# Role of nucleation in the structure evolution of a magnetorheological fluid

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A phenomenological model of nucleation-controlled structure evolution in dilute magnetorheological fluid is suggested. We find that the critical size of column nuclei is related to the magnetic field $H$, the increase of permeability $\delta\mu$ of the nuclei, and to the nucleus surface tension $\sigma$, by the relation $D_c \sim 16\pi\sigma/(H^2-H_c^2)\delta\mu$. The growth rate of columnar structure, and the field and volume fraction dependences of the separation between the columns are calculated, and are found to be given, respectively, by $d \sim t^{2/7}$, $d \sim H^{3/14}$, and $d \sim \phi^{1/7}$. These results fit the experimental data in ferrofluid emulsion systems very well.

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## I. INTRODUCTION

The interest in the evolution of structure in electrorheological (ER) and magnetorheological (MR) fluid has grown sharply in recent years. The dynamics of structure formation in ER and MR fluids are under extensive investigation [1–9]. The ferrofluid emulsion is a typical MR fluid under study, for which it is easy for researchers to choose the colloid particle size and to control the polydispersity of the particle sizes. It is an oil-in-water emulsion in which kerosene droplets contain about 6% by volume, of iron oxide grains, and the diameter of each droplet is around 0.5 $\mu$m. Each iron oxide grain has an average diameter of 9 nm, and has a permanent magnetic dipole moment corresponding to a single magnetic domain. Our major feature of these droplets arises from their superparamagnetic behavior. In the absence of an external magnetic field, these droplets have no permanent dipole moments, as the small magnetic grains within each droplet are randomly oriented due to their thermal motion. However, once an external magnetic field is applied, the orientation of magnetic grains is slightly rotated toward the field direction; this results in a dipole moment for each droplet. The magnitude of the magnetic dipole moment increases with the strength of the applied field until saturation is reached. Consequently these droplets interact through dipole forces which can be controlled by the magnitude of the external field.

There are two focuses of the research in ER and MR fluids: (1) the phase transition and the phase diagram [1–3], and (2) the growth rate of columnar structure [4–6]. These are related to the structure of the fluid. The structural changes greatly affect the rheology of the fluid, changing the low-viscosity, off-field fluid to a shear-thinning fluid whose viscosity can be many orders of magnitude greater. Most researchers are interested in the rheology of the fluid because of many potential magnetomechanical applications. The magnetic-field-induced phase behavior of ferrofluid emulsion is studied by light scattering and optical microscopy [1]. It is found that as the strength of an applied magnetic field increases at a slow enough rate, ferrofluid emulsion exhibits a gas to a nematic liquid phase transition at $H_{c_1}$ followed by a nematic liquid to solid phase transition at $H_{c_2}$. In the transition at $H_{c_1}$, randomly distributed emulsion droplets start to form chains at random positions and with various lengths. In the second transition at $H_{c_2}$, the fluctuation coupling is the dominant interaction, and it drives the chains to coalesce into separated columns which form a locally ordered columnar structure. When the field just exceeds $H_{c_2}$, it is found that in some areas chains are closer to one another than in other areas. These chains grow more rapidly with increasing field, and eventually become solid columns. This strongly indicates that nucleation plays an important role in the nematic liquid–columnar solid phase transition at $H_{c_2}$. Because of the cylindrical symmetry of the interchain potential, this is a two-dimensional phase transition in the plane orthogonal to the field lines. It turns out to be first order [7–9].

The growth rate is another important experimentally observable quantity which provides a sensitive test of the theories of structure evolution in MR and ER fluids. With a sudden application of a strong uniform external field, the average distance $d$ between columns, as a function of time $t$, field $H$ (or $E$), and volume fraction $\phi$ are investigated. One study was carried out for an ER fluid by assuming that coarsening is due to thermal fluctuations of chains [4]. This calculation resulted in a theoretical prediction for the coarsening of infinitely long chains: $d \sim t^{5/9}$, $d \sim E^{5/9}$, and $d \sim \phi^{2/3}$ However, the experimental result for a cell thickness of 0.7 mm shows that the chain coarsening varies in time in accordance with the power law $d \sim t^{2/5}$. The experimental situation corresponds to the case of cell thickness or width along the field direction essentially infinite due to image dipoles formed at the boundaries. Furthermore, recent experiments in ferrofluid emulsions demonstrate an even slower coarsening rate [9]. For a cell thickness greater than 300 $\mu$m, the number of droplets in a chain is found to be in the thousands; therefore the rate should show a tendency to approach the result of infinitely long chains. But surprisingly, a very slow power law of the form $d \sim t^{0.27}$,

 

$d \sim H^{0.22}$, and $d$ weakly dependent on $\phi$ was found. These exponents are only about half of those obtained from a previously existing theory [4].

