LVA 349.030

Thermodynamics of Nano-Structural Systems

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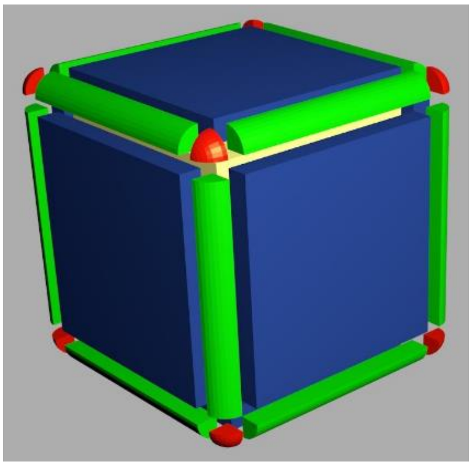
Extracurricular lecture series for students in Chemistry, Physics and Nano Science

2hr./3ECTS as a free elective subject   Prerequisite: basic course in thermodynamics

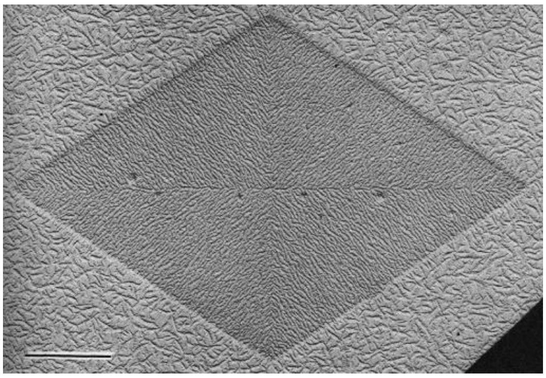
Registration via KUSSS or personally (KG620) until March 7th, 2021
First lecture in week 11 to be fixed after a short **introduction** on
Thursday, March 9th, 2023, 13:00 in KG606.

Motivation: In structured media interfaces and the corresponding interfacial tension play an important role, in particular when micrometer sizes are present. Capillarity as a scientific field goes back to the famous work of Gibbs (1875-1878) containing even ideas applicable for nanostructural systems, which, however, have been worked out systematically only recently (2018).

For the simple case of domains in the form of cubes with side length L as sketched in the figure, energetic (and other) properties consist of **four** parts: a **volumetric** contribution (yellow) proportional to L^3, **surface** contributions (blue) proportional to L^2, **edge** contributions (green) proportional to L^1, and **vertex** contributions (red) independent of L. It is obvious, that with decreasing side length of the cube $L \to 0$ the latter two contributions will dominate most properties.

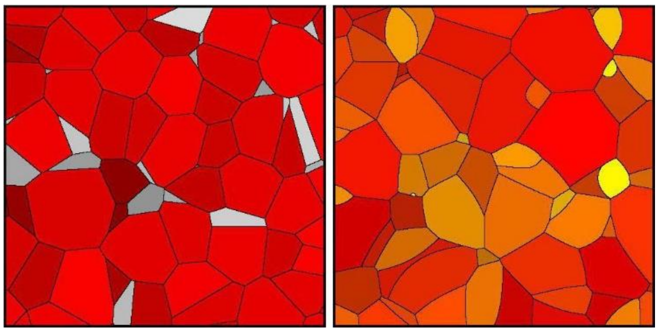


This behavior is also valid for general geometric forms of entities in solid, liquid or gas phases.



The Young-Laplace equation (1806) stating a simple proportionality between the pressure jump at an interface and the mean curvature of the interface (with the interfacial tension as proportionality constant) is frequently used nowadays. For small domains this relationship diverges, when the size decreases towards small values. In order to overcome this difficulty, size dependent interfacial tensions have been proposed, which, however, turn out to be misleading in systems with nanoscale structures. A general way to resolve this dilemma can be found using the works of Gibbs and Steiner (1840), which leads to a quite obvious extension of the classical form of the work differential in the first law of thermodynamics just by introduction of two additional energetic quantities.

In this series of lectures the general concepts of thermodynamic properties of nanostructural media are worked out. The use of all 4 basic energetic properties in such systems leads to important results for applications in **suspensions**, **aerosols** and for the description of **phase transitions** (nucleation).



Provisional chapters

0. Preface

1. Equilibrium thermodynamics of two-phase systems – classical approach
Classical representation of the basic laws of thermodynamics; phase diagrams; the Young-Laplace equation

2. Geometrical properties of bounded domains (bubbles, droplets, crystals, …)
The four basic geometric properties of bounded domains (Minkowski functionals); Steiner relations; local curvature properties of areas/surfaces/interfaces; the Minkowski functionals and their relations to curvature; an alternative characterization of Minkowski functionals; description of phase morphologies by Minkowski functionals

3. Fundamental energetic properties of nano-sized objects
The four basic energetic properties of structured media; estimates for the basic energetic properties of structured media

4. Equilibrium thermodynamics of two-phase systems – generalized approach
Generalized representation of the 1^{st} and 2^{nd} law of thermodynamics; the generalized Young-Laplace equation

5. Applications I: Nucleation in one-component systems
Extension of the nucleation theory of Becker and Döring; nucleation by coalescence; the temperature of homogeneous nucleation; the role of the item energy

6. Chemical potentials of interfaces
Generalized description of the internal energy in multi-component two-phase systems; evaluation for the thermodynamic equilibrium; Gibbs free energy and the generalized Gibbs-Duhem equation

7. Applications II
The surface tension of water/alcohol mixtures; stability of emulsions; the gas/liquid equilibrium of air/water – the generalized Kelvin equation

8. Outlook: Extensions to three- and four-phase systems