

# NONLINEAR OSCILLATION MODEL FOR EXPLAINING THE DISTRIBUTION OF POSITION DEVIATION IN SELF-ORGANIZED NANOPARTICLES

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A model for explaining deviations of positions in self-organized nanoparticles on a substrate from their corresponding positions in perfect organization is proposed. The model predictions were compared with SEM/TEM images and reported by some authors. We found a consistence between the model predictions with the data of Ag, Fe<sub>3</sub>O<sub>4</sub> and SiO<sub>2</sub> nanoparticles organization on various substrates.

*Keywords:* Nonlinear oscillation model; Hamaker equation; self-organization; nanoparticles.

## 1. Introduction

Self-organization of nanoparticles has attracted a great attention due to many potential applications in nanoelectronics, nanophotonics, magnetoelectronics, biochemical sensing, nanolithography, computer applications, etc.<sup>1–5</sup> However, most of the organization process was always accompanied by deviations of particle positions from perfect

organization.<sup>6–9</sup> Theoretical explanation is necessary to identify the reasons why such a deviation occurs and furthermore to control such deviation. Some theoretical studies have been proposed to explain self-organization of nanoparticles. An example is a theory based on bonding between two flat solid surfaces.<sup>10–12</sup> Using columbic and dipole–dipole energies, Talapin *et al.* proposed a

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model for explaining why the organization in a super hexagonal lattice is better than in face centered cubic lattice for nearly spherical PbS, PbSe and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanocrystals.<sup>13</sup>

Mostly, the models proposed by authors were not addressed to explain the deviation of nanoparticle positions from the perfect lattice points. The objective of this work is to propose an alternative model for describing this phenomenon. This model was based on the assumption that the deviation is mainly governed by oscillation of the nanoparticles during the liquid drying which is caused by Van der Waals interaction. The model predictions were then compared with several SEM/TEM images reported by several authors. An acceptable consistency between the model predictions and the experimental data was identified.

## 2. Methods

Suppose the distance between particles in perfect organization is  $r_0$ . The true distance might deviate from the distance position by  $r$ . We will determine the distribution of this deviation for a distinguishable particle assembly. If the number of particles deviating by  $r$  is  $n(r)$ , the density of state can be written as  $g(r) = cr^{D-1}$ , with  $c$  is a constant and  $D$  is the dimensionality of organization. The number of ways of distributing  $N$  particles so that there are  $n(r)$  particles at  $g(r)$  states is  $W = N! \prod_r g(r)^{n(r)} / n(r)!$ .<sup>14</sup> By assuming that both  $N$  and  $n(r)$  are very large, we may approximate

$$\ln W = N \ln N - N + \sum_r [n(r) \ln g(r) - n(r) \ln n(r) + n(r)]. \quad (1)$$

The total number of particles at all states and the total energy of all particles at any displacements are  $N = \sum_r n(r)$  and  $E = \sum_r n(r)\varepsilon(r)$ , respectively, with  $\varepsilon(r)$  is energy of a particle having a deviation  $r$  and assuming this energy is function of deviation only.

We minimize  $\ln W$  by applying constraints that both  $N$  and  $E$  are conserved, and introducing two Lagrange multipliers  $\alpha$  and  $\beta$  so that the “steady state” distribution reads  $n(r) = g(r)e^{\alpha}e^{\beta\varepsilon(r)}$ . Using the same reasons as discussed in statistics of gases,<sup>14</sup> we will identify that  $\beta = -1/kT$  with  $k$  is the Boltzmann constant and  $T$  is the absolute temperature,

and the explicit expression for  $n(r)$  becomes

$$n(r) = ce^{\alpha}r^{D-1}e^{-\varepsilon(r)/kT}. \quad (2)$$

The total number of particles is  $N = \int_0^{r_{\max}} n(r)dr$ . By assuming that  $r_{\max}$  is very large we may approximate  $N = \int_0^{\infty} n(r)dr$ .

