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A Diffusion Model of Field-Induced Aggregation in Ferrofluid Film *

FANG Wen-Xiao(方文啸), HE Zhen-Hui(何振辉)**, CHEN Di-Hu(陈弟虎), ZHAO Yan-E(赵燕娥)

State Key Laboratory of Optoelectronic Materials and Technologies, and Institute of Condensed Matter Physics, Sun Yat-sen University, Guangzhou 510275

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By introducing Arrhenius behaviour to the ferroparticles on the surface of the aggregated columnar structure in a diffusion model, equilibrium equations are set up. The solution of the equations shows that to keep the aggregated structures stable, a characteristic field is needed. The aggregation is enhanced by magnetic fields, yet suppressed as the temperature increases. Analysing the influence of the magnetic field on the interaction energy between the dipolar particles, we estimate the portion of the diffusing particles, and provide the agreeable ratio of the column radius over the centre-to-centre spacing between columns in a hexagonal columnar structure formed under a perpendicular magnetic field.

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When a certain external magnetic field is applied to a ferrofluid[1,2] film comprised of nanoparticles with an inherent magnetic moment, due to the magnetic dipolar interaction between the particles, aggregated structures can be formed especially in the presence of an applied magnetic field.[3−12] The study of the formation of these aggregated structures is very helpful for understanding the evolution of a dipolar system related to soft matter, and for the accurate controlling of the aggregated structures, which are expected for applications in optics[6−9] and magnetic storage. Theoretically, there have been three main approaches so far to investigate the formation of these aggregated structures. One is to simulate the motions of the ferroparticles by means of Monte Carlo method[13] and Brownian dynamics method.[14] Most of the simulation results demonstrated that ferroparticles can form chain-liked structures under an external magnetic field parallel to the ferrofluid film. In the framework of the thermal statistical approach (the second approach), Zubarev *et al.*[15] proved that the bulk aggregated structures occur provided that the total number of the particle is large enough. Assuming that single chains or drops are firstly formed by the particles, this approach would also predict the chain and drop transformations[15] in ferrofluid by comparing their free energy, as well as the rheological properties[16] by taking the chain interaction into account. The third approach[17−19] focuses on the aggregated structures, which are considered as a result of competition between the magnetic energy and the surface energy of the aggregated structures (sometimes including the configurational entropy in the studied system.[17]) In this approach, all of the particles were usually assumed to be involved in the aggregation to form columns formed under an external field perpendicular to the ferrofluid film plane. Although experiments have shown that some particles definitely disperse between those structures,[20,21] this approach satisfactorily explains the hexagonal structures obtained by solvent evaporation.[20] However, according to Ref. [17], the ratio between the radius and the spacing of the columns in the hexagonal structures is constant, which does not agree with the magnetic-field-induced aggregation experiments performed in a confined thin cell.[4−12] This means that to predict precisely the size of the field-induced aggregated structures formed in the ferrofluid film, the particles dispersed must be considered.

In this Letter, we setup a simplified diffusion model to deal with the dispersed particles by considering the particle diffusion flows between the columns with aggregated particles and the surrounding outside the columns (called space hereafter) with dispersed particles. In our diffusion model we focus on the equilibrium state of the columns. The predicted aggregation is in agreement with the experimental results performed by researchers.[4−8,10−12] We expect that the combination of the diffusion model with the well-developed minimization analysis [17−19] of the magnetic energy of the columns could achieve the goal of relatively accurate control of these structures.

The monodisperse ferroparticles are considered to be identical, having a spherical ferromagnetic core with radius r and a nonmagnetic shell with thickness of δ. For simplicity, interaction is taken into account only between the ferroparticles forming aggregation, while no interaction exists between the ferroparticles dispersed in the space due to the relatively long distance between the particles. Now let us consider a formed column. Due to the thermal fluctuation, the stable state of the column should be dominated by two diffusion flows of particles near the interface of the column and the space: one from the space to the column, induced by the Brownian motion of the particles, and the other from the column to space, con-

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**To whom correspondence should be addressed. Email: stshzh@mail.sysu.edu.cn

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strained by the adhesive potential well on the column surface. The particles arriving at the column surface were supposed to adhere to the column without rebounding back to the space and thus contribute to the growth of the column. The column keeps growing in a magnetic field until the two flows reach a dynamic equilibrium.

