C8863
Free Energy Calculations

3. Statistical Thermodynamics

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Introduction

Description of Physical Reality

- macroscopic (substances and mixtures, thermodynamics)
- microscopic (atoms and molecules, quantum mechanics, classic mechanics)

Thermodynamics

- state quantities
- state equations
- laws of thermodynamic

Mechanics

- particles and interactions among them
- equations of motion

Phenomenological vs Statistical Approach

Phenomenological Approach:

Thermodynamics examines the interrelationships between quantities that characterize the macroscopic state of the system and their changes during physical processes. Many of the features of the system can be evaluated without a thorough knowledge of its internal structure. This approach is based on several axiomatically pronounced (and experimentally confirmed) laws, which, in connection with the known properties of the system, served to derive other properties and relationships. The state of the system is described by means of state quantities and equations determining relations between state quantities.

Statistical Approach:

Statistical physics (statistical mechanics) puts two levels of description of physical reality in a relationship - macroscopic and microscopic. More traditionally, it deals with the investigation of the properties of macroscopic systems or systems, taking into account the microscopic structure of these systems (statistical thermodynamics). The founders were Ludwig Boltzmann and Josiah Willard Gibbs.

wikipedia.cz, upraveno

Statistical Thermodynamics

System and its properties

Consider a system that can be found in a variety of **microstates** (these are the quantum-mechanical states of the entire system — that is, all the molecules or atoms of the system) that change over time.

The **observable property** M of the system is then the **time average over the microstates** that the system gradually acquires over time:

$$\overline{M} = \frac{1}{t_{tot}} \int_{o}^{t_{tot}} M(t)dt$$

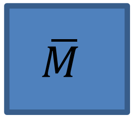
where *M(t)* is value of property M in a microstate, which the system gains at time *t*.

If the system is in equilibrium, for a sufficiently long t_{tot} measurement, the average value of the observable quantity is constant.

$$\frac{d\overline{M}(t_{tot})}{dt_{tot}} = 0$$

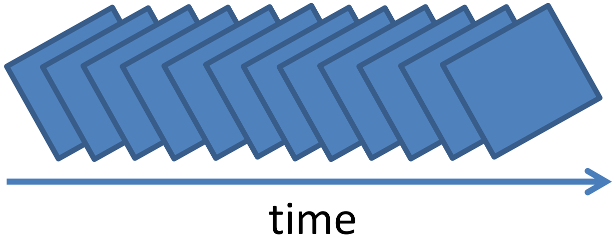
State vs Microstates

thermodynamic
state



$$\overline{M} = \frac{1}{t_{tot}} \int_{o}^{t_{tot}} M(t)dt$$

microstates

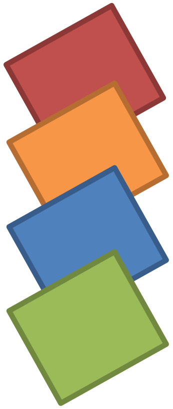


How many unique microstates are present in the time line?

$$dt \rightarrow 0$$

What is the typical size of dt?

example: four microstates



$$p_1 = \frac{3}{12}$$

$$p_2 = \frac{2}{12}$$

$$p_3 = \frac{3}{12}$$

$$p_4 = \frac{4}{12}$$

$$\overline{M} = \sum_{i=1}^{K} p_i M_i$$

Time vs ensemble averages

The evaluation of M(t) requires the solution of motion equations, which is an unsolvable task with respect to the large number of particles (atoms, molecules) from which the system consists.

