

Kinetics of the Active Nanoparticles

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We examined the behavior of active nanoparticles ensemble within the framework of canonical approach, taking into account the internal energy. We applied the anharmonic representation of the Hamilton function and analyzed the kinetics of the self-assembly using the phase-plane method. We discussed the transformations of the internal energy of nanoparticle into the kinetic energy.

Keywords: Active nanoparticles, Self-assembly, Hamilton function.

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1. INTRODUCTION

The development of nanoscience is related to high expectations in various fields of science (biology, medicine, electronics, etc.). The corresponding achievements are often connected with material science, while the design of a many advanced nanostructured materials will reduce the component size for different devices.

Despite the increased interest in the use of individual nanoparticles, the formation of nanoassemblies and their further coupling into the nanostructured materials have a greater practical application. Many realized objects – plastic metals, nanoparticle arrays with unique electronic properties, ultrasensitive chemical and biological sensors, etc. – confirm this fact [1].

There are two main methods of nanoassemblies fabrication: top-down and bottom-up. While the first method is based on different types of lithography, the second method is characterized by the self-organization process - self-assembly of atoms or molecules [2]. The last method is widespread in biology for the production of proteins and DNA molecules as well as various manipulations with cells. The self-assembly process occurs uniquely to each use because the components are very sensitive to the environmental parameters. Thus the technique of nanoparticles' self-assembly provides the new functional materials with unique properties.

Self-assembly allows creating structures in different dimensions: one-dimensional chains, two-dimensional arrays and sheets, and three-dimensional objects such as bubbles and crystals. Also the self-assembly involves a large number of nanoparticles, occurs parallel, and forms hierarchically structured materials. So for design of materials with desired properties the self-assembly becomes the most promising method [3].

But many challenges remain at the technology stage for developing materials based on nanoparticle assemblies. For mass production of such materials, one must thoroughly examine the kinetics of self-assembly. After all, rapid processes of the nanostructures synthesis are the most cost-effective.

The most widely and successfully self-assembly is applied for the formation of structures of colloidal particles. In our work we examine the kinetics for the set

of colloidal nanoparticles that can form nanostructures during self-assembly.

2. MAIN STATEMENTS

We rely on analytical description of the kinetics of active nanoparticles – where the term 'active' means that the particle has the excess of internal energy, which can be converted into other kinds of energy – on the basis of the canonical Hamilton system

$$\begin{aligned} \dot{q} &= \frac{\partial H}{\partial p}, \\ \dot{p} &= -\frac{\partial H}{\partial q}. \end{aligned} \quad (2.1)$$

Here dot denotes differentiation with respect to time, $\mathbf{q} = q_1, q_2, \dots, q_n$ and $\mathbf{p} = p_1, p_2, \dots, p_n$ are the n -dimensional coordinate and momentum. Hamilton function

$$H(\mathbf{q}, \mathbf{p}, t) = K(\mathbf{p}, t) + P(\mathbf{q}, t), \quad (2.2)$$

represents the total mechanical energy of the system – the sum of kinetic K and potential P energy.

For a self-consistent description of self-organized systems we should consider three degrees of freedom (the simplest example is the Lorenz system for atmospheric phenomena [4]). Besides the self-assembly dynamics is characterized by the dissipation of energy. In Ref.[5] the authors introduced a general theory of canonical dissipative systems using the couplings of the internal energy with the kinetic energy or with the total mechanical energy of the system. Developing this idea, we propose to apply the internal energy of the particle ε as a third degree of freedom (in addition to the coordinate and momentum).

Thus, taking into account the friction force and feedbacks with the internal energy, we obtain the system of equations

$$\dot{\mathbf{q}} = \frac{\partial H}{\partial \mathbf{p}}, \quad (2.3)$$

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$$\dot{\mathbf{p}} = -\frac{\partial H}{\partial \mathbf{q}} - \gamma \frac{\partial H}{\partial \mathbf{p}} + \beta \varepsilon \cdot F_1(H), \quad (2.4)$$

$$\dot{\varepsilon} = \frac{\varepsilon_e - \varepsilon}{\tau} - 2\mu\varepsilon \cdot F_2(H). \quad (2.5)$$

In the Eq. (2.4) we consider the friction force $\dot{\mathbf{p}} \propto -\gamma \mathbf{q}$ of a solid sphere in the liquid medium [6]. Here $\gamma = (6\pi R\eta_m) / m$ is a liquid friction coefficient, m and R are the mass and the size of the particle, η_m is a viscosity of the medium.

Eq. (2.5) is taken into account the relaxation and dissipation terms. The first term describes the relaxation of the internal energy to the value ε_e - which is defined by the external conditions - during the the corresponding relaxation time τ . The dissipation term describes the decrease of the internal energy after its transformation into kinetic or total mechanical energy. Moreover this transformation yields a positive contribution to the equation (2.4). The functions F_1 and F_2 are determined by the type of energy transformation (β and 2μ are the positive coupling constants).

