https://doi.org/10.15407/ujpe68.1.53

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TO THE DIMENSIONAL EFFECT IN NANOSTRUCTURED SYSTEMS

An expression for the Gibbs–Thomson formula in the nanometer interval from 1 to 10 nm is obtained, in which the surface energy σ_0 depends on the particle size r. It is shown that the account for the dependence $\sigma(r)$ changes the solubility of nanoparticles and the rate of their growth $\frac{dr}{dt}$, and, hence, the kinetics of the Ostwald ripening process in whole. This circumstance is especially important in the case of quantum dots obtained using the colloidal chemistry methods in the spherical form, with dimensions ranging from one to several nanometers.

K e y w o r d s: nanotechnology, nanostructured system, nanoparticle, surface energy, quantum dot, Ostwald ripening, Gibbs–Thomson effect.

1. Introduction

Nanostructured systems, which are the product of a nanotechnology, find exclusively important practical applications. Nanotechnology is a new interdisciplinary science. According to many experts, the progress in its development can be transformed into another (fourth) industrial revolution. Nanotechnology is associated with the creation of highly effective medicines and computers of unprecedented power, the implementation of "molecular manufactures" working on the basis of the "from bottom to up" principle, when a required nanostructure is pieced together from separate atoms and molecules, and so forth. A special role of the nanotechnology consists in the creation, implementation, and expansion of technological strategies resembling those that exist and operate in nature.

A new and very interesting phenomenon is observed in the world science. This is an interdisciplinary research performed on the basis of science and technology that are growing and complementing each other. As a result, new, absolutely unexpected properties are discovered in well-known substances, which makes it possible to create new materials and new technological methods. This phenomenon even was given a special name, the fusion or merging of technologies [1].

The production of nanostructured systems for special purposes in the framework of the merging of technologies, or structural materials strengthened by nanodispersed phases, or island films, or heterosystems with quantum dots (QDs), and so on implies the stability of their structure. However, the Ostwald ripening (OR), which is observed in those and similar systems, may be accompanied by an imbalance of their nanostructure and a partial – sometimes, complete – loss of their properties useful for practice that were acquired by the system during its synthesis.

C i t a t i o n: Vengrenovich R.D., Ivanskii B.V., Kryvetskyi V.I., Fesiv I.V., Yarema S.V. To the dimensional effect in nanostructured systems. *Ukr. J. Phys.* **68**, No. 1, 53 (2023). https://doi.org/10.15407/ujpe68.1.53.

Ц и т у в а н н я: Венгренович Р.Д., Іванський Б.В., Кривецький В.І., Фесів І.В., Ярема С.В. До розмірного ефекту в наноструктурних системах. *Укр. фіз. журн.* **68**, № 1, 53 (2023).

The essence of the OR phenomenon, which is a result of the Gibbs–Thomson effect, consists in that owing to the diffusional transfer of the substance from particles with a larger surface curvature to particles with a smaller one, the former particles dissolve and disappear, whereas the latter grow at the expense of the former. This process gives rise to a continuous growth of the average particle size and an unbalance in the initial microstructure.

The first theory describing the OR was the theory created by Lifshits, Slezov, and Wagner (LSW) [2–4]. It described well experimental data obtained in the micrometer interval of particle sizes. In particular, it was true the Lifshits–Slezov (LS) and Wagner (W) size distributions. With the development of the nanotechnology, the LSW theory was applied to nanostructured systems without any reservations and without working out the corresponding criteria. It turned out, however, that the classical version of the LSW theory is hardly applicable to describe experimental data obtained for nanometer-sized particles (nanoparticles, NPs).

In order to bring the LSW theory closer to practice, it was modified [5–8]. The idea consisted in that the modified theory should account for the specific features of OR in nanostructured systems. In particular, it can be a possibility of the NP growth (dissolution) simultaneously driven by two mechanisms, the diffusion and Wagner ones. As a result, in the modified LSW theory, instead of the NP size distribution, we have the generalized LSW (GLSW) distribution, which describes many more experimental curves than the LS and W distributions do.