On the other hand, spinodal decomposition (SD) mechanisms have predicted a very slow rate of nuclei growth [10]. Lifshitz and Slyozov predicted $\sim t^{1/3}$ behavior. It seems that these SD theoretical values are pretty close to the experimental result. However, the mechanisms are inconsistent with the optical microscopic observation of nucleation in the ferrofluid emulsion system, which will be discussed below. In this paper, we describe a nucleation mechanism, and then use a fluctuation coupling theory to explain the nematic liquid–columnar solid structure evolution and to account for the slow coarsening rate found in ferrofluid emulsion systems.

## II. COLUMNAR NUCLEATION MODEL

As is well known, in the first order phase transition there is always a possibility of metastable states and, hence, also of formation of nuclei [11]. For example, supercooled vapor in time condenses to a liquid; a superheated liquid is converted into vapor. This change occurs in the following manner. Owing to fluctuations, small quantities of a phase are formed in an originally homogeneous phase. For example, droplets in a stable vapor phase are always unstable, and eventually disappear. If the vapor is supercooled, however, they become stable and in time begin to grow and form a kind of center of condensation. The droplets must be sufficiently large in order to compensate for the unfavorable energy change when a liquid-vapor interface is formed. Thus there is a certain minimum or critical size necessary for a nucleus, as it is called, of a stable phase formed in a metastable phase, in order for it to become a center for formation of the later phase. The induced nematic liquid phase in the ferrofluid emulsion system is a metastable state, because of the short-range attractive interaction produced directly by dipole chains and the long-range fluctuation coupling between the chains. Within the metastable phase, nuclei will form and initiate the new phase. Nucleation can be of two types: (1) The system may begin in a heterogeneous phase. In that case, the transition occurs by what is often referred to as heterogeneous nucleation. (2) Spontaneous fluctuations can form nuclei which exceed the critical nucleus size. This is often termed homogeneous nucleation. Because the possibility of nucleating columns of the phase increases rapidly with increasing size of nuclei, the beginning of the phase transition is determined by the probability that nuclei of a minimum necessary size occur. The probability that a nucleus of this minimum size will form is proportional to $\exp(-R_{\min}/k_B T)$, where $T$ is the temperature and the energy barrier $R_{\min}$ is the work required to form such a critical nucleus. This nucleus is in unstable equilibrium with the medium: its shape is such that, at a given width of nucleus, the free energy of the body will be at a minimum, buts its width corresponds to a *maximum* of the free energy. Thus a critical nucleus corresponds to a saddle point of the free energy [11]. In an isotropic system the critical nucleus is spherical. But in the ferrofluid emulsion in the presence of a sufficiently strong external magnetic field, the structure formation begins by the chaining of droplets. The nuclei of columns consist of a few overlapping chains, and the shape of the nucleus is actually a long cylinder except at the ends where the width narrows. The nucleus shape has been discussed by several groups previously [12]; we do not intend to concentrate on it here. For simplicity, we assume that each nuclei is a uniform cylinder with square cross section.

The ferrofluid emulsion is confined within a cell of thickness $L$. In order to calculate the work required to form a critical nucleus $R_{\min}$, we use a mean-field approximation in which the initial state is taken to be uniform with all chains parallel to the $z$ axis (the direction of the external field). The permeability $\mu_i$ is taken to be its average value $\mu_0$ inside the sample. The final state is taken to consist of nuclei distributed periodically in space. Often, permeability is proportional to density, and, for a first order phase transition in the magnetic field, there should be a small jump of the magnetization and the permeability around the critical field $H_c$ where the nematic liquid crystal phase starts to evolve to a solid columnar structure. Hence, when $H > H_c$, we assume that the final state permeability in the region $|z| < L/2$ is given by the following expression with period $d$ in $x$ and $y$:

$$\mu_f(x,y) = \begin{cases} \mu_0 + \delta\mu & \text{for } |x| < D/2 \text{ and } |y| < D/2 \\ \mu_0 & \text{elsewhere}, \end{cases} \tag{1}$$

with $\delta\mu \ll \mu_0$. (Of course $\mu_i = \mu_f = 1$ for $|z| > L/2$.) $\delta\mu$ is due to the formation of the nuclei. $D$ is the width of the nuclei, and $d$ is the separation between adjacent nuclei with $d \gg D$. The chains are confined between $z = -L/2$ and $z = +L/2$; however, $L \gg d$, so the chains are long enough to be considered as infinite. In the mean-field approximation, we model the nucleation process as a transition from the initial state with free energy $\mathcal{F}_i$ to the final state with free energy $\mathcal{F}_f$. Our goal is to calculate $R_{\min}(D) = \mathcal{F}_f - \mathcal{F}_i$. By using Fourier's transformation, the permeability in the region $-L/2 < z < L/2$ can be rewritten as