Let us further suppose that the column as a cylinder with a mean particle concentration of n_c, and the mean particle concentration of in the space is n_s. For the lateral surface, the net flow per unit area j along the radial direction is given as

$$j = \frac{1}{2} n_s \gamma_s \Delta l - \frac{1}{2} n_c \gamma_c \Delta l, \tag{1}$$

where Δl is the particle mean free path dominated by the Brownian motion, and is assumed equal for the particle flows from column to space and that from space to column. The two terms in the right side correspond to the two flows discussed above respectively. Here γ_s and γ_c denotes the average numbers of particles per unit area per unit time moving from the space to the column and from the column surface to the space, respectively. In thermal dynamics, γ_s and γ_c should be related to particles' chemical potential in the space and that of the column. In consideration of the common liquid surrounding and the interactions existing only in the columns, γ_s is taken as γ_0 (the average number of jumps per unit area per unit time dominated by pure Brownian motion); while γ_c obeys the Arrhenius law expressed as $\gamma_0 \exp(-U/k_B T)$, where U is the potential energy constraining the particle from moving away to the space, and k_B and T Boltzmann's constant and the absolute temperature of the fluid, respectively. Since the potential energy in the space is taken as zero so that U can be considered as the absolute value of the adhesive interaction for the studied particle located on the surface of the columns. We assume that the value of the adhesive well U is uniform on the lateral surface for a certain external magnetic field. By considering the pure Brownian motion of the dispersed particle, γ_0 can be analytically solved. Ultimately, the diffusion equation at the lateral surface becomes

$$j = \frac{v}{3}\Big[n_s - n_c \exp\Big(-\frac{U}{k_B T}\Big)\Big], \tag{2}$$

where v is the average velocity of the particle. For the axial direction of the column, the only difference is the value of the adhesive well U due to the orientation effect of the dipolar interaction.

In consideration of the continuity of the flow, one can obtain instantly the radial column growth equation like

$$j = \dot{R} n_c, \tag{3}$$

where we have supposed that the particle concentration of the column is constant. Combining Eq. (2) with Eq. (3), one can see that the increase of the column radius lowers the particle concentration in the space, hence the growth rate $\dot{R}$ will be suppressed. When the flows come to a dynamic equilibrium, we have $j = 0$, and $\dot{R} = 0$. Then the equilibrium condition becomes $n_s = n_c \exp(-U/k_B T)$. Here it is emphasized that this can also be derived in terms of thermal statistical mechanism by equating fugacity (or chemical potentials) of particle in the column and that in the space. For aggregation along the axial direction, the column always elongates until being limited by the container.

As seen in Eq. (2), in an equilibrium state, the value of n_s can be deduced for a given finite potential well U and a given n_c, indicating that not all the particles aggregate. Let us define n_0 as the initial particle concentration (before magnetic field is applied). Since the total number N_0 of the particles (in both the space and the columns) is constant, the number N_c of the particles in the columns over N_0 can be derived as

$$\frac{N_c}{N_0} = \beta - \frac{(\beta - 1)}{1 - \exp(-U/k_B T)}, \tag{4}$$

where β is defined as n_c/n_0. The second term on the right-hand side of Eq. (4) indicates that the radio N_c/N_0 can be tuned by the value of the potential well on the surface of the column, which depends on the applied magnetic field. For a deep potential well, the ratio N_c/N_0 is high. In other words, more particles aggregate. For a sufficiently deep potential well, the ratio N_c/N_0 reaches a limitation value of unity, indicating that all the particles aggregate. On the other hand, for a given potential well, a critical initial particle concentration n_g is needed to form aggregation and given as

$$n_g = n_c \exp\Big(-\frac{U}{k_B T}\Big). \tag{5}$$

This also means the existence of a characteristic field H_c, above which the particles could form stable aggregation.