Let us consider two-dimensional organization of nanoparticles, the case which frequently observed in self-organization of nanoparticles on substrates, and mostly they arrange in hexagonal structures. In this structure, each particle is connected equidistantly to six other particles. Suppose  $\vec{R}_{0i}$  is the position of the  $i$ th particle at the perfect organization. The true position can be written as  $\vec{R}_i = \vec{R}_{0i} + \vec{r}_i$ , with  $\vec{r}_i$  as deviation from the perfect position. The interaction energy between the  $i$ th and  $j$ th particles can be written as  $\varphi(\vec{R}_i - \vec{R}_j) = \varphi[(\vec{R}_{0i} - \vec{R}_{0j}) + (\vec{r}_i - \vec{r}_j)]$ ,  $= \varphi(\vec{r}_{0ij} + \vec{r}_i - \vec{r}_j)$  with  $\vec{r}_{0ij} = \vec{R}_{0i} - \vec{R}_{0j}$  is the relative position between the  $i$ th and the  $j$ th particles at the perfect organization. In the hexagonal organization,  $|\vec{r}_{0ij}| = r_0$  for all  $i$  and  $j$  and  $\vec{r}_i - \vec{r}_j$  is the relative displacement between the  $i$ th and the  $j$ th particles in the true position. If displacements are small, or  $|\vec{r}_i| \ll r_0$  for all  $i$ , we can approximate

$$\phi(\vec{R}_i - \vec{R}_j) = \phi(\vec{r}_{0ij}) + \frac{1}{2}\gamma(\vec{r}_i - \vec{r}_j)^2, \quad (3)$$

with  $\gamma = \nabla^2\phi(\vec{R}_i - \vec{R}_j = \vec{r}_{0ij})$  is the spring constant.

At final drying process, we assume the prominent force acting on the particle as the Van der Waals one. The interaction potential between two spherical particles separated by  $x$  is  $\phi(x) = -(A/6) \times [d^2/2x^2 + d^2/2(x^2 - d^2) + \ln(1 - d^2/x^2)]$ , with  $A$  is the Hamaker constant and  $d$  is the particle diameter.<sup>15</sup> Based on this potential energy, we can derive the spring constant as  $\gamma = \partial^2\phi/\partial x^2|_{r_0}$ .

Equation (3) suggests that the interaction energy between particles can be replaced by the elastic energy under the assumption that the displacements are very small compared to the particle distance. The spring constant of this elastic energy is derived from the Van der Waals energy.

Consider a unit of hexagonal cell containing one particle at the center and the six other particles are distributed equidistantly around it [see Fig. 1(a)]. If the central particle is deviated by  $r$  toward one of the six springs [see Fig. 1(b)], we can show that the

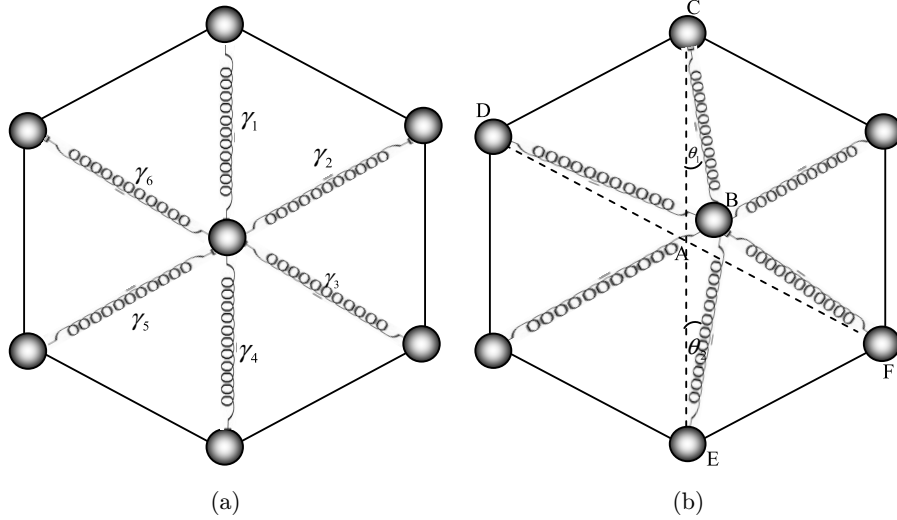


Fig. 1. (a) All particles occupy the perfect positions in a hexagonal organization and (b) The center particle is deviated by  $r$  from the perfect positions.