For this reason, in statistical thermodynamics, the ensemble average of the quantity is used instead of the time average:

$$\overline{M} = \sum_{i=1}^{K} p_i M_i$$

p_i – probability of microstate *i*
M_i – value of mechanical property of microstate i
K – number of microstates

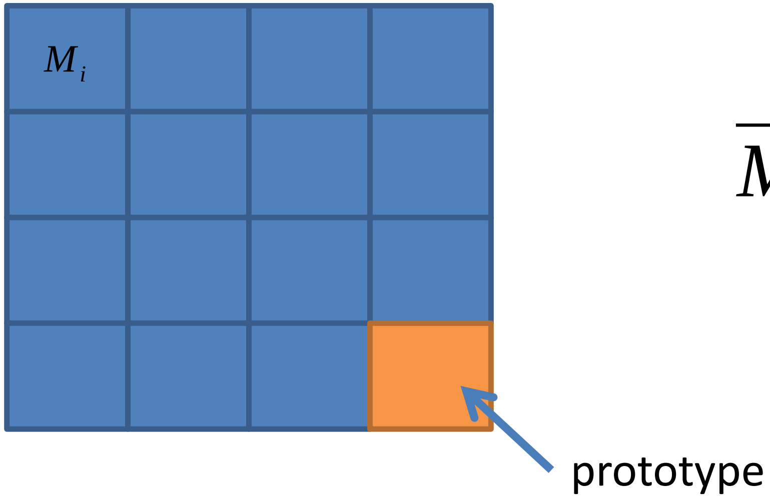
Ergodic hypothesis (postulate) argues that both approaches (time and ensemble) for calculating the average provide the same outcome.

Statistical thermodynamics deals with evaluation of probabilities p_i.

Statistical Ensemble

The **statistical ensemble** (Gibbs ensemble) is a thought construction in which a set is created by a large number of copies of a system (prototype) whose thermodynamic properties we want to determine. Each prototype replica is located in one of available microstates. The interactions between the prototype replicas are very weak (practically negligible), however, sufficient to maintain **thermodynamic equilibrium**.

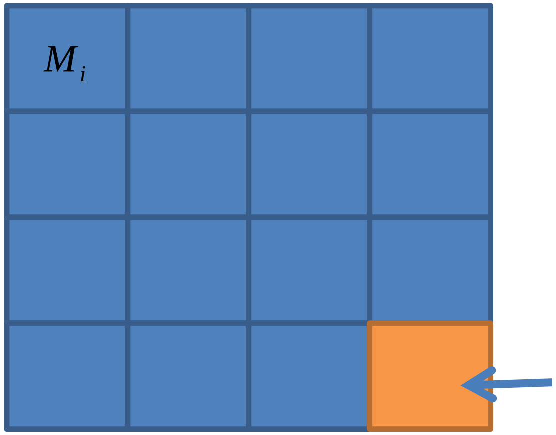
Statistical Approach:



$$\overline{M} = \sum_{i=1}^{K} p_i M_i \qquad p_i = \frac{n_i}{L} = ?$$

L	– number of prototypes
K	– number of microstates
n_i	– number of prototypes in microstate i
p_i	– probability of microstate *i*

Properties of Prototype (System)



prototype

L – number of prototype copies

Intensive properties:

$$T_e = T \quad \text{(temperature)}$$

$$p_e = p \quad \text{(pressure)}$$

Extensive properties:

$$U_e = LU \quad \text{(internal energy)}$$

$$S_e = LS \quad \text{(entropy)}$$

$$F_e = LF \quad \text{(Helmholtz energy)}$$

properties of ensemble

properties of prototype (system)

Number of Ensemble Realizations

Statistical ensemble can be created in many different ways. The number of possible implementations for a given number of prototypes in a given microstate n_i (distribution of microstates) is given by **the statistical weight of the distribution W**:

$$\underbrace{W(n_1,\ldots,n_K)}_{\text{distribution of microstates}} = \frac{\overbrace{L!}^{\text{number of all combinations}}}{\underbrace{\prod_{i=1}^{K} n_i!}_{\text{correction for indistinguishability of microstates}}}$$

L – number of prototype copies
K – number of microstates
n_i – number of prototypes in microstate i

