# Peculiarities of nano-structured systems:
## Thermodynamic (*top-down*) and quantum (*bottom-up*) issues

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The subject is a continuation of the GEFTA 2010 lecture "Macro/meso/micro/nano world: temperature and thermal physics" now focusing instead idiosyncrasy of the pair heat-temperature to the new degree of freedom which is *dimension*. Involved nanostructured systems have a rich history beginning with a colloidal solution - heterogeneous mixture in which the particle size of the substance is intermediate between a true solution and a suspension, *i.e.*, between 1-1000 nm (even smoke from a fire is a good example). Imperative status has a colloidal gold as a suspension (or colloid) of submicron-sized particles of gold in a fluid (water) or glass providing an intense red color (for particles <100 nm ) or blue purple (for larger particles). J. Herschel invented in 1842 a photographic process called chrysotype that used colloidal gold to record images on paper. Some properties of inherent nanoparticles were investigated using the term micro-clusters (which term was used for the first time in 1661 by English chemist R. Boyle) and associated with the Alchemist process of multiplied division. Modern description 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 size is in order of ($^3\sqrt{N}$ 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 a model metal clusters information describing systems up to 80 atoms. The number of atoms of a nanoparticle can be derived from the Loschmidt number giving $2.6 \times 10^{19}$ 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-called Planck's mass that amounts to $2.17 \times 10^5$ g of which specifies the boundary of the 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 polyhedral, the whole space could be filled by appropriate packing of the congruent specimen 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 infinitely faceted ultimate sphere of radius, r, (A/V $\cong$ 2/r). Abatement of the restrictions of a regular symmetry in nanoworld leads to the appearance of icosahedral packing with unusual pentagonal symmetry (*i.e.* quasi-particles) 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 specially associated behavior in terms of superatoms exhibiting the quantum properties of nanoclusters (i.e. *quantum nature* of nanaostes).

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 non-isotropic stress, $dw_{surf} = \gamma\, dA$, where the scalar parameter $\gamma$ (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 $\varepsilon$*) 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 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 $T_\infty$) or temperature (from $T_\infty$ to $T_r$ under constant) so that the change in the difference of bulk chemical potentials $\Delta\mu$ is compensated by negative $2\gamma V_{am}(1/r)$. Certainly there exists further particularizing models such as liquid skin melting (LSM) assuming that melting starts on the particle surface creating thus a thin surface layer of the thickness $\delta$ (an adjustable parameter) so that $T/T_\infty = 1-(2V\gamma/(\Delta H(r-\delta)))$ eventually including the shape dependability $T/T_\infty = 1-(A/V\Delta H)(\gamma_{sol} - \gamma_{liq})$ where for a sphere A/V equals 3/r. Another impact relates to the particle volume contraction $\Delta V$ due to the internal over-pressure which often results in the internal phase transition. Also the mixing enthalpy $\Delta H_{mix}$ (and Gibbs energy $\Delta G$) depends on the particle size and the atomic distribution which may vary from the flat to curved surface owing to the cause of curvature yielding thus a surface interface segregation. There are yet unsolved specifics of melting due to the characteristic of the interface, such as coherent (with a small elastic deformation due to the small differences of atomic arrangements) and incoherent (with a large elastic deformation due to the significant differences in atomic arrangements). On the temperature dependence of melting for nanoparticles of indium in the matrix of alumina prepared through different techniques it was experimentally observed a opposite temperature behavior of particles obtained by extreme melt-fast-quenching (firmly built-in the matrices thus having little volume flexibility) and those loosely integrated particle (produced by intensive ball milling having thus more space within the matrices) exhibiting classically assumed decrease of melting temperature upon the diminishing particle diameter (d). Correspondingly, it is necessary to consider the effect of the particle-matrix interaction in the case of polymeric nanocomposites wherein nanoobjects (often nanofibres) are continuously surrounded by a rigid solid phase often as a core-shell structure, the interior being covered with a thin surface layer of another material (filament surface chemically ached, oxidized, etc). 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.

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