresponding change in free energy is given as

$$\begin{aligned}\Delta A &= \left(\frac{\partial A}{\partial N_A}\right)_{N_B,N_C,N_D,T,V} dN_A + \left(\frac{\partial B}{\partial N_B}\right)_{N_A,N_C,N_D,T,V} dN_B \\ &\quad + \left(\frac{\partial C}{\partial N_C}\right)_{N_A,N_B,N_D,T,V} dN_C + \left(\frac{\partial D}{\partial N_D}\right)_{N_A,N_B,N_C,T,V} dN_D \\ &= \mu_A dN_A + \mu_B dN_B + \mu_C dN_C + \mu_D dN_D \end{aligned} \tag{13.18}$$

In a chemical reaction the relative the change in the number of particles (the ratio of dN_A to dN_B etc.) is not arbitrary but determined by the stoichiometric coefficients ν_A, ν_B, ν_C, and ν_D in eq. 13.1. That is, if the number of particles of sustance A changes by $-\nu_A \cdot N$, the number of particles in the other three substances have to change by $-\nu_B \cdot N$, $\nu_C \cdot N$, and $\nu_D \cdot N$ (forward reaction). Thus, eq. 13.18 becomes

$$\Delta A = -\nu_A\mu_A - \nu_B\mu_B + \nu_C\mu_C + \nu_D\mu_D \tag{13.19}$$

In equilibrium $\Delta A = 0$ and hence

$$\nu_A\mu_A + \nu_B\mu_B = \nu_C\mu_C + \nu_D\mu_D \tag{13.20}$$

13.2 Exchange reaction in two-atomic molecules

A exchange reaction in two atomic molecules is

$$A_2 + B_2 \leftrightarrows 2AB\,. \tag{13.21}$$

Note that number of particles does not change during the reactions, i.e. $\Delta\nu = \nu_{AB} - \nu_B - \nu_B = 0$. Hence the equilibrium constant is independent of the volume and only depends on the temperature.

$$\begin{aligned} K &= \frac{\left(q_{AB}/v\right)^2}{q_A/v q_B/v} \cdot \exp\left(-\frac{\Delta\epsilon_0}{k_B T}\right) \\ &= \frac{q_C^{\nu_C} q_D^{\nu_D}}{q_A^{\nu_A} q_B^{\nu_B}} \cdot \exp\left(-\frac{\Delta\epsilon_0}{k_B T}\right) \end{aligned} \tag{13.22}$$

We approximate the single-particle partition function as

$$\begin{aligned} q_k &= q_{\text{trans}} \cdot q_{\text{vib}} \cdot q_{\text{rot}} \cdot q_e \cdot q_n \cdot \\ &= q_{\text{trans}} \cdot q_{\text{vib}} \cdot q_{\text{rot}} \cdot q_e \cdot q_n \cdot e^{-\epsilon_0/k_B T}\,. \end{aligned} \tag{13.23}$$

We use the approximation from chapter 8 and 9 and obtain

$$q_k = \left(\frac{2\pi m_k k_B T}{h^2}\right)^{3/2} V \cdot \frac{1}{1-\exp\left[-\frac{\Theta_{\text{vib},k}}{T}\right]} \cdot \frac{1}{\sigma_k}\frac{T}{\Theta_{\text{rot},k}} \cdot g_{e,0,k} \cdot \prod_{i=1}^{2}(2I_{i,k}+1) \cdot e^{-\epsilon_{0,k}/k_B T} \tag{13.24}$$

where m_k is the mass, $\Theta_{\text{vib},k}$ is the vibrational characteristic temperature, $\Theta_{\text{rot},k}$ is the rotational characteristic temperature, σ_k is the symmetry factor, $g_{e,0,k}$ is the degenerace of the electronic ground state, and $\epsilon_{0,k}$ is the ground state energy of of substance k. $I_{i,k}$ is the spin of the ith in a molecule of substance k. Inserting eq. 13.24 into eq. 13.21 yields

$$\begin{aligned} K &= \left(\frac{m_{AB}^2}{m_{A_2} m_{B_2}}\right)^{3/2} \cdot \frac{z_{\text{vib},AB}^2}{z_{\text{vib},A_2} z_{\text{vib},B_2}} \cdot 4 \cdot \frac{\Theta_{\text{rot},A_2}\Theta_{\text{rot},B_2}}{\Theta_{\text{rot},AB}^2} \cdot \frac{g_{e,0,AB}^2}{g_{e,0,A_2} g_{e,0,B_2}} \cdot e^{-\Delta\epsilon_0/k_B T} \\ &= f_{\text{trans}} \cdot f_{\text{vib}} \cdot f_{\text{rot}} \cdot f_{\text{e}} \cdot e^{-\Delta\epsilon_0/k_B T} \end{aligned} \tag{13.25}$$