$$\mu_f(x,y) = \mu_0 + \delta\mu \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} A_{mn} \sin\left[\frac{m\pi D}{d}\right] \cos\left[\frac{2m\pi}{d} x\right] \times \sin\left[\frac{n\pi D}{d}\right] \cos\left[\frac{2n\pi}{d} y\right], \tag{2}$$

where $A_{mn} = (2-\delta_{m0})(2-\delta_{n0})/(\pi^2 mn)$. (The $m=0$ and $n=0$ terms require taking a limit.) We assume that the magnetic permeability tensor is diagonal and isotropic. Thus we write $\vec{B}_i = \mu_i \vec{H}_i$ and $\vec{B}_f = \mu_f \vec{H}_f$ for the initial and final states, respectively. By solving Maxwell's equations with boundary conditions, up through terms of first order in $\delta\mu$, we find for the field $\vec{H}_f^{(i)}$ in $|z| < L/2$ and $\vec{H}_f^{(0)}$ in $|z| > L/2$:

$$H_{fx}^{(i)}=\delta\mu\sum_{m,n=0}^{\infty}\frac{m}{\sqrt{m^2+n^2}}S_{mn}s_{mx}c_{ny}\sinh(2r_{mn}z)\ ,$$
$$H_{fx}^{(0)}=\delta\mu\,\mathrm{sgn}(z)\sum_{m,n=0}^{\infty}\frac{m}{\sqrt{m^2+n^2}}T_{mn}s_{mx}c_{ny}\exp(-2r_{mn}|z|)\ , \tag{3}$$
$$H_{fz}^{(i)}=\frac{H_0}{\mu_0}-\delta\mu\sum_{m,n=0}^{\infty}S_{mn}c_{mx}c_{ny}\cosh(2r_{mn}z)\ ,$$
$$H_{fz}^{(0)}=H_0+\delta\mu\sum_{m,n=0}^{\infty}T_{mn}c_{mx}c_{ny}\exp(-2r_{mn}|z|)\ , \tag{4}$$

where

$$S_{mn}\equiv\frac{H_0}{\mu_0}A_{mn}\sin\left[\frac{m\pi D}{d}\right]\sin\left[\frac{n\pi D}{d}\right]\Big/[\sinh(Lr_{mn})+\mu_0\cosh(Lr_{mn})]\ ,$$
$$T_{mn}\equiv S_{mn}\exp(Lr_{mn})\sinh(Lr_{mn})\ , \tag{5}$$
$$s_{mx}\equiv\sin\left(\frac{2m\pi}{d}x\right),\quad c_{ny}\equiv\cos\left(\frac{2n\pi}{d}y\right),\ \text{etc.}\ ,$$
$$r_{mn}\equiv\frac{\pi\sqrt{m^2+n^2}}{d}\ ,$$

where $H_0$ is the external applied field. Because there is a symmetry between $x$ and $y$ components, $H_{fy}^{(i)}$ and $H_{fy}^{(0)}$ can be obtained from the expressions for $H_{fx}^{(i)}$ and $H_{fx}^{(0)}$ by interchanging $x$ with $y$, and $m$ with $n$. The calculation of $R_{\min}$ due to formation of nuclei in a magnetic field, may be carried out similar to Privorotskii [13]. The work $R_{\min}$ necessary to form nuclei is

$$R_{\min}=\int d^3x[g_f(\rho_f,T,\vec{H}+\delta\vec{H})-g_i(\rho_i,T,\vec{H})]+\int\sigma ds\ , \tag{6}$$

where $g_f$ and $g_i$ are the Gibbs free energy densities in the final and initial states, respectively. $\vec{H}=(H_0/\mu_0)\hat{z}$ is the magnetic field in the absence of nuclei, and $\delta\vec{H}$ is the change due to the formation of the nucleus. $\sigma$ is the surface tension, and $\int\sigma ds$ is the contribution of the domain (nucleus) boundary to the free energy.

The Gibbs free energy density $g$ is given by [13]

$$g(\rho,T,H)=g^{(0)}(\rho,T)-\frac{1}{4\pi}\int_0^H\mathbf{B}\cdot d\mathbf{H}\ , \tag{7}$$

where $g^0(\rho,T)$ is the Gibb's free energy density in the absence of a magnetic field, as a function of density and temperature. $\rho=m_m n_m+m_n n_n$ is the density of MR fluid, where $n_m$ and $n_n$ are the numbers of magnetic droplets and solvent molecules per unit volume of ferrofluid emulsion, and $m_m$ and $m_n$ are their masses, respectively. $\mathbf{B}$ and $\mathbf{H}$ are the magnetic induction and field, respectively. Writing $\mathbf{B}_i=\mu_i\mathbf{H}_i$, etc. for the Gibbs free energy density in the initial state, we obtain

$$g_i=g_i^{(0)}(\rho_i,T)-\frac{1}{8\pi}H_0^2/\mu_i\ . \tag{8}$$

In the final state, outside and inside the nuclei, to the first order in $\delta\mu$,

