# Research of instability development of nanoparticle surface shape

Tamara N. Pogosian Sergey A. Chivilikhin Igor Yu. Popov
Victor V. Gusarov
edo-chan@mail.ru

**Abstract**

Due to the influence of a mass diffusion flux of droplets or the vapors mass flux on a surface from a gas phase, instability development of the nanoparticle surface shape happens. That is theoretically investigated in this work.

Growth of the condensed phase caused by diffusion deposition of substance from a gas phase on a surface of liquid or a solid body is accompanied by distortion of a form of this surface. The reason of such distortion is influence of a surface form on distribution of a mass flux along it. Emergence of a local unevenness on a surface for the casual reasons causes local increase of a mass flux that leads to perturbation growth. Without the factors which are smoothing a surface, perturbation of a surface accrue, and the less length of perturbation wave is, the more its growth rate is. Cause of formation of fractal structure on a surface [1]- [3] is such kind of instability. It can also lead to formation of fractal clusters [4] and nanoclusters [5]. Capillary forces are needed to achieve the opposite effect. They cause decrease of perturbations of a free surface. Stability or instability of perturbation depends on what of factors will prevail. It can cause forming different character of the structures on a surface - from system of the ordered waves to fractals. The similar reasons define fractal character of a surface of nanoscale clusters.

## 1 Formulation of the problem

Mathematical model approach is used in this article to investigate the influence of a mass diffusion flux on nanoparticle growth. For the description of a nanoparticle the liquid-drop model is used. The unperturbed surface is considered as an ideal sphere. The mass stream can be calculated in quasi–steady–state approximation using quasi–steady–state equation of diffusion: $\Delta C = 0$, with boundary conditions $C|_{r=R} = 0$, $C|_{r\to\infty} = C_\infty$. Here $C$ is concentration of the dissolved substance in liquid, $r$ is radial coordinate, $R$ is nanoparticle radius.

## 2 Calculations

With taking into consideration that perturbations of particle surface influence the field of concentration, we are looking for the solution of the diffusion equation in the form of summing up not perturbed decision and perturbed one: $C = C^{(0)} + \tilde{C}$, where $C^{(0)} = C_\infty(1 - R/r)$. The equation for the perturbation of concentration caused by perturbation of a surface form looks like $\Delta\tilde{C} = 0$, or in spherical coordinates:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\tilde{C}}{\partial r}\right)+\frac{1}{r^2 sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial\tilde{C}}{\partial\theta}\right)+\frac{1}{r^2 sin^2\theta}\frac{\partial^2\tilde{C}}{\partial\varphi^2}=0. \tag{1}$$

Boundary conditions to (1) look like $\tilde{C}|_{r=R}=C_\infty\tilde{r}/R,\ \tilde{C}|_{r\to\infty}=0$, where $\tilde{r}$ is perturbation of the nanoparticle surface.

Being limited to consideration of axisymmetric perturbation $\tilde{r}(\theta)$, $\tilde{C}(r,\theta)$ submit the decision (1) in the form of expanding in series of Legendre polynomials:

$$\tilde{C}=\frac{C_\infty}{R}\sum_{n=0}^{\propto}a_n\left(\frac{R}{r}\right)^{n+1}P_n(cos\theta), \tag{2}$$

where $a_n$ is expansion coefficients of perturbation $\tilde{r}$ in series of Legendre polynomials. For determination of dependence of these coefficients from time, we will write down the equation of evolution of a surface form:

$$\frac{\partial\tilde{r}}{\partial t}=V_P+V_D, \tag{3}$$

where $V_P$ is movement velocity of liquid on a particle surface, $V_D=j/\rho$ is velocity of a surface movement at the expense of a mass diffusion flux. Here $J=-D\partial C/\partial r|_{r=R},\rho$ is density of the particle. Using (3) and [6], we get the required equation of evolution of expansion coefficients $a_n$ in the shape of:

$$\frac{\mathrm{d}a_n}{\mathrm{d}t}=\frac{V}{R}\left(n+1\right)a_n-\frac{\sigma}{2\mu R_0}\gamma_n a_n, \tag{4}$$

where $V=DC_\infty/(\rho R_0)$ is unperturbed velocity of sphere radius growth, $\gamma_n=n(n+2)(2n+1)/(2n^2+4n+3)$. The first term in the right part of (4) describes increase of perturbation of a surface at the expense of mass diffusion flux. The second term, written down according to [6], corresponds to attenuation of perturbation of a liquid-drop surface with viscosity $\mu$ and surface tension coefficient $\sigma$. The solution of (4) is:

$$a_n(t)=a_n(0)exp\left(\left(V(n+1)-\frac{\sigma}{2\mu}\gamma_n\right)\frac{t}{R_0}\right).$$

