**7. Statistical mechanics**

**7.1. The Problem**

Consider the concept of pressure. One can start from the dimensional analysis:



This follows also from the molecular considerations. Each molecule has a momentum (on average) . The flux of the molecules colliding with the surface of our reservoir is I. The factor of 2 originates from the fact that the molecules reflect from the surface. The flux can also be described as , where n is the concentration of the particles.

At each collision, the particle may have different amount of kinetic energy (momentum), but there are many particles. Very many. So we feel only a time-averaged value.

Averaging over time: 

In equilibrium, nothing depends on time, so **we can substitute the averaging over time with the averaging over realizations (events)**.



Here:

-possible values of the function (in discrete case) = realizations

- probability to get the particular realization

- probability density of the system’s states

- is a number of systems (points in Gamma-space) that have and 

- is the number of configurational points on the phase trajectory.

We want to find 

**7.2. Basic concepts and definitions**

Definition: **Ergodic system** = a system for which a time-average is equal to an average over realizations.

Example: A jar with 50 black and 50 white balls. In it is a window. We shake the jar and look into this window every second for 100 years, noticing the color of a ball in that window. Eventually and realize that we see black in 50% of cases and white in 50%. **This system is ergodic**.

Now, 2 black balls have stick to the bottom of the jar. As a result, our time-averaged results will be different from what we know based on the proportions of the differently colored balls in the jar. **This system is not ergodic**.

Another example: A 1-D Harmonic oscillator.

Note: All the derivations in a standard statistical mechanics are correct only for ergodic systems.

Definition: **-space**. A space of a single molecule: 6-dimensional. An image of 1 molecule is 6-dimensional point. An image of 1 mole of molecules is 6 x 1023 – 6 dimensional points.

Definition: **-space**. A space of a mole of molecules: 6 x 6 x 1023 – dimensional. An image of 1 mole of molecules is a single 6 x 6 x 1023 dimensional point.

Definition: points in the**-**space are called **configurational points**.

Definition: **Phase trajectory** – is a sequence of the configurational points.

Definition: **Microstate** (configuration, 1 configurational point) – is defined by positions and momenta of all particles in a system.

Definition: **Macrostate** – is defined by all macroscopic parameters (P, T, V, etc.) of a system.

Definition: **Gibbs’ ensemble** – is a collection of microstates corresponding to a given macrostate.

Classification:

* **Microcanonical** (NVE, meaning N = const, V = const, E = const)
* **Canonical** (NVT, possible energy exchange with the environment such that )
* **Grand canonical** (µTV, possible energy exchange, and mass exchange, such that and )

Theorem: Phase trajectory does not intersect itself.

**Proof**: ad absurdum: Assume there is a point of self-intersection 🡺 if we choose it as a starting point, there will be several pathways of system evolution 🡺 contradiction with the determinism of classical mechanics.

Theorem (Liouville): The density of configurational points is constant along the phase trajectory.

**Proof**: We start with a continuity equation, which states:



 is a flux in the phase space, where 

So:



Here we used Hamiltonian equations of motion

Substituting everything back to the continuity equation, we obtain:

.

Which proves the theorem.

Ergodic hypothesis: During its evolution, a system will visit all points of a phase space belonging to a given energy level. That is: .

In other words: All microstates with the same energy are equally probable

Consequences: **Boltzmann** ( N! ) = = = **Gibbs** (Th Liouvile + Ergodic hypothesis)

**7.3. Maxwell-Boltzmann distribution**

Assume the macroscopic parameters (N, V, E, T, etc.) are defined. They define certain constraints on the set of points in the phase space (microstates) that are consistent with this macrostate. For instance, for a harmonic oscillator, different total energy values will define different circles. Each circle, in this case is a “volume” of the phase space that corresponds to given total energy.

One can subdivide a phase space volume into many small cells of width and . Although Boltzmann merely hypothesized this, one can recall the uncertainty principle, which suggests these width could be related to each other. The number of such cells is large, but finite, if V and E are fixed.

Further, the following constraints are present:





Here, is the number of particles in the cell with index *i*, is the total number of particles, is the energy of the cell with index *i*, is the total energy of the system.

The main assumptions of the Boltzmann’s theory:

1. All microstates are equally probable
2. Macrostate is defined by defining the number of particles is each cell of the phase space: 
3. Each macrostate is realized by a certain number of microstates
4. Equilibrium state is the one that is realized by the largest number of microstates

Using the constraints and the assumptions, we can derive the distribution. First, the number of microstates is given by:



The numerator describes the total number of permutations of N particles. Each term in the denominator accounts for all permutations of particles in the cell k. This is needed, because the particles are indistinguishable.

Example: consider 6 particles in 3 cells.

1. If the distributions is: , then . There is only 1 way to distribute 6 particles into a given cell. We don’t care into which cell the particles are put.
2. If the distributions is: , then . As you can see this is a uniform distribution, and is realized by the largest number of microstates.

The maximum of coincides with the maximum of , but the latter is easier to work with. Using the Sterling approximation, , which is satisfied for large N, we obtain:



In the last equation, we utilized the condition on the total number of particles.

To find general distribution, we find maximum of , but under given constraints. This can be achieved via the unconstrained maximization of the functional . The extremum condition is:



So, we obtain:



This is, essentially, our main result. The coefficient A can be found from the normalization condition:



Finally,

 is the probability to find system in the state with energy 

This is called a **Maxwell-Boltzmann distribution**.

**7.4. Gibbs ensembles and distributions**

***A. Microcanonical distribution***.

This case follows directly from the Liouville theorem:

 for .

Here, the constant value, , is of course different for different total energy layers and .