$$g_{\text{out}}=g_{\text{out}}^{(0)}(\rho_{\text{out}},T)-\frac{1}{8\pi}\frac{H_0^2}{\mu_i}-\frac{1}{8\pi}\frac{\mu_{\text{out}}}{\bar{\mu}^2}(H_0^2-H_{0c}^2) \tag{9}$$

and

$$g_{\text{in}}=g_{\text{in}}^{(0)}(\rho_{\text{in}},T)-\frac{1}{8\pi}\frac{H_{0c}^2}{\mu_i}-\frac{1}{8\pi}\frac{\mu_{\text{in}}}{\bar{\mu}^2}(H_0^2-H_{0c}^2)\ . \tag{10}$$

Here we have considered only the limit $L\to\infty$, and the boundary condition gives $H_i=H_0/\mu_i$ and $H_{\text{in}}=H_{\text{out}}=H_0/\bar{\mu}$, where $\bar{\mu}$ is the average susceptibility in the final state; $\bar{\mu}=\mu_i+\delta\mu A_n/A$, $\delta\mu\equiv\mu_{\text{in}}-\mu_{\text{out}}$. $H_{0c}$ is the external field for which the susceptibility jumps from the value $\mu_i$ to $\mu_{\text{out}}$ outside the nuclei and $\mu_{\text{in}}$ inside. Actually $H_{0c}$ is close to $H_{c2}$ mentioned in Sec. I, which is the critical external field for the structure to start evolution from the induced nematic liquid crystal to the columnar solid structure. Per nuclei, $R_{\min}$ is given by

$$R_{\min}=[\sigma(\partial A_n)+g_{\text{in}}A_n+g_{\text{out}}(A-A_n)-g_i A]L\ . \tag{11}$$

Here $\sigma(\partial A_n)L$ is a surface tension term. If we assume the nuclei have circular cross section with diameter $D$,

$$R_{\min}/L=\sigma\pi D+\frac{\pi D^2}{4}\left[\Delta g-\frac{1}{8\pi}(H_0^2-H_{0c}^2)\frac{\delta\mu}{\bar{\mu}^2}\right]+\cdots\ , \tag{12}$$

where $\Delta g\equiv g_{\text{in}}^{(0)}-g_{\text{out}}^{(0)}$, and the terms left off are independent of $A_n$. Here we see that $R_{\min}$ exhibits the expected maximum in $D$ when $D=D_c$, where

$$D_c=\frac{2\sigma}{\frac{1}{8\pi}(H_0^2-H_{0c}^2)\frac{\delta\mu}{\bar{\mu}^2}-\Delta g}\ . \tag{13}$$

$D_c$ goes to infinity when $H_0=\tilde{H}_0$, where

$$\tilde{H}_0=\left[H_{0c}^2+\frac{8\pi\bar{\mu}^2}{\delta\mu}\Delta g\right]^{1/2} . \tag{14}$$

Usually, the experiments make the density of ferrofluid emulsion droplets to match the density of solvent in order to avoid sedimentation of magnetic droplets. In that case, $\Delta g \equiv g_{\text{in}}^{(0)}-g_{\text{out}}^{(0)}\simeq 0$. Thus

$$D_c=\frac{16\pi\sigma}{(H_0^2-H_{0c}^2)\frac{\delta\mu}{\bar{\mu}^2}} \tag{15}$$

or

$$D_c=\frac{16\pi\sigma}{(H^2-H_c^2)\delta\mu} . \tag{16}$$

The interpretation of this equation is that if the external field is below $H_{0c}$, no stable nuclei is formed; but above $H_{0c}$, the critical size of nuclei is finite, and stable nuclei occur. Hence for a given field $H_0$ the nuclei must have a diameter larger than $D_c$ in order to be stable. When $D<D_c$, a decrease of the size $D$ is energetically favorable and the nucleus will be absorbed; when $D>D_c$, an increase of $D$ is favorable and the nucleus will grow. In Eq. (16) $D_c\sim|H-H_c|^{-1}$ indicates that when $H\Longrightarrow H_c$, the critical size of nuclei is infinite. If a higher field is applied, the critical size of the nucleus will become finite, and some nucleate columns with $D>D_c$ would be stabilized.

