Thermal Physics of Nanostructured Materials: Thermodynamic (Top-Down) and Quantum (Bottom-Up) Issues

Jaroslav Šesták

New Technology - Research Centre in the Westbohemian Region, West Bohemian University, Universitní 8, CZ-30114 Pilsen

sestak@fzu.cz

The subject is focusing on the newly adjusted thermodynamic degree of freedom which is *dimension*. Nanoworld thermodynamic groundwork unfolds from a single phase division into α and β separated by interface the curvature of which request the higher pressure on the concave side with respect to the surrounding, p, i.e., $p_\alpha > p_\beta = p$ (Young-Laplace effect). It can happen by splitting up (division, cleavage) or nucleation, as well as by elastic deformation (strain) of already existing surface due to the impact if isotropic or nonisotropis stress, $dw_{surf} = \gamma\, dA$, where the scalar parameter γ (defined as a specific surface energy) is always positive (due to the stability criteria) and is independent on the surface, A. Performed work, $dw_{surf} = f\, dA_{elast} = f\, A\, d\varepsilon$, causes elastic deformation (*strain* ε) of the original surface assuming $d\varepsilon = dA/A$. Unite specific surface work is called surface stress, f, and possesses generally tensor denomination but for isotropous environment become scalar following $w_{surf} = f\, A_{elast}$. As a result we can say that any nanosystem possesses its size as an extra degree of freedom, equilibrium of which requires a modification of traditional macroscopic thermodynamics. Everything factually originates from the Kelvin historical relation, $p/p_\infty = 2V\gamma/(RTr)$, and the related equation for temperatures, $T/T_\infty = 2V\gamma/(\Delta H\, r)$. In the other words it means that if we want to create any equilibrium modification for a variation of curvature upon the change of external conditions (T, p) we have to change either pressure (from $p_{\beta\infty}$ to $p_{\beta r}$ under constant T_∞) or temperature (from T_∞ to T_r under constant$_\infty$) so that the change in the difference of bulk chemical potentials $\Delta\mu$ is compensated by negative $2\gamma V_{\alpha m}(1/r)$. It associates similar effect as rapidly changed temperature when observing real shapes kinetic phase diagrams (temperature shifts) providing a new space for novel thermophysical studies including impact of eccentricity of heat transfer, heat capacities or phase relations in nanodimensional space. Modern descripttion came with the paper introducing the term 'microcluster' as a new phase of matter and book showing that they cannot be formed fully accidentally but the atoms are combined according some 'magic numbers' (e.g. Fibonacci following the calcium clusters series 561, 923, 1415, 2057, etc). The particle is in order of size ($\sqrt[3]{N}\, d$) where N is the number of atoms and d is their diameter showing that for d~2-3 A is N~2-10 nm. There exists metal model clusters describing systems up to 80 atoms. The number of atoms of a nanoparticle can be derived from the Loschmidt number giving 2.6×10^{19} atoms in a cubic cm of a substance so that about 10^4 atoms are contained in nanoparticle cube with a side of 100 nm. It associates with a notion of the so-cooled Planck's mass amounting 2.17×10^{5}g and specifying the boundary of quantum world. In a crystallographic view spheres of a given radius or regular tetrahedral with a given edge can be assumed as the most closely packed in space, i.e., crowded so that the ratio between the filled part of the space and the unfilled part would be as large as possible. Using polyhedra the whole space could be filled by appropriate packing of the congruent specimens of these polyhedra starting e.g. from a cube, adge, a, (surface/volume: $A/V \cong 6/a$), terehedron, via penta-, hexa-, hepta-, nona-, deca-, dodeca-, icosa-, triaconta-, hexaconta-, enneaconta-, up to an infinite faceted ultimate sphere of radius, r, ($A/V \cong 2/r$). Another important process of covering a space with polyhedra is the so called stellation, following the historical Kepler constructions (year 1611) of the first two other stellar polyhedron from dodecahedron. This multiplication process of self-repetition yields the specificity of a self-similar system which shows statistically the same properties at many scales and which is well known as sourced on the Koch curves (i.e. snowflakes), further defining the self-similarity dimension in the sphere of fractals expressing thus the complexity of an object and giving the intermediary to chaos (supposing both ways from the top to bottom and vice versa). Similarly assumed clustering is close to the real

pattern of a structure evolution from disorder (chaos), local ordering up to periodic structures sometimes including structural code or even inorganic gene and became close to the topic of chemistry beyond the molecule and special associated as superatoms exhibiting the quantum properties of nanoclusters (i.e. quantum nature of nanostes).

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