net force experienced by this particle is  $F_r = -3\gamma(r + r^3/2r_0^2)$  and the potential energy is

$$\varepsilon = - \int_0^r F_r dr = \frac{3}{2}\gamma r^2(1 + \lambda r^2), \quad (4)$$

with  $\lambda = 1/4r_0^2$ . We can consider  $\lambda$  as a perturbation constant. This energy expression behaves as nonlinear oscillation equation<sup>16</sup> and has been used to explain the dynamics of coupled domain walls oscillations.<sup>17</sup>

Using Eq. (4) for calculating the total number of particles we will have  $ce^\alpha = 2N\sqrt{6\gamma\lambda/\pi kT} \exp[-3\gamma/8\lambda kT]/\text{erfc}[\sqrt{3\gamma/8\lambda kT}]$ , with  $\text{erfc}[x]$  is the error function. With this result, the final expression for particle deviation distribution becomes

$$n(r) \approx \frac{2N\sqrt{\frac{6\gamma\lambda}{\pi kT}}}{\text{erfc}\left[\sqrt{\frac{3\gamma}{8\lambda kT}}\right]} e^{-3\gamma/8\lambda kT} r e^{-\frac{3}{2}\gamma r^2(1+\lambda r^2)/kT} \quad (5)$$

and the root mean square of particle deviation from the perfect position is

$$\sqrt{\langle r^2 \rangle} = \left\{ \frac{1}{6\lambda} \left[ \frac{(2\sqrt{6\lambda kT/\pi\gamma} \exp[-3\gamma/8\lambda kT])}{\text{erfc}[\sqrt{3\gamma/8\lambda kT}]} - 3 \right] \right\}^{1/2}. \quad (6)$$

We also derived the force and potential energy experienced by a particle deviated from its equilibrium position in a square structure. The

expressions for the force and the potential energy are  $F_r = -2\gamma(r + r^3/2r_0^2)$  and  $\varepsilon = \gamma r^2(1 + \lambda r^2)$ , respectively, with  $\lambda = 1/4r_0^2$ . Both expressions are nearly the same as the expressions for particle in the hexagonal structure.

### 3. Results and Discussion

We verified the model predictions with the observed data reported by several authors. Because most of the observed nanoparticle organization occurred in the hexagonal structure, at the present work, comparison between the experimental data and theoretical predictions are performed for such structure. Figure 2(a) shows the TEM images of silver nanoparticles on a substrate<sup>18</sup> and the corresponding distribution of particle deviation from perfect position predicted by the present model. Measurement from the image we obtained that the particle diameter and the average distance are 4.8 nm and 7.66 nm, respectively, and the average deviation of particle organization is 0.51 nm. The average distance was determined by averaging the distances of hundreds of particles in the images, or  $r_0 = \sum_{ij} R_{ij}/N_{ij}$  where  $R_{ij}$  is the distance between the  $i$ th and the  $j$ th particle in the images and  $N_{ij}$  is the number of pairs counted. The average deviation was calculated by  $\sqrt{\langle r^2 \rangle} = \sqrt{\sum_{ij} (R_{ij} - r_0)^2/N_{ij}}$ .

The Hamaker constant of silver particle is  $A_{Ag} = 5.10 \cdot 10^{-19}$  J.<sup>19</sup> Using this data, the theoretical spring constant is  $29.9 \times 10^{-22}$  J/nm<sup>2</sup>. We have