## III. NUCLEATION-CONTROLLED COARSENING

Equation (16) indicates that, during the coarsening, there are two types of nucleate columns created: the stable columns with $D>D_c$, and the unstable columns with $D<D_c$. The existence of the nucleation as described above has been confirmed qualitatively by microscopic observation of the structure evolution in ferrofluid emulsions We find that the coarsening consists of two separate processes: (1) Growth of the stable nuclei. During the coarsening, two types of nucleate columns, the stable columns with $D>D_c$ and the unstable columns with $D<D_c$, coexist. The stable nucleate columns absorb the unstable columns by capturing its chains individually. (2) Merging of the nuclei. During their growth, two nuclei may very quickly move together and merge into one larger nucleus, which then continues to grow. In brief, the growth process happens between a stable column nuclei and an unstable column nucleate, whereas the merging process occurs between stable nuclei. The overall coarsening rates result from the compounding of these two separate processes. Our experimental observations show that the two processes coexist and alternatively occur. The occurrence of processes (1) and (2), however, may need different collision times and have different probability. When the magnetic field is high enough, it takes a longer time for process (1) than process (2) to occur, and process (1) is observed to happen much more frequently [9]. As a result, although the merging process plays an important role in the coarsening process, the growth rate in MR fluid is determined mainly by the growth process of the stable nucleate columns. Our model therefore emphasizes this growth. A model was proposed for ER fluid in which the fluctuating field could drive a chain to move toward another chain and then to clump together into a baby column. These columns coalesce again and form the second generation of columns, so on and so forth, up to the final columnar structure [4]. All columns at each stage have an equal opportunity of coalescing, and no one of them has preference. This model describes process (2) (or merging of the nuclei), which may be dominant for ER fluids, but not for our ferrofluid emulsion systems.

In our model, the nucleate columns with $D<D_c$ are created and destroyed instantly. The columns with $D>D_c$ capture the individual chains from the unstable columns and recruit them for their growth. The basic coupling responsible for the growth rate is the interaction between a stable column and a single chain, rather than the interaction between two columns. We believe that in a certain region of volume fractions, the coupling between a chain and a column stems from a fluctuating field induced by the dipole density fluctuation [14] because of Peierls-Landau instability. This effect is crucially important in the nematic liquid phase where each chain is a one-dimensional subsystem [15]. We do not expect the ordinary dipole-dipole interactions to cause the chains to clump together because the long-range dipole-dipole interactions are screened, leading to an exponential decay with the distance between chains. Suppose that a chain is undergoing small longitudinal fluctuations, with droplet position $z_l=l2a+U_l$, where $U_l$ is the displacement of the $l$th droplet and $a$ is the droplet radius. The local density at long wavelengths is $n(z)=1/(2a+U_{l+1}-U_l)\approx(1/2a)(1-[\partial U(z)]/\partial z)$. The field induced by a fluctuating chain, a distance $\rho$ away, is [14,15]

$$H_z(\rho,z)\approx\frac{m}{\rho^2}\int d\psi\, F(\psi)n(\rho\psi+z) , \tag{17}$$

where $m$ is the magnetic dipole moment and $F(\psi)\equiv(2\psi^2-1)/(\psi^2+1)^{5/2}$. The fluctuation field induced by a column is given by

$$H_z(\rho,z)\approx\sum_{i=1}^{N}\frac{m}{|\vec{\rho}-\vec{\rho}_i|^2}\int d\psi\, F(\psi)n_i(|\vec{\rho}-\vec{\rho}_i|\psi+z) , \tag{18}$$

where $N$ is the number of chains in the column. The field-field correlation function is

$$\langle H_z(\rho,z)H_z^*(\rho,z')\rangle\approx\sum_{i=1}^{N}\sum_{j=1}^{N}\frac{m^2}{|\vec{\rho}-\vec{\rho}_i|^2|\vec{\rho}-\vec{\rho}_j|^2}\int\int d\psi\, d\psi' F(\psi)F(\psi')\langle n_i(|\vec{\rho}-\vec{\rho}_i|\psi+z)n_j^*(|\vec{\rho}-\vec{\rho}_j|\psi'+z')\rangle . \tag{19}$$

The density-density correlation is

$$\langle n_i(z)n_j^*(z')\rangle \approx \frac{1}{4a^2}\left[1+\left\langle \frac{\partial U_i(z)}{\partial z}\frac{\partial U_j^*(z')}{\partial z'}\right\rangle\right] = \frac{1}{4a^2}\left[1+\sum_{k,k'}\exp(ikz-ik'z')kk'\langle U_i(k)U_j^*(k')\rangle\right] . \quad (20)$$

During the coarsening, we assume that the stable columns are not laterally tightly fused, so that phonons excited in the different chains are not coherent to each other. Taking any reasonable interdroplet potential and using the equipartition theorem, we obtain

$$\langle U_i(k)U_j^*(k')\rangle \approx \langle U_i(k)U_i^*(k')\rangle\delta_{ij} \sim \frac{k_BT}{m^2/a^5}(k^2a^2)^{-1}\delta_{ij}\delta_{k,k'} . \quad (21)$$