Nevertheless, there exist some experimental histograms that are not described by any of the LS, W, and GLSW theoretical curves. This fact means that not all factors that govern the OR process in nanostructured systems are taken into account in the available theories. First of all, this concerns the structural size effect, where the particle size is a critical quantity [1].

In this work, we will try to show how the size effect (within an interval from 1 to 10 nm) can affect the solubility of NPs and, therefore, the OR kinetics.

2. Solubility of Nanoparticles from One to Ten Nanometers in Dimensions

The solute concentration C_r at the interface particle–solution (the solubility) is described by the well-known Gibbs–Thomson formula

$$C_r = C_\infty \ell^{\frac{2\sigma_0 \upsilon_m}{kT}\frac{1}{r}}, \tag{1}$$

where C_∞ is the equilibrium concentration at a plane interface, σ_0 is the specific surface energy, υ_m is the volume of a solute atom, k is the Boltzmann constant, and r is the particle radius. As a rule, formula (1) is written in the form

$$C_r = C_\infty \left(1 + \frac{2\sigma_0 \upsilon_m}{kT}\frac{1}{r}\right), \tag{2}$$

where the smallness of the power exponent in Eq. (1) is taken into account.

Particles (structural elements) in nanostructured systems can be of various shapes: spherical, flat (disk-shaped), in the form of a spherical segment (dome-shaped), and others; and the solution can be the supersaturated steam, supersaturated liquid (melt), supersaturated solid phase (solid solution), and others. Expression (1) not only allows one to better understand the physical essence of the Gibbs–Thomson effect, but it is one of the most important relationships in the OR theory. It makes it possible to determine the growth rate $\frac{dr}{dt}$ in the OR process, and, hence, to formulate a closed system of integro-differential equations whose solution enables the complete determination of the OR kinetics, i.e., the time evolution of such parameters as the solute concentration $\langle C\rangle$, the supersaturation $\Delta = \langle C\rangle - C_\infty$, the critical, r_k, maximum, r_g, and average sizes of NPs, their concentration, size distribution, and so forth.

In formula (1), the parameter σ_0 is considered to be constant. However, it turned out that the structural-size effect is observed in the NP size interval from 1 up to 100 nm. It consists in that if the NP size is smaller than 10 nm, σ_0 is not a constant anymore, but depends on the NP size [1]. Taking this circumstance into account, formula (1) for the NP size interval from 1 to 10 nm takes the form

$$C_r = C_\infty \ell^{\frac{2\sigma \upsilon_m}{kT}\frac{1}{r}}. \tag{3}$$

If we consider, in the first approximation, that

$$\sigma = \sigma_0 \frac{r_0}{r}, \tag{4}$$

where $r_0 \approx 10$ nm, then Eq. (3) can be rewritten as follows:

$$C_r = C_\infty \ell^{\frac{2\sigma_0 r_0 \upsilon_m}{kT}\frac{1}{r^2}} \approx C_\infty \left(1 + \frac{2\sigma_0 r_0 \upsilon_m}{kT}\frac{1}{r^2}\right). \tag{5}$$

Thus, in Eq. (5), the exponent power is reciprocal not to the NP radius, but to its square. This means that the solubility of NPs drastically increases in the indicated size interval and, accordingly, their instability also grows, which ultimately changes the OR kinetics.

Expression (5) corresponds to spherical NPs. In order to obtain corresponding formulas for NPs of any geometric shape, then, when modeling the structural elements of a nanostructured system, it is necessary to use a transient expression for the Gibbs–Thomson formula in the form [8]

$$C_r = C_\infty \ell^{\frac{\upsilon_m}{kT}\Delta P} \approx C_\infty \left(1 + \frac{\upsilon_m}{kT}\Delta P\right), \tag{6}$$

where ΔP is the additional pressure under the curved NP surface. The additional Laplace pressure ΔP can be expressed via the particle size by equating the work executed by the pressure, when the NP volume changes by dV and the reduction of the free surface energy: $\Delta P dV = \sigma dS$ or