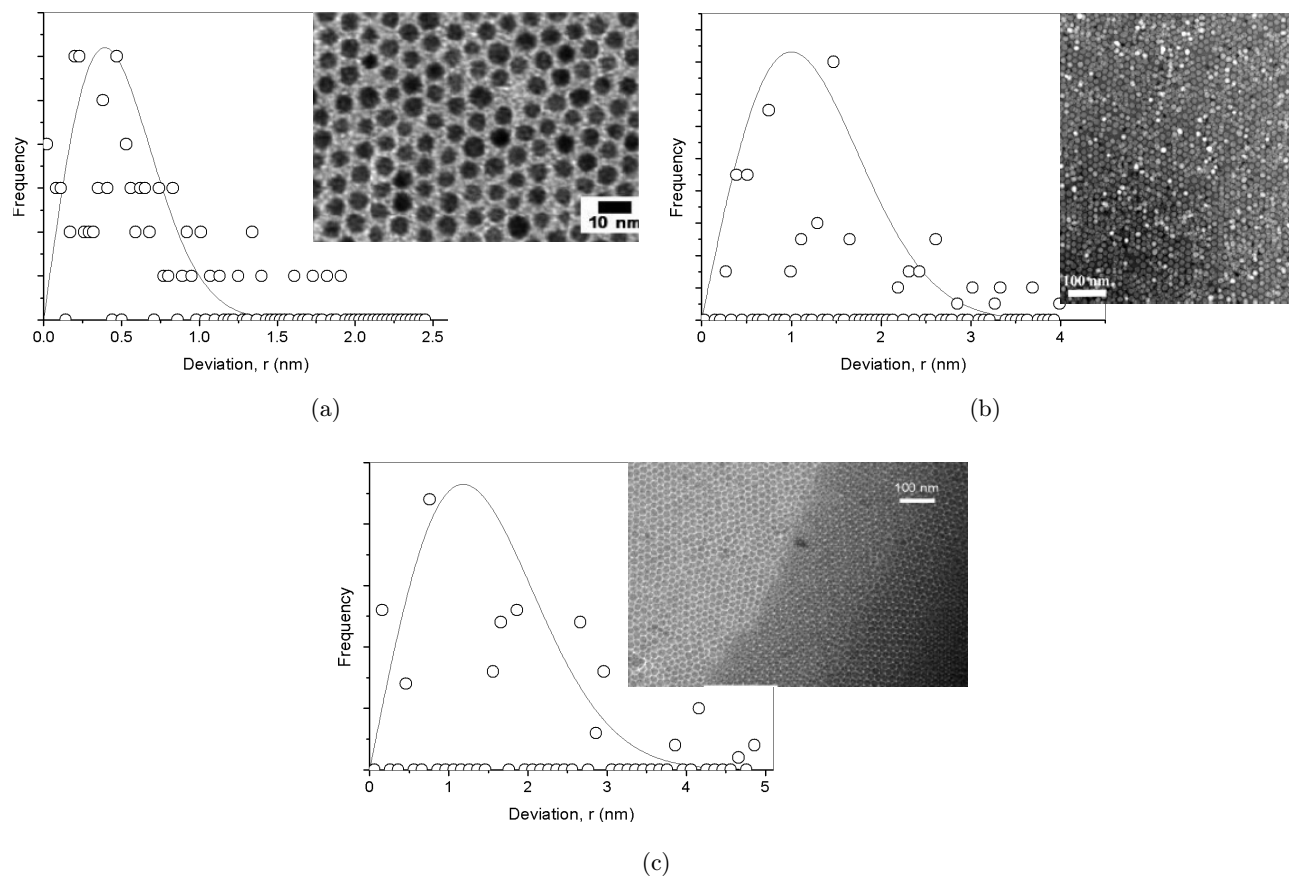


Fig. 2. TEM or SEM images of nanoparticles organized on substrates and the corresponding distribution of particle deviation from perfect position: symbols are calculated from the images and lines are fitting data using Eq. (5). (a) Silver nanoparticles,<sup>18</sup> (b)  $\text{Fe}_3\text{O}_4$  nanoparticles,<sup>20</sup> and (c)  $\text{SiO}_2$  nanoparticles.<sup>23</sup> The fitting parameters used in simulation appear in Table 1. Copyrights from: (a) American Chemical Society.com, (b) Institute of Physics and (c) American Chemical Society.com.

tried to calculate the deviation [see Eq. (6)] using this spring constant and identified a great discrepancy with the experimental data. We then tried other values of the spring constant and finally obtained a good comparison with the experimental data using a spring constant which was three times larger. Using this larger spring constant, we simulated the average deviation of the particle position, 0.55 nm, which is very close to the experimental data.