The long-wavelength approximation has been used because the most significant contribution to the field comes from the long-wavelength fluctuations. The coupling constant is proportional to $m^2/a^5$. Substituting Eqs. (20) and (21) into Eq. (19), the field-field correlation function can be rewritten as

$$\langle H_z(\rho,z)H_z^*(\rho,z')\rangle \sim k_BT\sum_{i=1}^{N}\frac{a^2}{|\vec{\rho}-\vec{\rho}_i|^5}\int d\psi F(\psi)F\left[\psi+\frac{z-z'}{|\vec{\rho}-\vec{\rho}_i|}\right] . \quad (22)$$

The mean square field induced by fluctuations of a column is

$$\langle |H_z(\rho)|^2\rangle \sim k_BT\sum_{i=1}^{N}\frac{a^2}{|\vec{\rho}-\vec{\rho}_i|^5}\int d\psi[F(\psi)]^2 . \quad (23)$$

Since the size of the column is typically much smaller than the separation between the stable and the unstable columns, at a transverse distance $\rho$ from this column the fluctuation induced field, or the square root mean field, is

$$H_f \equiv \sqrt{\langle H_z^2\rangle} \sim \frac{\sqrt{k_BTNa^2}}{\rho^{5/2}} \sim \frac{\sqrt{k_BTR^2}}{\rho^{5/2}} , \quad (24)$$

where $N\sim R^2/a^2$, with $R$ is the column radius. A droplet in a chain located at a distance $\rho$ from the nucleate column has a dipole moment $\kappa a^3H$. It will experience a force which is of the order of magnitude.

$$F_d \sim \frac{\sqrt{k_BT}\,\kappa Ha^3R}{\rho^{7/2}} , \quad (25)$$

where $\kappa=(\mu-\mu')/(\mu+2\mu')$, where the permeability $\mu$ of ferrofluid decreases with an increasing field, and $\mu'$ is the permeability outside the droplet. The force might be either repulsive or attractive, depending on the exact configuration of the fluctuating column and chain. However, the attractive configurations should be dominant because they are energetically favorable to the system. The attractive force would drive the chains to coalesce. The time scale for collision can be obtained by equating the force $F_d(\rho)$ to the viscous force, that is

$$C\eta a\frac{d\rho}{dt}=F_d , \quad (26)$$

where $\eta$ is the solvent viscosity, $d\rho/dt$ is the velocity of the chain moving to the nucleate column, and $C$ is a constant. Since $R\sim\phi^{1/2}\rho$, where $\phi$ is the volume fraction, we obtain the collision time

$$t_c \sim \eta(k_BT)^{-1/2}(\kappa H)^{-1}a^{-2}\phi^{-1/2}\rho^{7/2} . \quad (27)$$

As we pointed out, the dominant process responsible for the growth rate is the accretion process of stable nucleate columns; hence the growth rate is actually the time scale for the chains in the unstable nucleus to be drawn to the stable column. Since the radius of the unstable nucleate columns is much smaller than the separation between the stable and the unstable columns, the averaging $\rho$ in Eq. (27) is equivalent to the characteristic length $d$, here taken to be the mean separation between columns. We can now find the qualitative dependences of $d$, on the growth rate, the field, and the volume fraction as follows:

$$\begin{aligned} &d\sim t^{\alpha} , \quad \alpha=\tfrac{2}{7} , \\ &d\sim(\kappa H)^{2/7}\sim H^{\beta} , \quad \beta=\tfrac{3}{14} , \\ &d\sim\phi^{\gamma} , \quad \gamma=\tfrac{1}{7} , \\ &d\sim\eta^{\zeta} , \quad \zeta=-\tfrac{2}{7} , \end{aligned} \quad (28)$$

where the field dependence of $\kappa$ is related to the Langevin function. We carried out a numerical, statistical mechanical calculation of $\kappa(H)$. The result indicated that $\kappa\sim H^{-1/4}$ for 50 G $<H<$ 400 G, which was used in the second of Eqs. (28).

## IV. COMPARISON WITH THE EXPERIMENTAL RESULTS

The structural evolution of the ferrofluid emulsion is studied using optical microscopy and static light scattering techniques, which have been described in detail elsewhere [9]. Comparison of our theoretical model with the experimental results is listed in Table I, and thereafter explained.

(a) There are three sets of experimental data for the 3% volume fraction sample. (i) The light scattering measurement shows a power law of the form $d\sim t^{0.27}$ as shown in Fig. 1, where the droplet diameter is 0.4 $\mu$m, the sample thickness is 300 $\mu$m, and field is 450 G. (ii) For the sam-

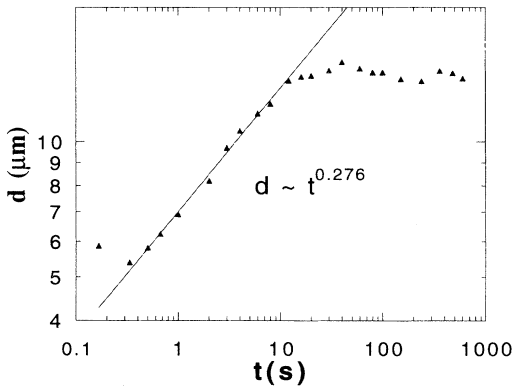


FIG. 1. Coarsening rate measured by light scattering for $\phi=0.03$ samples with $2a=0.44$ $\mu$m, $L=300$ $\mu$m, and $H=450$ G.