For a reaction, the ratio of the nuclear partition functions is alwas 1 since

$$\frac{\prod_{i=1}^{2}(2I_{i,AB}+1)^2}{\prod_{j=1}^{2}(2I_{j,A_2}+1)\prod_{l=1}^{2}(2I_{l,B_2}+1)} = \frac{(2I_A+1)(2I_B+1)(2I_A+1)(2I_B+1)}{(2I_A+1)(2I_A+1)(2I_B+1)(2I_B+1)} = 1 \tag{13.26}$$

Example: formation of hydrogen iodine HI is form from its elements in an exchange reaction

$$H_2 + I_2 \leftrightarrows 2HI\,. \tag{13.27}$$

where we use the most abundant isotope forms of the molecules: ${}^1H_2$, ${}^{127}I_2$ and ${}^1H^{127}I$. The electronic ground states in H_2, I_2, and HI are not degenerate and hence

$$\frac{g_{e,0,AB}^2}{g_{e,0,A_2} g_{e,0,B_2}} = 1 \tag{13.28}$$

The characteristic rotational temperatures are $\Theta_{\mathsf{rot},H_2} = 85.36$ K, $\Theta_{\mathsf{rot},I_2} = 0.0537$ K, and $\Theta_{\mathsf{rot},HI} = 9.246$ K yielding

$$\frac{\Theta_{\mathsf{rot},H_2}\Theta_{\mathsf{rot},I_2}}{\Theta_{\mathsf{rot},HI}^2} = \frac{85.36 \cdot 0.0537}{9.246^2} = 0.054 \tag{13.29}$$

For the ratios of the translational partition functions we obtain

$$\begin{aligned}\left(\frac{m_{AB}^2}{m_{A_2} m_{B_2}}\right)^{3/2} &= \left(\frac{(127+1)^2}{(1+1)\cdot(127+127)} \frac{(a.m.u)^2}{a.m.u. \cdot a.m.u}\right)^{3/2} \\ &= 32.25^{3/2} = 183.16\end{aligned} \tag{13.30}$$

The electronic ground state energies are $D_{0,H_2} = 4.4773$ eV, $D_{0,I_2} = 1.544$ eV, and $D_{0,HI} = 3.053$ eV, yielding

$$\Delta\epsilon_{0,e} = (2 \cdot 3.053 - 4.4773 - 1.544)\ \text{eV} = 0.085\ \text{eV} = 1.36 \cdot 10^{-20}\ \text{J} \tag{13.31}$$

Note that the contributions of the vibrational states to the equlibrium constant depends on the temperature. We here use precalculated vibrational partition functions, which contain the ground state energy

T/K	$z_{\mathsf{vib},HI}$	z_{vib,H_2}	z_{vib,I_2}
298.15	1.000	1.000	1.553
500.00	1.007	1.000	2.703
1000.00	1.014	1.000	3.013

For the equilibrium constant we obtain

T/K	f_{trans}	f_{vib}	f_{rot}	f_{e}	$-\Delta\epsilon_0/k_BT$	K
298.15	183.16	0.6439	$4 \cdot 0.054$	1	-3.305	
500.00	183.16	0.3752	$4 \cdot 0.054$	1	-1.971	
1000.00	183.16	0.3328	$4 \cdot 0.054$	1	-0.986	

14 The activated complex

In chemical reaction, substrates pass a transition state - the so-called activated complex

$$A + B \leftrightarrows C \tag{14.1}$$

In the statistical thermodynamical theory of the activated complex $(AB)^\dagger$, this complex is treated as a separated and independent chemical species which is in equilibrium with the substrates and products. The reaction equation is extended

$$A + B \leftrightarrows (AB)^\dagger \rightarrow C\,. \tag{14.2}$$

During the reaction, the concentration if of the activated complex is very small compared to the concentration of the educts and products. Thus, for the equlibrium constant for the formation of the activated complex (first part of the reaction scheme) we have

$$K_c^\dagger \;=\; \frac{c_{(AB)^\dagger}}{c_A\, c_B} \ll 1\,. \tag{14.3}$$

The concentrations are again dimensionless properties $c_k = N_k/v$ with $v = V/V_0$. The overall reaction rate depends on the rate with which the complex reacts into the products.