The comparison was also performed for  $\text{Fe}_3\text{O}_4$  nanoparticles<sup>20</sup> [see Fig. 2(b)]. Measurement on the TEM image showed the average particle diameter is 6.6 nm and the average deviation is 1.18 nm. The Hamaker constant of  $\text{Fe}_3\text{O}_4$  is  $2.1 \times 10^{-19}$  J.<sup>21,22</sup> Using this data we obtained the theoretical spring constant of  $4.56 \times 10^{-22}$  J/nm<sup>2</sup>. In the simulation, we used a spring constant of three times larger and obtained the simulated average deviation of 1.39 nm which is very close to the measured data.

Finally, the comparison was also done for silica nanoparticles<sup>23</sup> [see Fig. 2(c)]. The measured average diameter and average deviation are 15 nm and 1.62 nm, respectively. Using the Hamaker constant of  $6.6 \times 10^{-20}$  J,<sup>24</sup> we obtained the theoretical spring constant of  $2.60 \times 10^{-22}$  J/nm<sup>2</sup>. In the simulation, a better comparison with the experimental data was obtained by using four times larger spring constant, where the simulated particle deviation is 1.71 nm. Table 1 summarizes the measured data and the simulated results.

The better fittings obtained using spring constants of three or four times larger than the spring constants derived theoretically can be explained as follow. In the model proposed here, the force experienced by a particle was assumed only the Van der Waals force due to other particles. Indeed, this is not the only force experienced by the particle. Other forces such as Van der Waals force between particle and substrate (flat surface) and drag force

Table 1. The fitting parameters, measured data and simulated data.

Organized nanoparticles	Spring constant ( $\times 10^{-22}$ J/nm <sup>2</sup> )		Root mean square of deviation (nm)	
	Derived from Van der Waals energy	Used in this simulation	Measured from TEM/SEM images	Calculated in this simulation
Silver <sup>18</sup>	29.9	$3 \times 29.9$	0.51	0.55
Fe <sub>3</sub> O <sub>4</sub> <sup>20</sup>	4.56	$3 \times 4.56$	1.15	1.39
SiO <sub>2</sub> <sup>23</sup>	2.60	$4 \times 2.60$	1.71	1.62

due to relative motion with respect to fluid during evaporation will contribute also on the total force on the particle. The potential of this interaction is  $\phi_{ps} = -Ad/12z$ , with  $d$  and  $z$  are, respectively, the separation between the particle and the substrate.<sup>24</sup> The typical magnitude of  $z$  is 4 Å,<sup>25</sup> so the potential of interaction can be written as:  $\phi_{ps} = -A'd$  with  $A' = (A/48).10^{10}$  J/m. By assuming  $A \approx 10^{-19}$  J (see Refs. 21, 22 and 24) and  $d \approx 10$  nm as observation above, we approximated  $\phi_{ps} \cong 10^{-20}$  J, which is around several times larger than the spherical-spherical Van der Waals potential (about  $\phi_{pp} \cong 10^{-21}$  J).

Castellanos<sup>26</sup> showed that the Van der Waals force between particle and flat surface can be two times larger than the Van der Waals force between particles. If we have determined the spring constant derived by considering only interaction between particles, the more realistic spring constant used in simulation should be around three times larger when considering also interaction between particles and flat surface. The effective spring constant might

be much larger when considering all other interactions. This is likely the reason why the spring constant of three or four times larger than the spring constant derived by considering only Van der Waals interaction between particles have given better fittings. However, extensive work must be done to confirm this hypothesis so that the theory will be applicable for explaining organization of any particles on any substrates.