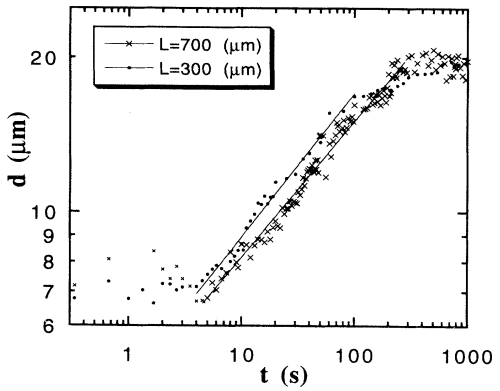


FIG. 2. Two microscopic measurements of coarsening rate. The dots denote the experiment (ii), with droplet diameter 0.3 $\mu$m and cell thickness 300 $\mu$m under a magnetic field of 380 G. The crosses are for experiment (iii), with droplet diameter 0.26 $\mu$m and cell thickness 700 $\mu$m under magnetic field of 390 G.

ple with a diameter of 0.3 $\mu$m and a thickness of 300 $\mu$m under the magnetic field 380 G, the optical microscopy measurement of the coarsening rate shows $d\sim t^{0.28}$. (iii) For the sample with a diameter of 0.26 $\mu$m and a thickness of 700 $\mu$m under the magnetic field 390 G, it is found that $d\sim t^{0.263}$ in the microscopy measurement. Both (ii) and (iii) are shown in Fig. 2. All measurements are very close to our theoretical result $d\sim t^{0.286}$. Since the chain length is proportional to $\lambda^{2/3}$ where $\lambda\approx\kappa^2H^2a^3/k_BT$, for the sample with a diameter of 0.3 $\mu$m under $H=400$ G, the chain length is about 300 $\mu$m [15]. If the length of the chain is increased by increasing $\lambda$, the exponent $\alpha$ may tend toward the value $\frac{2}{7}\approx0.286$, which is theoretically obtained by assuming infinite chain length.

(b) The field dependence of the separation between the columns was measured by light scattering, which is shown in Fig. 3 with $d\sim H^{0.22}$. This is in good agreement with our theoretical value $d\sim H^{0.21}$.

(c) The same measurement was performed for various volume fractions with the same cell thickness 100 $\mu$m. It was found that all follow a similar power-law relation, $d\sim t^{\alpha}$. Figure 4 indicates that the volume fraction dependence of separation $d$ fits our theoretical result $d\sim\phi^{1/7}$ very well.

(d) Although the coarsening rates, or $\alpha$, are the same as obtained in both microscopy measurements of (ii) and (iii), different saturation times and saturation separations are found, which are given by $t_{s2}=87$ s with $d_{s2}=16.4$ $\mu$m, and $t_{s3}=265$ s with $d_{s3}=19.5$ $\mu$m. $t_{s3}$ is more than twice $t_{s2}$. At first glance, this looks like a puzzle. But from Eq. (27) we have

$$\frac{t_{s_2}}{t_{s_3}}\approx\left[\frac{T_2}{T_3}\right]^{-1}\frac{\eta(T_2)}{\eta(T_3)}\left[\frac{a_3\lambda_3}{a_2\lambda_2}\right]^{1/2}\times\left[\frac{\phi_2}{\phi_3}\right]^{-1/2}\left[\frac{d_{s_2}}{d_{s_3}}\right]^{7/2}. \tag{29}$$

TABLE I. Comparison with experimental results.

| Power law | Theoretical values | Experimental values |
|---|---|---|
| $d\sim t^{\alpha}$ | $\alpha=\frac{2}{7}\approx0.286$ | $\alpha\approx0.27$ |
| $d\sim H^{\beta}$ | $\beta=\frac{3}{14}\approx0.21$ | $\beta\approx0.22$ |
| $d\sim\phi^{\gamma}$ | $\gamma=\frac{1}{7}\approx0.14$ | $\gamma\approx0.17$ |
| $d\sim(\sqrt{T}/\eta(T))^{\zeta}$ | $\zeta=\frac{2}{7}$ | $\zeta=?$ |
| $t_c\sim H^{-\nu}$ | $\nu\approx\frac{3}{4}=0.75$ | $\nu\approx0.81$ |