For a hexagonal columnar structure with a column radius of R and a centre-to-centre spacing of d, we can derive

$$\frac{R^2}{d^2} = \frac{\sqrt{3}}{2\pi}\Big[1 - \frac{\beta - 1}{\beta}\frac{1}{1 - \exp(-U/k_B T)}\Big]. \tag{6}$$

If all of the particles aggregate under a sufficiently deep potential well, the square of the ratio R/d will saturate at $\sqrt{3}/2\pi\beta$ in agreement with Ref. [17].

To further study the aggregation, the value of U should be determined according to the dipolar interaction between the particles and the van der Waals interaction and steric interaction between the shells. To explore the effect of the magnetic field, here only dipolar interaction is taken into account (the other interactions could be included as a background independent on the magnetic field). Next, we derive the average dipolar interaction between position-fixed ferroparticles under an external magnetic field. Firstly the aggregating particles forming the columns are assumed

to show weakly interacting superparamagnetism at room temperature, so that we can introduce a mean interaction field. The average interaction energy for an aggregating particle located on the surface of the column can be obtained by solving the following equations,

$$U_d = \alpha U_0 L^2(\lambda), \quad \lambda = \frac{m_0(H_e + H_d)}{k_B T},$$

$$U_0 = \frac{m_0^2}{4\pi\mu_0(2r)^3}, \tag{7}$$

$$U_d = -m_0 L(\lambda) H_d, \tag{8}$$

where m_0 is the magnetic moment of the particle, H_d the mean dipolar field on the studied position contributed by the surrounding particles. $L(\lambda)$ is the Langevin function, written as $\coth\lambda - 1/\lambda$. The factor α depends on the position of the studied particle and the surface and inner structure of the column,[22] whose typical value is given in the range from $-2r^3/(r+\delta)^3$ to $-3r^3/(r+\delta)^3$ for a stable adhesive position on the surface of a column. By combining Eq. (7) with Eq. (8), U_d can be solved numerically for a given α. For a system with large particles, the absolute value of dipolar potential energy for a certain α increases very fast with the external magnetic field.

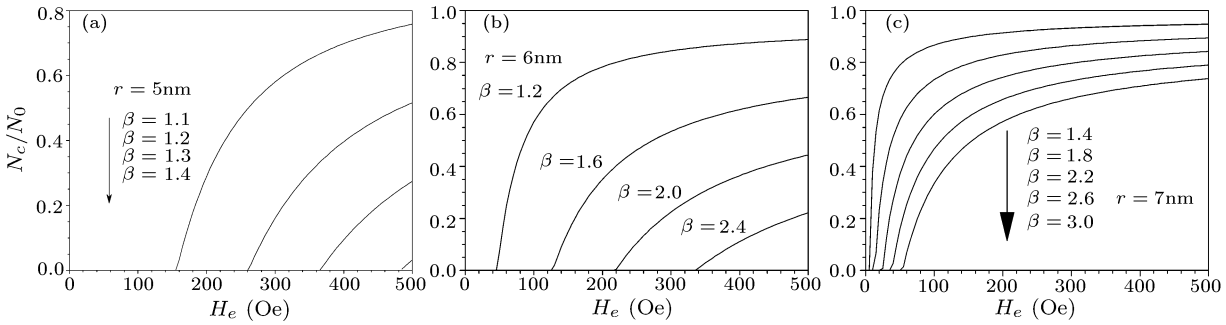

Fig. 1. Dependences of the ratio N_c/N_0 on the external magnetic field for different β and particle radius r: (a) $r = 5$ nm, (b) $r = 6$ nm, (c) $r = 7$ nm. The thickness of the nonmagnetic shell is 2 nm. The temperature of the ferrofluid film is 300 K.