$$\Delta P = \frac{\sigma_0 r_0}{r}\frac{dS}{dV}. \tag{7}$$

In particular, for a dome-shaped particle in the form of a spherical segment,

$$\Delta P = \frac{2\sigma_0 r_0}{r^2}\sin\theta\frac{\alpha_2(\theta)}{\alpha_1(\theta)}, \tag{8}$$

where θ is the contact angle [8, 9], so that

$$C_r = C_\infty \ell^{\frac{2\sigma_0 r_0 \upsilon_m}{kT}\sin\theta\frac{\alpha_2(\theta)}{\alpha_1(\theta)}\frac{1}{r^2}} \approx$$

$$\approx C_\infty \left(1 + \frac{2\sigma_0 r_0 \upsilon_m}{kT}\sin\theta\frac{\alpha_2(\theta)}{\alpha_1(\theta)}\frac{1}{r^2}\right). \tag{9}$$

In the case of disk-shaped particles that look like a cylinder of height h and radius r, and are embedded into a supersaturated solution of adatoms on a flat surface,

$$C_r = C_\infty \ell^{\frac{\sigma_0 r_0 \upsilon_m}{kT}\frac{1}{r^2}} \approx C_\infty \left(1 + \frac{\sigma_0 r_0 \upsilon_m}{kT}\frac{1}{r^2}\right), \tag{10}$$

if $h = \text{const}$, and

$$C_r = C_\infty \ell^{\frac{4}{3}\frac{\sigma_0 r_0 \upsilon_m}{kT}\frac{1}{r^2}} \approx$$

$$\approx C_\infty \left(1 + \frac{4}{3}\frac{\sigma_0 r_0 \upsilon_m}{kT}\frac{1}{r^2}\right), \tag{11}$$

if $h/r = \text{const}$.

Sometimes, pyramidal QDs in heterostructures are modeled as cone-shaped NPs so that

$$C_r = C_\infty \ell^{\frac{2\sigma_0 r_0 \upsilon_m}{kT}\sqrt{1+\frac{1}{a^2}}\frac{1}{r^2}} \approx$$

$$\approx C_\infty \left(1 + \frac{2\sigma_0 r_0 \upsilon_m}{kT}\sqrt{1+\frac{1}{a^2}}\frac{1}{r^2}\right), \tag{12}$$

where $a = \frac{h}{r} = \text{const}$, h is the cone height, and r is the cone base radius.

3. Conclusions

In order to determine the growth rate $\frac{dr}{dt}$ for particles in the nanometer size interval from 1 to 10 nm in the course of OR, it is necessary to know the Gibbs–Thomson formula for this interval. The dependence of the superficial energy σ on the particle radius, $\sigma(r)$, in its classical version testifies to possible changes in the solubility and the growth rate $\frac{dr}{dt}$ for NPs, and, therefore, in the OR kinetics. This is especially important for QDs synthesized using the colloidal chemistry methods in the form of spherical NPs, whose sizes vary from one to several nanometers.

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Received 27.01.20.
Translated from Ukrainian by O.I. Voitenko

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ДО РОЗМІРНОГО ЕФЕКТУ
В НАНОСТРУКТУРНИХ СИСТЕМАХ

Узагальнено формулу Ґіббса–Томсона для нанометрового діапазону від 1 до 10 нм, в якому величина поверхневої енергії σ_0 залежить від розмірів частинок. Показано, що врахування залежності $\sigma(r)$ приводить до зміни розчинності наночастинок і швидкості їх росту $\frac{dr}{dt}$, а відтак і до зміни кінетики всього процесу оствальдівського дозрівання. Це особливо важливо у випадку квантових точок, отримуваних методами колоїдної хімії, у вигляді сферичних частинок, розміри яких коливаються від одного до декількох нанометрів.

Ключові слова: нанотехнологія, наноструктурна система, наночастинка, поверхнева енергія, квантова точка, оствальдівське дозрівання, ефект Ґіббса–Томсона.