

LVA 349.030

Thermodynamics of Nanostructural Systems

Gerhard Eder

Institute of Polymer Science

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: until March 7th, 2021

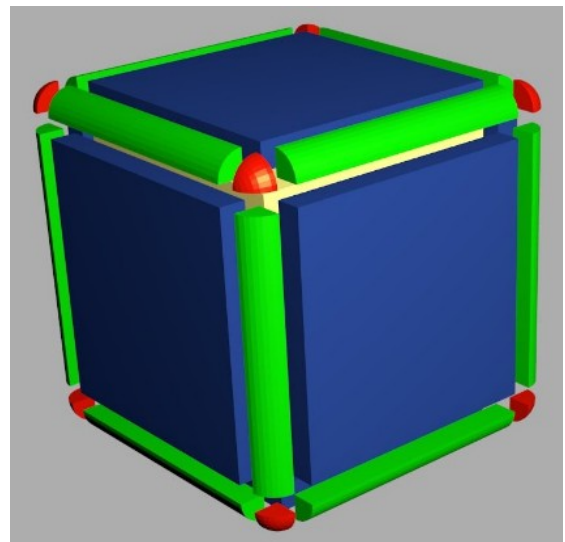
First lecture in week 11 to be fixed after a short

introduction (via Zoom, link in KUSSS) on **Tuesday, March 9th, 2021, 13:00**

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).

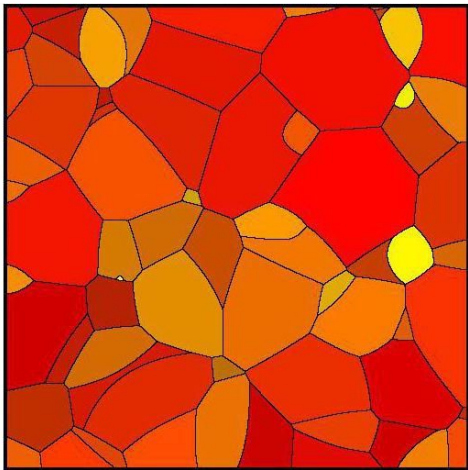
The Young-Laplace equation (1806) stating a simple proportionality between the pressure jump at an interface and the mean curvature of the interface (with the interfacial tension as proportionality constant) is frequently used nowadays. For small domains this relationship diverges, when the size decreases 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.

For the simple case of domains in the form of cubes as sketched in the figure these quantities refer to the contribution of the molecules forming the edges (green) and the



vertices (red). It is obvious, that with decreasing side length of the cube $L \rightarrow 0$ the volumetric contribution (yellow) goes towards zero proportionally to L^3 , the surface contribution (blue) with L^2 , the edge contribution with L^1 , leaving the constant vertex contribution. This behavior is valid also for general geometric forms of entities in solid, liquid or gas phase. Therefore, the most important contribution to the total energy proceeds from the volumetric contribution via surface contribution via edge contribution to the vertex contribution when going from macroscopic systems towards smaller and smaller scales.

In this lecture series the general concepts of thermodynamic properties of nanostructured media are worked out. The use of all 4 basic energetic properties of



structured media leads to important results for applications in suspensions, aerosols and for nucleation models. As an example, in one component systems near the equilibrium l/s-coexistence line it turns out, that stable (non-growable) clusters in the liquid phase can already be present. Finally, some perspectives will be presented for three- and four-phase systems, in which in addition to contact interfaces also contact lines (between 3 different phases) and contact vertices (between 4 different phases) and related contact angles show up.

Provisional chapters:

1. Equilibrium thermodynamics of two-phase systems – classical approach
Classical representation of the basic laws of thermodynamics; phase diagrams; interfacial tension and the Young-Laplace equation; conceptual problems with the classical approach
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 surfaces/interfaces
3. Fundamental energetic properties of nanostructural two-phase systems
Internal vs. external work; the four basic energetic properties of structured media; estimates
4. Equilibrium thermodynamics of two-phase systems – generalized approach
Generalized representation of the 1st and 2nd law of thermodynamics; the generalized Young-Laplace equation
5. Chemical potentials of interfaces
Extensions for multi-component systems; generalized Kelvin equation; Cahn/Hilliard theory
6. Applications
Thermodynamic stability of clusters; homogeneous nucleation; self-nucleation; stability of emulsions and aerosols
7. Extensions to three- and four-phase systems
Contact areas, contact curves, contact vertices; contact angles; heterogeneous nucleation
8. Consequences for non-equilibrium thermodynamics and outlook
Kinetics of phase transitions; generalized Becker-Döring theory; outlook