Pravděpodobnost výskytu mikrostavu

The probability of microstate in the ensemble is given as a weighted average over all possible implementations (distribution of microstates) of the ensemble:

$$p_i = \frac{\sum_j^{realizace} W_j \boxed{\frac{n_{i,j}}{L}}}{\sum_j^{realizace} W_j}$$

← probability for implementation with W_j

Since L is a large number, there is a realization for which the statistical weight of the distribution W* dominates over others.

$$W^*(n_1^*, \ldots, n_K^*) >> W_{others}$$

Maximum of Statistical Weight

$$W^*(n_1^*,\ldots,n_K^*) = \frac{L!}{\prod_{i=1}^{K} n_i!} \rightarrow \max!$$

We are searching for a representation of microstates in which the statistical weight gains its maximum.

Probability of microstate in realization of ensemble with maximum statistical weight:

$$W^*(n_1^*,\ldots,n_K^*) >> W_{ostatní}$$

$$p_i = \frac{\sum_j^{realizace} W_j \frac{n_{i,j}}{L}}{\sum_j^{realizace} W_j} \approx \frac{W^*}{W^*}\frac{n_i^*}{L} = \frac{n_i^*}{L}$$

There is just one distribution of the prototype microstates that uniquely determines the most likely composition of the statistical ensemble and hence the thermodynamic properties of the prototype.

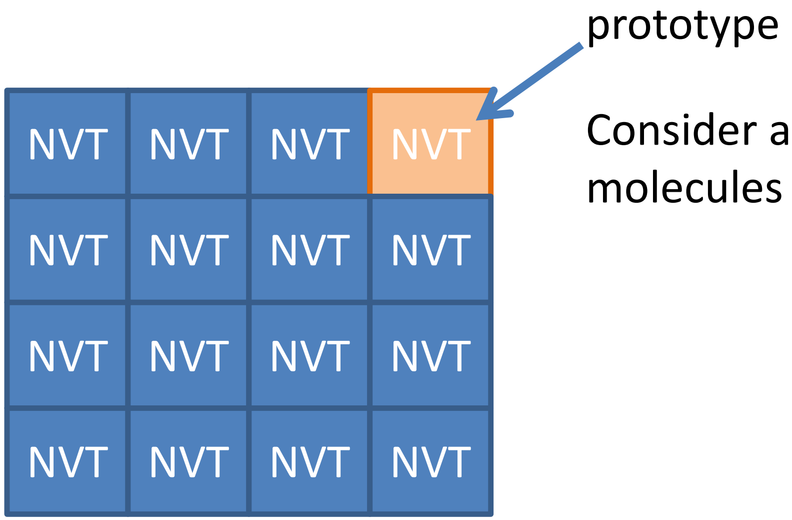
Types of Statistical Ensembles

The properties of the statistical ensemble must fulfill predefined conditions, which then influence the maximum statistical weight.

The most common types of statistical ensembles include:

- **microcanonical ensemble** (NVE) - the prototype contains a constant number of particles, has a constant volume and energy
- **canonical ensemble** (NVT) – the prototype contains a constant number of particles, has a constant volume and temperature
- **grandcanonical ensemble** (μVT) - the prototype has a constant chemical potential, volume, and temperature

Canonical Ansemble



prototype

NVT	NVT	NVT	NVT
NVT	NVT	NVT	NVT
NVT	NVT	NVT	NVT
NVT	NVT	NVT	NVT

Consider a system (prototype) that has a constant number of molecules and a constant volume.

The energy of the ensemble is equal to the sum of the energies of the prototype copies (the copies do not interact) :

$$E = \sum_{i=1}^{L} E_i$$

Statistical Weight and Entropy

It can be shown that the statistical weight W is related to the entropy of the statistical ensemble S_e.