It is important to mention that at $n\to\infty$, the equation becomes $a_n(t)=a_n(0)exp\left(n\left(V-\sigma/(2\mu)\right)t/R_0\right)$. That means that if $V>\sigma/(2\mu)$, coefficients of expansion correspond to unstable harmonics and speed of instability development increases with index growth, what corresponds to formation of fractal structure of a surface.

Obviously it is still needed to find $a_n(0)$ through initial perturbation of a surface. Let initial perturbation be expanded in series of Legendre polynomials too: $h_0(\theta)=\sum a_n(0)P_n(cos\theta)$. Using orthogonality condition of polynoms, we receive:

$$a_n(0)=\frac{2n+1}{2}\int_0^\pi h_0(\_theta)sin(\theta)P_n(cos\theta)d\theta.$$

To sum it up, the law of evolution of perturbation of a surface takes on form:

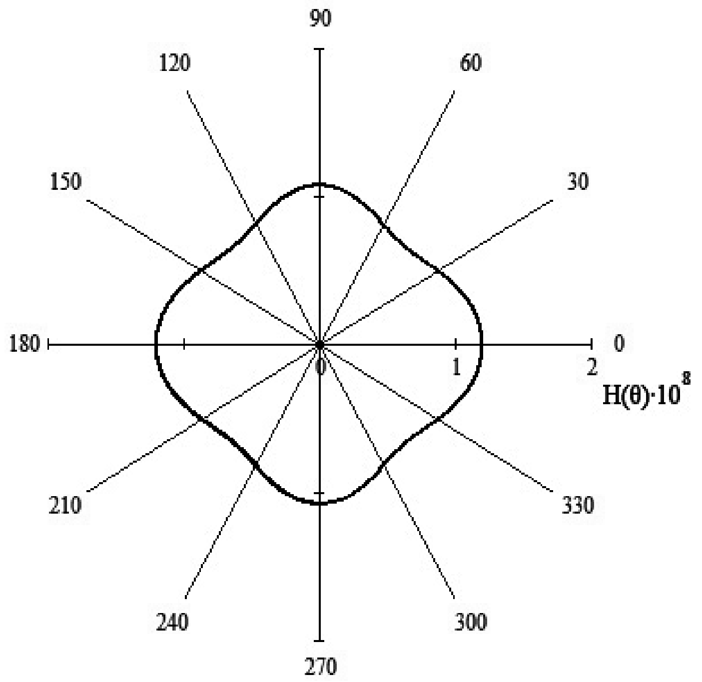


Figure 1: Polar plot $H(\theta)$:sum of particle radius and initial perturbation $h_0(t) = \alpha R_0 P_4(cos\theta)$, $R_0 = 10$ nm.

$$h(\theta, t) = \sum_{n=1}^{\infty} a_n(t) P_n(cos\theta).$$

Radial growth of a nanoparticle could be found from:

$$\frac{\mathrm{d}R}{\mathrm{d}t} = \frac{DC_\infty}{\rho R}, R(t) = \sqrt{R_0^2 + 2VR_0 t}.$$

## 3 Example

To give an example, it is necessary to take into consideration that values have to be approached to real physical quantities. Using approximations to the true values, it is possible to prove reality of the law of evolution of perturbation of a surface form.

For an example, we will consider initial perturbation in a form $h_0(t) = \alpha R_0 P_2(cos\theta)$, where $R_0$=10 nm, $\alpha = 0.2$. No matter what will be unperturbed velocity of sphere radius growth, surface tension coefficient and viscosity, the picture of perturbation, calculated under the law at $t = 0$, and the picture of initial perturbation (Fig. 1)will be the same. That speaks well for the received law of evolution.