Now, substituting $U = -U_d$ into Eq. (4), we study the aggregation quantitatively. As shown in Fig. 1, the diffusing particles in the space become considerable in a low applied magnetic field, especially for the ferrofluid consisting of small particles. Another interesting character is the characteristic field which is highly sensitive to β for system of ferroparticles of 5 nm, yet much less sensitive for that of 7 nm. This can be easily explained by the dependence of the potential well on the particle size and the magnetic field.

To compare Eq. (6) with the experimental data, the values of n_0 and n_c must be set. In real ferrofluid, n_0 and n_c are often expressed as $\Phi_0/((4\pi/3)r^3)$ and $\Phi_c/[(4\pi/3)(r+\delta)^3]$, respectively, where Φ_0 is the initial ferroparticle volume fraction in the ferrofluid related directly to the measurable saturated magnetization, Φ_c the average package volume fraction of the particles in the columns depending on the particles packing inside the column. Note that here we suppose the shell of the particle is incompressible. In fact, the aggregates may consist of small regions with an energetically favoured close packing, separated by less densely packed transition regions. The predicted ratios of R/d are compared with the experimental results in Ref. [7] performed by Yang *et al.*, in which the ordered structures were formed under a perpendicular magnetic field in a kerosene-based $MnFe_2O_4$ ferrofluid film. To obtain the experimental curve of $R/d \sim H_e$, we extract the values of R and d in the reference and calculate the values of R/d. The bulk magnetization and mass density of $MnFe_2O_4$ are set to be 0.5 T and 5.0 g/cm^3 (Ref. [23]), and the mass density of kerosene as 0.8 g/cm^3, respectively. By equating the square of the saturation ratio R/d to the theoretical saturation value of $\sqrt{3}/2\pi\beta$, we find that the value of Φ_c is a function of the initial particle concentration. For a low initial particle concentration, the evaluated Φ_c is about 0.10, while for a high one it is about 0.46. For simplicity and the purpose of illuminating the physics nature in the model, Φ_c is chosen to be 0.2. Figure 2 shows the predicted R/d of the hexagonal structures with the particle radius of 6 nm, 6.5 nm and 7 nm, in comparison with the experimental data. As can be seen, the experimental data almost fall between the two theoretical curves of 6.5 nm and 7 nm. For a ferrofluid with particle radius of 5 nm, the characteristic field is above 500 Oe, which is not shown in Fig. 2. In comparison to the theoretical curve of 7 nm, the experimental data indicate a possibly higher characteristic field, and a slightly higher saturation ratio of R/d. These deviations implicate a distribution of particle size and probably more complicate particle packing inside the column. As a matter of fact, the real ferrofluid usually contains incompletely homogeneous particle. Note that higher values of Φ_c or lower absolute values of α would lead to curve-shift to higher field. Our theoretical result is also in agreement with the experimental data reported in Refs. [5,6].

The effect of the circumstance temperature can also be discussed. As we can deduce from Eqs. (4), (7) and (8), the increase of the circumstance temperature leads to the increase of the probability for the aggre-

gating particles on the surface of the column to move to the space and the decrease of the absolute value of the dipolar interaction under a certain magnetic field. Figure 3 shows us less particles aggregating and lower ratio R/d in the hexagonal structure with the increase of the temperature. The experiments about the effect of temperature on the structure formation in the ferrofluid film were performed by Yang *et al.*,[11] who confirmed that a higher external magnetic field was required to make the particles aggregate at a higher temperature. This is in agreement with our prediction. Experimentally it was also found[12] that a sufficiently high temperature could destroy the columnar structure at a certain magnetic field. As is expected, we found that higher characteristic field H_c (shown in Fig. 3) is needed to form aggregation at higher temperature.