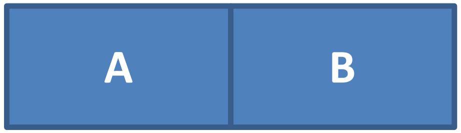
$$\boxed{S_e = k_B \ln W}$$

k_B – Boltzmann constant

k_B – is not one due to definition of temperature

Finding the maximum statistical weight is equivalent to finding the state of the ensemble (and also the prototype) with maximum entropy.

1) *W* is property of a state, therefore, it must be a state function
2) *W* is extensive property



two statistical ensembles in equilibrium

$$W = W_A W_B \longrightarrow \ln W = \ln W_A W_B = \ln W_A + \ln W_B$$

$$S = S_A + S_B$$

3) At T = 0, all prototypes will be in one microstate (with the lowest energy), W = 1 → S = 0 (consistent with the third thermodynamic law).
4) The definition is consistent with other thermodynamic properties that will be further derived.

Maximum Entropy of Canonical Ensemble

$$S_e = k_b \ln W(n_1,\ldots,n_K) = k_b \ln \frac{L!}{\prod_{i=1}^{K} n_i!} \to \max!$$

We are looking for a representation of microstates (distributions) in which the entropy of the statistical ensemble reaches its maximum.

Stirling approximation is used to find the maximum:

$$\ln x! \approx x \ln x - x$$

In addition, the extreme must meet the following binding conditions:

$$E = \sum_{i=1}^{K} n_i E_i \qquad N = \sum_{i=1}^{K} n_i$$

Indeterminate Coefficient Method

Extreme search with binding conditions – Lagrange method

$$\ln W(n_1,\ldots,n_K) + \alpha\underline{(E - \sum_{i=1}^{K} n_i E_i)} + \beta\underline{(N - \sum_{i=1}^{K} n_i)} \rightarrow \max!$$

Lagrange multiplicators

$$\frac{d}{dn_i}\left(\ln W(n_1,\ldots,n_K) + \alpha(E - \sum_{i=1}^{K} n_i E_i) + \beta(N - \sum_{i=1}^{K} n_i) \right) = 0$$

Results

Partial result:

$$n_i^* = e^{-\alpha} e^{-\beta E_i}$$

Lagrange multiplicators:

$$e^{-\alpha} = \frac{N}{\sum_{j=1}^{K} e^{-\beta E_j}}$$

$$\beta = \frac{1}{k_B T}$$

k_B – Boltzmann constant

T – absolute temperature

Final result:

$$p_i^* = \frac{e^{-\beta E_i}}{\sum_{j=1}^{K} e^{-\beta E_j}} = \frac{e^{-\beta E_i}}{Q}$$

Canonical partition function:

$$\boxed{Q = \sum_{j=1}^{K} e^{-\beta E_j}}$$

normalization constant

A range of thermodynamic properties of a system can be determined from partition function.

Thermodynamic Properties

Internal Energy:

$$\boxed{U = k_B T \left(\frac{\partial \ln Q}{\partial \ln T} \right)_{N,V}}$$

$$U = \sum_{i=1}^{K} E_i p_i^* = \frac{\sum_{i=1}^{K} E_i e^{-\beta E_i}}{\sum_{j=1}^{K} e^{-\beta E_j}} = \frac{\sum_{i=1}^{K} E_i e^{-\beta E_i}}{Q}$$

Entropy:

$$\boxed{S = \frac{U}{T} + k \ln Q}$$

Helmholtz Energy F:

$$F = U - TS$$

$$\boxed{F = -k_B T \ln Q}$$

Summary

Canonical partition function:

discrete microstates
(from quantum chemical calculations)

$$Q = \sum_{j=1}^{K} e^{-\beta E_j}$$

continuous microstates
(from molecular dynamics simulations)

$$Q = \iint_{\Omega} e^{-H(x,p)} d\boldsymbol{x} d\boldsymbol{p}$$

phase space of give thermodynamic state

Helmholtz energy F:

$$F = -k_B T \ln Q$$