The smoothness of particle or substrate surface might generate additional force on the particles. As described by Castellanos,<sup>26</sup> changing the roughness can change the Van der Waals force to several orders of magnitude. Difference in roughness might be the factor responsible for producing four times larger effective spring constant on SiO<sub>2</sub> organization. However, further investigation is still required to prove this proposal.

Figure 3 shows the distribution of deviation for particles having different mean diameters. This simulation was applied to particles of a specific material on the same substrate. The deviation decreases as the mean diameter increases. It is caused by increasing in the Van der Waals interaction among the particles to imply the strengthening of the spring constant which ultimately decreases the deviation.

For further advantage, if the effective particle diameter is increased by adsorbing polymers, polymer brushes or surfactants on the particle surface,<sup>27</sup> the deviation becomes smaller. When the coating material is finally removed, the end-product will be self-organized nanoparticles at small deviation.

Figure 4 shows that the deviation increases with increasing the temperature of colloid during organization process. This can be understood in terms of higher kinetic energy of the particle to increase the random (Brownian) movement of the particles.

Although this model was applied for organizations in hexagonal structure, however, it can be

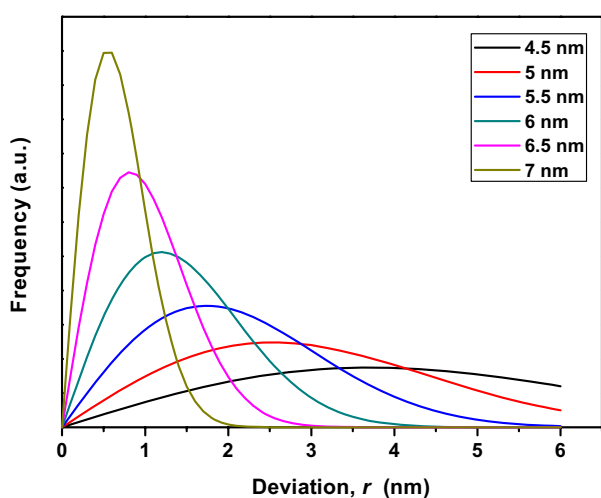


Fig. 3. The profile of deviation distribution for different nanoparticle mean diameters.

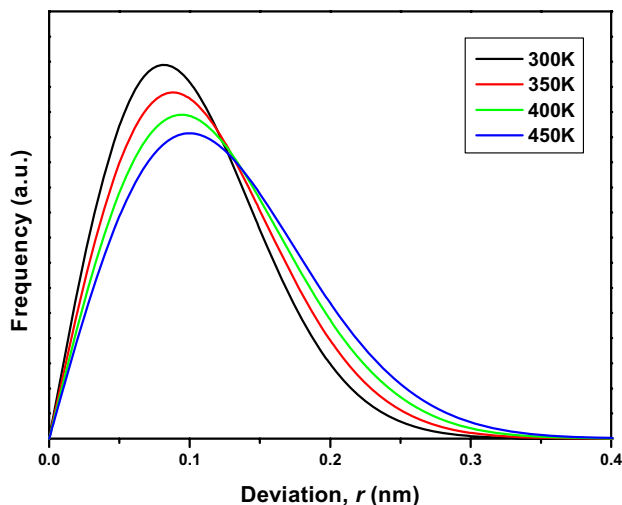


Fig. 4. The profile of deviation distribution for several temperatures. For higher temperatures, the root mean square of deviation is greater.

applied for other organizations by reformulating the expression of interaction energy. The model can also be made more precise by taking into account other interactions that have not been considered in this work.

#### 4. Conclusion

The deviation of nanoparticle positions in self-organized sample relative to the corresponding positions in perfect organization has been explained by a nonlinear oscillation model. The model predictions well fit experimental observations on the organizations of Ag, Fe<sub>3</sub>O<sub>4</sub> and SiO<sub>2</sub> nanoparticles. Better fittings were obtained by using larger spring constant compared to the theoretical ones. Interaction between particles and substrates and their surfaces smoothness likely contributed to increasing the effective spring constant. The model might be extended to explain other organized phenomena of nearly organized phenomena even in living things, such as flock of birds or school of fishes.

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