Let $D = 10^{-4} m^2/s$, $C_\infty/\rho = 10^{-2}$, $\sigma = 0.3 N/m$, $\mu = 0.0018 kg/(m \cdot s)$. With increase in time it is possible to observe increase in perturbation (Fig. 2).

For the same parameters except $\mu = 0.0011 kg/(m \cdot s)$, with increase in time it is possible to observe the opposite effect, there is a tendency to perturbation relaxation and taking the form of the ideal sphere by nanoparticle (Fig. 3).

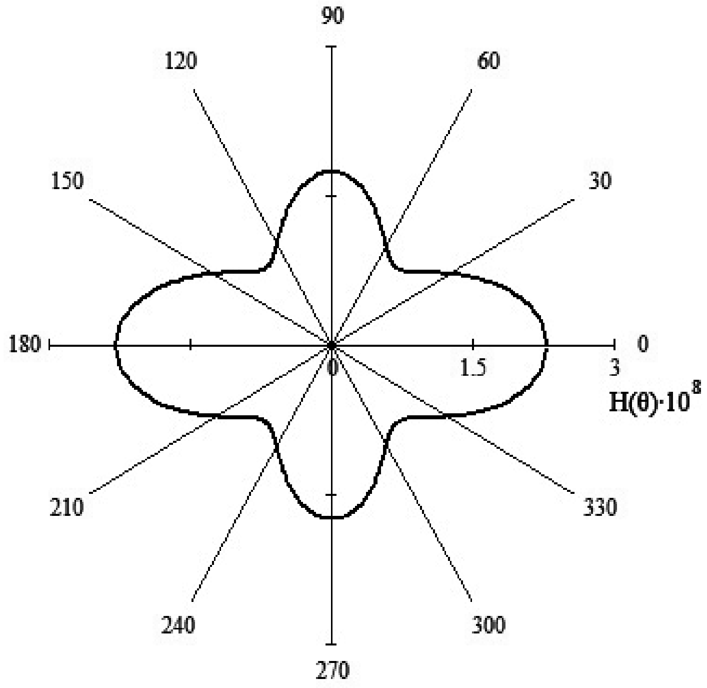


Figure 2: Polar plot $H(\theta) = R + h(\theta)$, calculated under the received law of evolution at $t = 10^{-10}s$, where $D = 10^{-4}m^2/s$, $C_\infty/\rho = 10^{-2}$, $R_0 = 10$ nm, $\sigma = 0.3N/m$, $\mu = 0.0018kg/(m \cdot s)$

It follows from this that the important role in research of the law of evolution of perturbation of a surface form is played by system parameters.

## 4 Analysis

For the analysis of parameters entering under an exhibitor in coefficients at Legendre polynomials, it is better to observe them as ratio $\sigma/(2\mu V)$, mark it as $k$.

In the (Fig. 4) the line of ratio of parameters $k$ divided into areas is presented. Left area marked as B is an area of a ratio of parameters at which all harmonicas, since the first, are responsible for growth of perturbation development. Right area marked as A is an area of a ratio of parameters at which all harmonicas are responsible for a relaxation of the perturbation surface. Between these main areas there is located the infinite set of decreasing areas where the part of harmonicas starts being responsible for instability. So, for example, below a straight line $k = 2$ the first harmonica starts bringing instability in perturbation development while all the others aim for a relaxation. Below a straight line $k = 1.425$ the second harmonica joins the first one and so on, until a straight line with $k = 1$ will be reached. The value of a straight line below which the n-harmonica starts making a contribution to instability of perturbation development, can be calculated from:

$$k = \frac{\sigma}{2\mu V} = \frac{(n+1)(2n^2+4n+3)}{n(n+2)(2n+1)},$$

where $n = 1, 2, ...\infty$.