$$-\frac{dc_A}{dt} \;=\; \nu_r c_{(AB)^\dagger} = \nu_r K_c^\dagger c_A c_B\,. \tag{14.4}$$

Both the equilibrium constant of the activated complex $K_c^\dagger$ and its decay rate ν_r can be calculated using statistical thermodynamics.

14.1 Decay rate of the actived complex

Consider the reaction

$$D + H_2 \leftrightarrows (D - H - H)^\dagger \rightarrow DH + H\,. \tag{14.5}$$

The decay of the process will proceed along one of its vibrational normal modes. Assuming that the three atoms are aligned linearly in the complex, the anti-symmetric stretch vibration will lead to the decay of the complex. The force constant of this vibration is so small that the complex will decay during the first vibration. Thus, the decay rate of the complex is equal to the vibrational frequency of this particular mode

$$\nu_r \;=\; \nu^* \tag{14.6}$$

Thus,

- Find the transition state structure of the reaction.
- Perform a normal mode analysis for this structure.
- Find the normal mode along which the complex will decay. The frequency associated to this mode is the decay rate ν_r of the complex.

14.2 The equilibrium constant of the formation of the activated complex.

The equilibrium constant is expressed in terms of the single-particle partition functions

$$K_c^\dagger \;=\; \frac{q_{(AB)^\dagger}/v}{q_B/v\; q_B/v} \tag{14.7}$$

Let's consider the single-particle partition function of the activated complex more closely. The vibrational partition function is given as a product of the vibrational partition functio of all normal modes

$$q_{\mathsf{vib}}((AB)^\dagger) \;=\; \prod_{i=1}^{3N_{\mathsf{atoms}}-6} q_{\mathsf{vib}}(\Theta_{\mathsf{vib},i})$$

$$= \quad q_{\text{vib}}(\Theta_{\text{vib},r}) \prod_{i=1,\, i\neq r}^{3N_{\text{atoms}}-5} q_{\text{vib}}(\Theta_{\text{vib},i}) \tag{14.8}$$

where $\Theta_{\text{vib},i}$ is the characteristic vibrational temperature of the ith normal mode and r is the index of the reactive mode. The characteristic vibrational temperature of the reactive mode is low and hence the high-temperature approximation is appropriate

$$q_{\text{vib}}(\Theta_{\text{vib},r}) \quad \approx \quad \frac{k_B T}{h\nu^*} \,. \tag{14.9}$$

We define a "truncated partition function" for the activated complex

$$\begin{aligned} q &= \frac{k_B T}{h\nu^*} \left[\prod_{i=1,\, i\neq r}^{3N_{\text{atoms}}-6} q_{\text{vib}}(\Theta_{\text{vib},i}) \right] q_{\text{trans}}\, q_{\text{rot}}\, q_e\, q_n \\ &= \frac{k_B T}{h\nu^*} q'_{(AB)^\dagger} \end{aligned} \tag{14.10}$$

and obtain for the equilibrium constant

$$K_c^\dagger \quad = \quad \frac{k_B T}{h\nu^*} \frac{q'_{(AB)^\dagger}/v}{q_B/v\; q_B/v} \tag{14.11}$$

14.3 The reaction rate of a bimolecular reaction

Inserting eq. 14.11 and 14.6 into eq. 14.4 yields

$$\begin{aligned} -\frac{dc_A}{dt} &= \nu^* \frac{k_B T}{h\nu^*} \frac{q'_{(AB)^\dagger}/v}{q_B/v\; q_B/v} c_A c_B \\ &= \frac{k_B T}{h} \frac{q'_{(AB)^\dagger}/v}{q_B/v\; q_B/v} c_A c_B \,. \end{aligned} \tag{14.12}$$