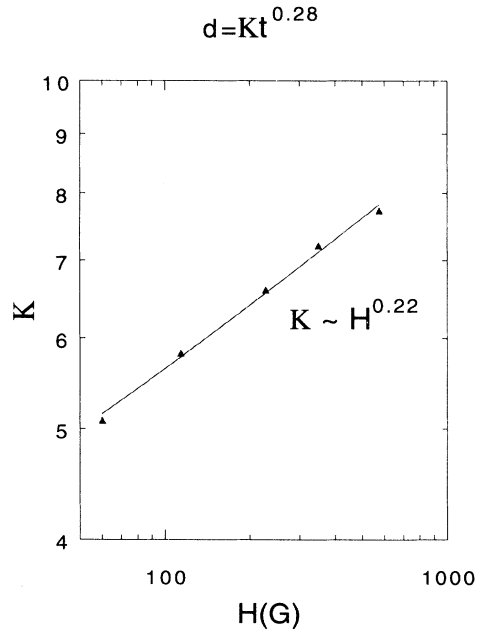


FIG. 3. The dependence of separation on field $H$, measured by light scattering, where $L=200$ $\mu$m and $2a=0.44$ $\mu$m.

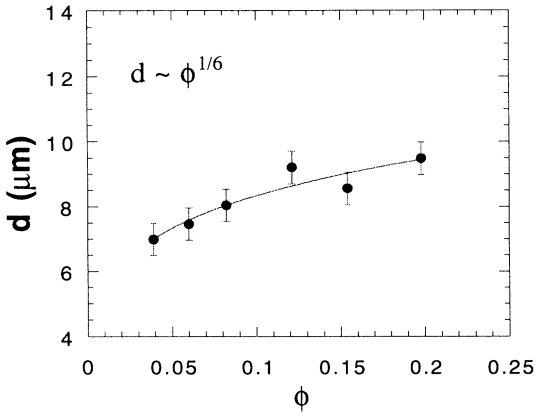


FIG. 4. The dependence of separation on the volume fraction $\phi$, obtained for $L=100$ $\mu$m, $H=380$ G, and $2a=0.5$ $\mu$m.

Substituting all parameters into the right-hand side of Eq. (29), and setting $T_3=T_2$, we obtain $(a_3\lambda_3/a_2\lambda_2)^{1/2}(d_{s_2}/d_{s_3})^{7/2}=0.42$, which is close to the experimental data given by $t_{s_2}/t_{s_3}\approx 87s/265s\approx 0.33$.

(e) The dependence of the growth rate on magnetic field in ferrofluid emulsion is found [9] to be $\sim H^{0.81}$, which is the same as what was measured in ER fluid [4]. From Eq. (27) the growth rate increases as $H^{0.75}$. This good agreement between calculation and measurement rules out the direct dipole-dipole interaction mechanism responsible for the coarsening process, and provides significant evidence for fluctuation theory as suggested by Halsey and Toor [14].

(f) Usually, in the growth rate measurement for ER fluid, $\lambda$ is much larger than that in ferrofluid emulsion system, and the existence of imaging charges in ER fluid enhances the symmetry along the chain direction. Hence photons excited in the different chains of a stable column would be coherent with each other. In that case, the fluctuation electric field $E_f$, Eq. (24), becomes $E_f\sim(\sqrt{k_BTN^2a^2/\rho^{5/2}})\sim(\sqrt{k_BTR^4/a^2/\rho^{5/2}})$, which is proportional to $R^2$, instead of $R$. Thus we find $d\sim t^{2/5}$ and the field dependence of the growth rate $t^{-1}\sim\kappa E\sim E^{0.7\sim0.85}$, here $\kappa=(\epsilon-\epsilon')/(\epsilon+2\epsilon')$, which weakly declines with increasing field, and $\epsilon$ is the dielectric constants. This result fits experimental data $d\sim t^{2/5}$ and $t^{-1}\sim E^{0.8}$ very well [4]. Also, it predicts $d\sim(\kappa E)^{2/5}\sim E^{0.28\sim0.38}$ and $d\sim\phi^{2/5}$, which needs further experiments in ER fluids to test it.

Although our calculation gives a slow rate as the SD mechanism, there are essential differences between the SD and nucleation mechanisms. First, SD requires no thermal activation energy; that is, it occurs in the unstable rather than in the metastable region of a phase diagram. Second, in the nucleation mechanism the additional phase starts from small regions, the nuclei, which then proceed to grow in extent. In the SD mechanism the composition changes gradually in both directions from the average; the growth is not in extent but in amplitude of density with a characteristic wavelength. Third, in nucleation, a surface energy barrier is necessary, but, for SD, no surface energy barrier is needed. Hence a very high degree of connectivity is a good indication of the SD mechanism. Our experimental results show the lack of the characteristics of the SD mechanism. We believe that the mechanism of coarsening is nucleation and its growth, and the dominant interaction for coarsening of the columns is the fluctuation coupling caused by the Peierls-Landau instability.

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