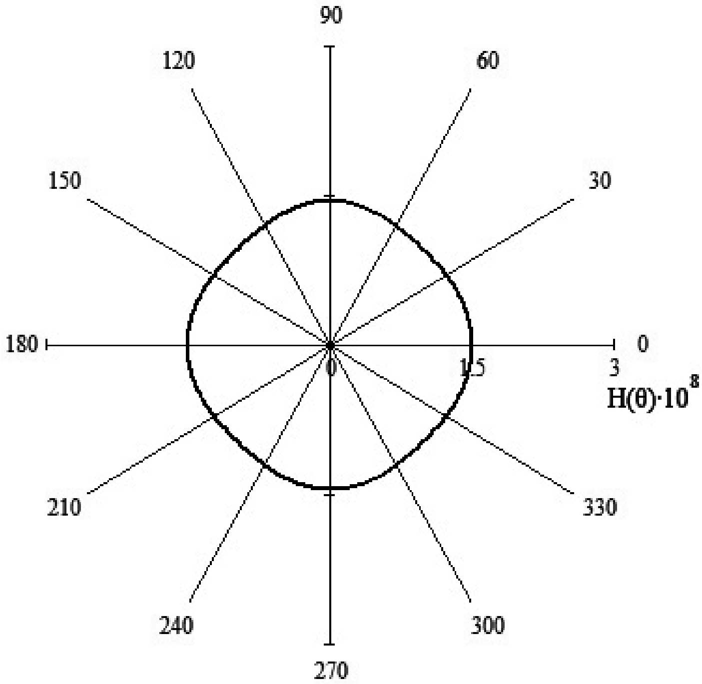


Figure 3: Polar plot $H(\theta) = R + h(\theta)$, calculated under the received law of evolution at $t = 10^{-10}s$, where $D = 10^{-4}m^2/s$, $C_\infty/\rho = 10^{-2}$, $R_0 = 10$ nm, $\sigma = 0.3N/m$, $\mu = 0.0011kg/(m \cdot s)$

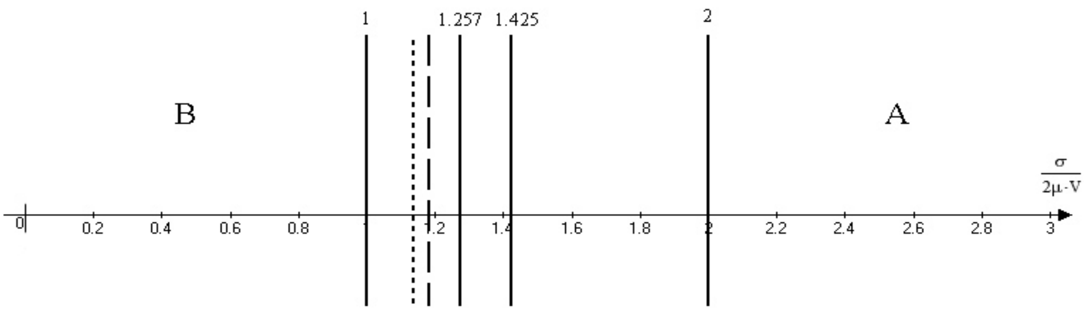


Figure 4: Line of ratio of parameters $\sigma/(2\mu V)$ divided into areas: A is an area of a ratio of parameters at which all harmonicas are responsible for a relaxation of the perturbation surface; B is an area of a ratio of parameters at which all harmonicas are responsible for growth of perturbation development.

Thus knowing one of parameters of system it is possible to pick up optimum their ratios for achievement of this or that effect.

## 5 Conclusions

In work the law of evolution of perturbation of a surface of a nanoparticle is received. Various modes of development of the perturbation surface concerning parameters are investigated. There are revealed modes at which the surface of a nanoparticle loses stability, and modes at which there is a relaxation of perturbation of a free surface. The most actual is finding conditions for formation of fractal structure of a surface. This condition is excess of growth rate of a nanoparticle of some critical velocity. And this critical velocity must be bigger than surface tension coefficient divided into the doubled effective coefficient of viscosity.

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*T.N.Pogosian, S.A.Chivilikhin and I.Yu.Popov St. - Petersburg State University of Information Technologies, Mechanics and Optics, Kronverkskiy, 49, Saint-Petersburg, 197101,Russia; V.V.Gusarov - Saint-Petersburg State Institute of Technology (Technical University), Moskovsky, 26, 190013, Saint-Petersburg, Russia*