The rate constant is

$$k_r = \frac{k_B T}{h} \frac{q'_{(AB)^\dagger}/v}{q_B/v\; q_B/v} \tag{14.13}$$

and reformulated with respect to a common reference energy

$$k_r \quad = \quad \frac{k_B T}{h} \frac{q'^0_{(AB)^\dagger}/v}{q^0_B/v\; q^0_B/v} \exp\left(-\frac{\Delta\epsilon^\dagger}{k_B T}\right) \,. \tag{14.14}$$

where

$$\Delta\epsilon^\dagger \quad = \quad \epsilon_{0,(AB)^\dagger} - \epsilon_{0,A} - \epsilon_{0,B} \tag{14.15}$$

is the activation energy. The pre-exponential factor has units of s^{-1}, i.e. it is a rate. This molecular reaction rate is related to a molar reaction rate by

$$k_{r,m} \quad = \quad k_r N_A = \frac{RT}{h} \frac{q'^0_{(AB)^\dagger}/v}{q^0_B/v\; q^0_B/v} \exp\left(-\frac{\Delta\epsilon^\dagger}{k_B T}\right) \tag{14.16}$$

where N_A is Avogadro's number and R is gas constant.

14.4 Example: exchange reaction between D and H_2

Consider again the reaction

$$D + H_2 \rightarrow DH + H \tag{14.17}$$

The activated complex $D - H - H$ has $3N - 5 = 4$ normal modes, of which three do not lead to a decay of the complex

- a symmetric stretch vibration: $\tilde{\nu}_s = 1740$ cm^{-1} ($\Theta_s = 2508K$)
- a two-fold degenerate bending vibration: $\tilde{\nu}_\delta = 930$ cm^{-1} ($\Theta_s = 1339K$)

The frequency of the reactive normal mode cancels in the equation for the rate constant. The characteristic rotational temperatur is $\Theta_{\text{rot}} = 9.799$ K. The molar rate constant is given as

$$\begin{aligned} k_{r,m} &= \frac{RT}{h}\frac{1}{V^0}\frac{q_{\text{trans},C}/V}{q_{\text{trans},H_2}/V\, q_{\text{trans},D}/V}\cdot\frac{q_{\text{rot},C}}{q_{\text{rot},H_2}}\cdot\frac{q_{\text{vib},C}}{q_{\text{vib},H_2}}\cdot\frac{g_{e,0,C}}{g_{e,0,H_2}g_{e,0,D}}\cdot\exp\left(-\frac{\Delta\epsilon^\dagger}{k_BT}\right) \\ &= A\cdot\exp\left(-\frac{\Delta\epsilon^\dagger}{k_BT}\right) \end{aligned} \tag{14.18}$$

where we used that the rotational and vibrational partition function of a single atom (i.e. D) is 1. The degeneracy of the electronic ground state of D and of the activated complex is 2, thus

$$\frac{g_{e,0,C}}{g_{e,0,H_2}g_{e,0,D}} = 1 \tag{14.19}$$

Using the approximations from chapters 8 and 9, we obtain for the pre-exponential factor

$$A = \frac{RT}{h}\frac{1}{V^0}\left(\frac{h^2}{2\pi k_BT}\right)^{3/2}\left(\frac{m_C}{m_{H_2}m_D}\right)\frac{I_c\sigma}{I_{H_2}}\frac{\left(1-e^{-h\nu_s/k_BT}\right)^{-1}\left(1-e^{-h\nu_\delta/k_BT}\right)^{-2}}{\left(1-e^{-h\nu_{H_2}/k_BT}\right)^{-1}} \tag{14.20}$$

Inserting all the properties in SI units and choosing $V_0 = 1$ cm$^3 = 1\cdot10^{-6}$ m^3 yields

$$A = 1.26\cdot10^{14}\ \text{mol}^{-1}s^{-1} \qquad (V_0 = 1\ \text{cm}^3) \tag{14.21}$$

The experimental value is $A = 0.49\cdot10^{14}$ mol$^{-1}s^{-1}$.

Despite the large number of assumption which we used in the derivation of the reaction rate, the theory of the activated complex yields a result which has the correct order of magnitude. The theory of the activated complex is useful to understand how the reaction rate changes if the substrates change. For example the pre-exponential factor in the analogous reaction

$$CH_3 + H_2 \rightarrow CH_4 + H \tag{14.22}$$

is two orders of magnitude smaller because one has to take the rotational partition function of CH_3 into account.