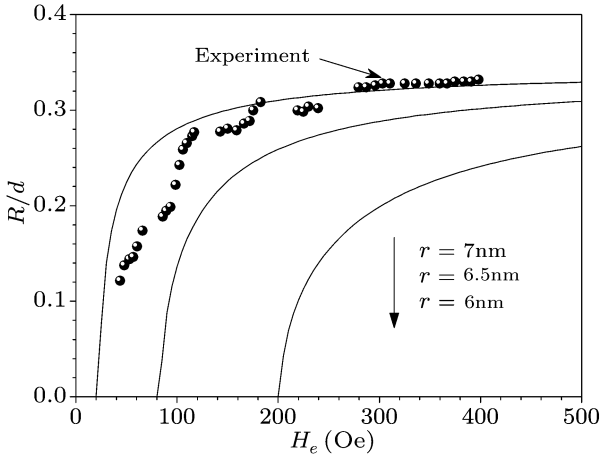

Fig. 2. Theoretical results of the ratio between the radius R of the hexagonal columnar structure and the spacing d between the columns, as a function of the external magnetic field H_e, in comparison with the experimental result by extracting the data obtained by Yang *et al.*[7] The ferrofluid magnetization M_s is 17.63 emu/g, the ferrofluid temperature is set at 300 K, the volume fraction of the particles in the column Phi_c is set at 0.20, and the thickness of the shell is 2 nm.

We also examine the role of the interaction between the columns on the ratio R/d. The mean interaction field induced by all neighbouring columns can be approximated roughly as $H_{dc} = -\dfrac{N_R V_m \Phi_c M_s L(\lambda)}{4\pi\mu_0 d^3}$, where V_m is the volume of the column, N_R is a factor summing up the column interactions and equal to a limit about 8.6227 (equal to 6 in the case of the near neighbouring columns counted), and λ should be rewritten as $m_0(H_e+H_d+H_{dc})/k_BT$. As a negative modification of the external magnetic field, the column interactions lead to a decrease of the ratio R/d (and N_c/N_0) with the increase of L.[24] This was also qualitatively confirmed by the experiments in Ref. [7]. Since the column interaction is supposed to act against the external field, the diffusion model could give at least an upper limit of the ratio R/d by neglecting the column interactions.

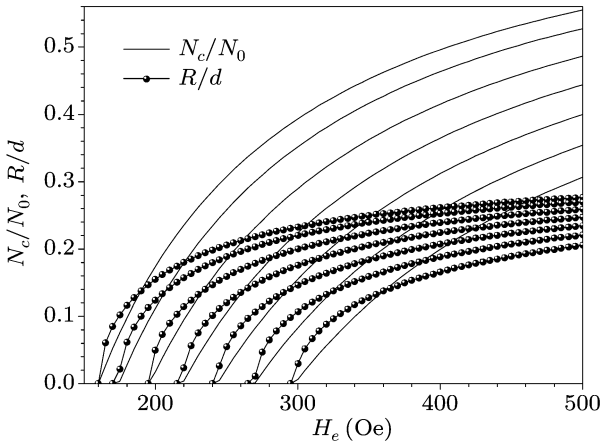

Fig. 3. Ratios N_c/N_0 or R/d of a hexagonal columnar structure as a function of the external magnetic field H_e at temperatures of 273 K, 280 K, 290 K, 300 K, 310 K, 320 K and 330 K, respectively (from top to bottom). The value of β is 2, and the radius of the particle is 6 nm.

In conclusion, we derive the ratio between the number of the aggregating particles and the total particles in the ferrofluid, as well as the agreeable ratio between the radius of the column and the centre-to-centre spacing between two columns in a hexagonal structure. The predicted magnetic-field enhanced and thermally suppressed aggregations are also in agreement with the published observations. Our ultimate goal is to demonstrate the possibly considerable portion of particles dispersed in the space between the columns, and remind one to think about it in the free energy minimization analysis,[17–19] especially for small-particle ferrofluid films.

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