Consider the differential of the probability to find a system in a given energy state:

,

Here  is the phase space volume that corresponds to energy interval ,

 is the energy density of states

In other words, for the microcanonical distribution we obtain:



A discrete analog will be:



With the constant, given from the normalization condition: , so:

 - **microcanonical Gibbs distribution**.

Example:

Consider computing for 1 particle:



in the last equation, we have switched to polar coordinates.

When integrating over all 6 degrees of freedom, one obtains:



So, you can see that the phase space volume is equal to the product of the volumes in coordinate (cube or any arbitrary shape of volume V) and momentum (sphere) spaces.

Assuming we deal with a free particle, the momentum and total energy are related as: .

So: 

Then, we can compute the density of states:



For a system of N non-interacting particles, we obtain, by analogy:



***B. Canonical distribution***.

Consider a system with energy and the number of particles . The system of interest is immersed into a bigger system (thermostat) with energy  and the number of particles , such that:





We allow energy exchange, between the system and thermostat, but such that .

A microcanonical distribution is applicable to the overall system (“system” + thermostat), so we have:



This expression means – the probability to find the system in a state with energy and the thermostat in a state with energy .

Because of the condition, the system and thermostat can be considered independent, so:



Introduce a new function:



Because of , we can apply a Taylor expansion in terms of :



So, .

Here, we dropped the dependence on the energy of thermostat, , because it is much larger than the energy of the target system.

Here , and is called **statistical temperature**.

can be determined from the normalization conditions, leading to:



This is **canonical Gibbs distribution** – same as Maxwell-Boltzmann distribution

***C. Thermal equilibrium***.

Consider two systems, 1 and 2, which are in equilibrium with each other and are statistically independent.

The probability to have energy is system 1 is . Analogously, for the system 2, we have: .

For the combined system 1+2, we get:



Because the number of states in the combined system is just the product of the numbers of states in each sub-system (since 1 and 2 are statistically-independent):



Then, we look at the condition:



If we assume energy additivity, , then the above equality can be satisfied only if:

.

This is nothing but the 0-th law (postulate) of thermodynamics – thesis about existence of the temperature function that takes the same values for all parts of a system that are in equilibrium with each other. That is why the constant is called statistical temperature.

Recall the fundamental Gibbs’ equation:



From which we obtain: at the same time, we have: .

One can see the following connections:



and



***D. Grand canonical distribution***.

The construction is similar as for the canonical one, only we also allow exchange of the particles. Analogously to the canonical situation, the exchange is assumed to be sufficiently small:

.

A microcanonical distribution is applicable to the overall system (“system” + thermostat), so we have:



This expression means – the probability to find the system in a state with energy and number of particles and the thermostat in a state with energyand number of particles .

Because of the and conditions, the system and thermostat can be considered independent, so:



Introduce a new function:



Because of  and , we can apply a Taylor expansion in terms of and :



So,

.

Here, we have defined  - **chemical potential**

From the normalization, we obtain the distribution:

 - **grand canonical distribution**

**7.5. Partition function and its relationship with thermodynamic functions**.

In the above derivations, we utilized:

 canonical partition function

 grand canonical partition function

Important: The partition function is defined up to a multiplicative factor. The factor is related to the choice of the zero energy level. Indeed, if all energy levels are shifted by a constant value: , the partition function changes as: . It is common to choose energy levels such that zero on the energy scale corresponds to energy of the system at absolute zero, 

1. **Internal energy:** 

Proof:



2. **Average number of particles:**

Proof:



3. **Helmholtz free energy**: 

Proof: In phenomenological thermodynamics, we have derived equation 

Using the first expression, we get:



from which we immediately obtain the main result

4. **Entropy**: 

Proof: This results follows from simple algebra and relationships between thermodynamics functions



5. **Pressure**: 

One can use relationships between thermodynamic variables to derive all other relationships.

**7.6. Calculation of molecular partition function**.

**A. General formulation**

The total partition function of N particles can be represented as:



Here, N! accounts for the quantum-mechanical indistinguishability of particles,

- is the **molecular partition function** (for a single particle, in the ideal gas approximation): accounts for internal degrees of freedom of each independent particle

- **configurational integral** – accounts for interactions between particles of the gas (real gases)

The total energy of each particle can be represented as a sum of various contributions:



Correspondingly, the molecular partition function factorizes:



**B. Computing the configurational integral**



Each spatial coordinate is 3-dimensional, so the overall integral is 6N-dimensional.

Assume pair-wise interactions:



Definition: Mayer’s function 

Then



Where 

Consider computing using the hard spheres potential:





**C. Computing the electronic partition function**



Here,  is **practical partition function**.

We can compute it, because we know all the energy gaps, , but the electronic energy of the ground state can vary depending on chosen conventions.

are the degeneracies of electronic states.

Since the electronic energy levels are usually well separated from the ground state level, the electronic partition function (practical) is just the degeneracy of the ground electronic state.

Exceptions:

* Metals (gaps are small)
* High temperature

**D. Computing translational partition function**



Here, we utilized the integral



**E. Computing vibrational partition function**

Harmonic oscillator model: , where vibrational frequency,

yields the energy levels: .

The energy of the ground state is chosen to be zero (consider it absorbed into the term when splitting the partition function into the practical one and the gauge term). Then,



Real N-atomic molecule contains 3N-6 vibrations (3N-5 in linear molecule). Frequencies of all modes may be different, so the resulting molecular vibrational partition energy will be a product of the contributions from all modes:



**F. Computing rotational partition function**

Rigid rotor model yields rotational energy levels: , where is a rotational constant, is the component of the inertia tensor.

The degeneracies of the levels are: 

Thus,



**effective rotational temperature**.

symmetry number (e.g. H-Cl = 1, Cl-Cl = 2, NH3 = 3, etc.)

There are two main cases:

**Classical**: , then the summation can be replaced by the integration:



**Quantum**:  - explicit summation