3. DISCUSSION

We consider the transformation of the internal energy into the kinetic energy of the system. Instead of Eqs (2.3)-(2.5) we get

$$\dot{q} = \frac{\partial H}{\partial p}, \quad (3.1)$$

$$\dot{p} = -\frac{\partial H}{\partial q} - \gamma \frac{\partial H}{\partial p} + \beta \varepsilon \frac{\partial H}{\partial p}, \quad (3.2)$$

$$\dot{\varepsilon} = \frac{\varepsilon_e - \varepsilon}{\tau} - 2\mu\varepsilon \cdot K(p). \quad (3.3)$$

For harmonic motion of the particle the Hamiltonian function appears as

$$H_0 = \frac{p^2}{2m} + \frac{m\omega^2 q^2}{2}, \quad (3.4)$$

where m is a particle mass, and ω is a natural frequency. But due to the influence of the environment the particle motion looks like anharmonic so we rely on

$$H_0 = \frac{p^2}{2m} + \frac{m\omega^2 q^2}{2} + \alpha_1 q^3 + \beta_1 q^4, \quad (3.5)$$

where α_1 and β_1 are the coefficients of the third and fourth order corrections to the function (3.4) respectively.

Substituting Eq. (3.5) into Eqs. (3.1)-(3.3) we get the system

$$\begin{aligned} \dot{q} &= \frac{p}{m}, \\ \dot{p} &= -m\omega^2 q - 3\alpha_1 q^2 - 4\beta_1 q^3 - \gamma \frac{p}{m} + \beta \varepsilon \frac{p}{m}, \\ \dot{\varepsilon} &= \frac{\varepsilon_e - \varepsilon}{\tau} - 2\mu\varepsilon \frac{p^2}{m}. \end{aligned} \quad (3.6)$$

Firstly analyzing the system (3.6) we should consider the appropriate approximation – internal energy varies faster than any other degree of freedom. Secondly because of the great number of constants we can introduce the dimensionless variables. As a result the system (3.6) is reduced to a simplified form

$$\begin{aligned} \dot{q} &= p, \\ \dot{p} &= -\chi q - \kappa q^2 - \eta q^3 - p + \frac{\varepsilon p}{1 + p^2}. \end{aligned} \quad (3.7)$$

This system of two differential equations (3.7) has three singular points corresponding to the equilibrium states of the system. Introducing additional terms in the system (3.1) - (3.3) we can take into account additional effects (including the interaction between the particles) and as a result the amount of singular points will be increased.

We consider one of the singular points O (0,0), the Lyapunov exponents (the criterion of chaos) of which take the form

$$\lambda_{1,2} = \frac{\varepsilon_e - 1}{2} \pm \sqrt{\left(\frac{\varepsilon_e - 1}{2}\right)^2 - \chi} \quad (3.8)$$

By analyzing the possible values of the Lyapunov exponents we can qualitatively describe the type of the nanoparticles' motion (corresponding phase diagram and Lyapunov exponents are shown in Fig.1).

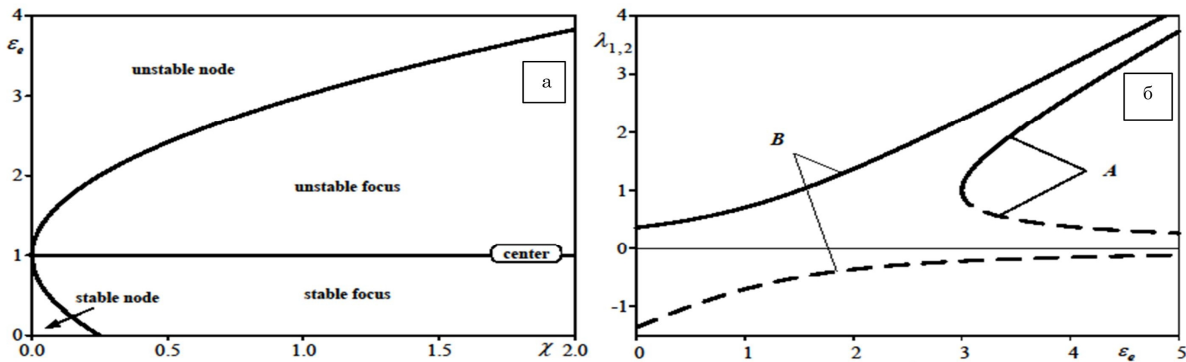


Fig. 1 – Stability diagram for the equilibrium point O (a); Lyapunov exponents for equilibrium points A and B at $\chi = 1$, $\kappa = 3$, $\eta = 2$ (solid lines correspond to λ_1 , dashed to $-\lambda_2$) (b).

For example, the quick self-assembly process may be associated with a stable node (nanoparticles can quickly assemble in the equilibrium point), slower self-assembly process is realized if we have focus in the phase portrait (the kinetics of the system reminds a damped oscillatory motion). For $\varepsilon_e > 1$ we have only unstable regime for point O, when all particles tend to leave this state and there is no self-assembly.

4. CONCLUSION

We proposed a model allowing to describe the kinetics of the active nanoparticles on the basis of the canonical Hamiltonian approach. Considering the internal energy of the particle, we arrived to the system

of three differential equations describing the self-assembly of the particles. Within the adiabatic approximation the kinetics of the system may be considered.

Analyzing the obtained results, we can talk not only about the possibility of nanoparticles' self-assembly, but also about the coordinates and the velocity of the process realization. So controlling the environment parameters and the initial states of the particles, we can manage the self-assembly process. These studies can be used in medicine (e.g. for targeted drug delivery), in material science (for the design of materials with desired architecture), in electronics (for a nanocircuits), in chemistry (for the control of catalytic reactions), etc.

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