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Domain structures in thin layers of a ferrocolloid

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Abstract. — We consider the problem of formation of structures composed of identical domains in a ferrocolloid that fills a space between two closely situated parallel planes under action of a normal external magnetic field. Those structures begin to arise under conditions favouring the phase separation of the ferrocolloid. An inhomogeneous system including two equivalent colloidal phases would ultimately evolve due to Ostwald ripening, but for a scaling effect of the planes that stops the evolution at a certain level and makes for the resulting domain structure being stable. A method to find out main characteristics of the domains, such as their size and concentration, is developed for both chaotic and regular (ordered) structures.

1. Introduction.

Numerous experiments, among which those in [1-5] should be cited, evidence a ferrocolloid layer between parallel boundaries to lose its thermodynamic stability if the strength of an externally applied normal magnetic field exceeds some critical value. As a result, a system of cylindrical domains develops, the concentration of magnetic particles inside the domains being considerably higher than that in the ambient parent colloidal phase. Such a transformation from an original homogeneous state to that with a stable domain arrangement resembles to all appearances a phase transition of the first type. A similar phenomenon of the emergence of domains is also specific to thin layers of an electrorheological suspension under action of a constant electrostatic field [6]. Visually, the mentioned domains are like domains in solid magnetics or vortice structures that are sometimes generated in superconductors of the second type.

The authors are aware of the only attempt to theoretically explain the origination of the domains by assuming the reason of this phenomenon to be due to the break of thermodynamic stability of ferrocolloids in sufficiently strong fields and to an ensuing process of spinodal decomposition [7, 8]. The theory of these papers leads, however, to a conclusion that the particle concentration has to vary smoothly, almost sinusoidally, along the layer plane.
Such a conclusion does not correspond in the least to available experimental evidence, according to which all the domains are practically of a cylindrical shape and possess easily discernible sharp boundaries. This cannot be explained with the aid of almost sinusoidally varying concentration fields. Moreover, it has been shown in [4] that there is merely a comparatively small number of randomly positioned domains if the external field is either weak or of reasonably moderate intensity, so that the domain assemblage surely reminds of a two-dimensional ideal gas. The domains become capable of forming an ordered lattice only at a condition of their concentration being sufficiently high, what demands a rather strong field. At last, it has been rigorously proved [9] that the layer boundaries cannot exert a stabilizing influence on an early stage of spinodal decomposition which happens to be relevant to the theory of [7, 8].

A main physical reason for the origination of domain systems seems to be clear enough. The dipole interparticle interaction in magnetic dispersions results in an effective attraction between the particles which significantly increases as the strength of an external orienting magnetic field a dispersion is exposed to grow [10, 11]. The attraction tends to cause condensation of the particles whereas the particle thermal motion opposes this process. If the dispersion concentration is sufficiently high and/or its temperature is sufficiently low, the dispersion thermodynamic stability cannot be maintained, and a process of phase separation of the dispersion into two phases with different concentrations of the particles evolves. Such a process is quite similar to that commonly observed in molecular systems undergoing a first type phase transition [10-13]. Examples of transformations of the same nature in colloids in which the interparticle attraction is of another physical origin can be found in [14, 15].

A constant external magnetic field intensifies attraction of particles of a ferrocolloid and so favours its separation into two colloidal phases. The process of phase separation starts with the formation of initial critical nuclei of a new phase that give rise to dropwise aggregates which are elongated in the external field direction [12]. If the ferrocolloid were unbounded, the aggregates would incessantly grow till Ostwald ripening begins to dominate the new phase evolution, when larger aggregate continue to increase in size at the expense of smaller ones.

A finite distance between the layer boundaries sets, however, a limit to such a process as compared with that in the bulk. When the aggregate size comes to equal this distance, any aggregate can continue to grow only in the radial direction, that is, in the layer plane. Then the aggregate radius eventually grows under a condition of constant length, and the aggregate virtually transforms into a domain. This results, of course, in strengthening of the aggregate demagnetization field and ultimately causes an energy expenditure to become too high to provide for the domain growth over a certain critical size.

In what follows, this qualitative picture is proved to be correct and main properties of resulting stable domain arrangements are found out and discussed at some length.

2. Chaotic arrangements.

Consider an assemblage of nearly cylindrical domains of radius \( a \) in a ferrocolloid layer of thickness \( 2l \) between parallel plates. The ferrocolloid is subject to an external magnetic field of strength \( H_0 \) which is directed normally to the plates. Let us introduce the volume concentration \( \phi_d \) of magnetic particles in each domain, also a surface concentration of the domains themselves that represents the fraction occupied by domain crossections in the layer plane and equals \( s = \pi a^2 n \), \( n \) being understood as the number of the domains per unit area of this plane. In accordance with the majority of experimental data, we assume right away the domains to be thin, what means the domain radius \( a \) to be much smaller than the layer thickness \( l \), \( a \ll l \).

Our intended goal consists, first, in identifying conditions at which there exists a ther-
moderately equilibrium domain arrangement within the ferrocolloid layer and, second, in finding out properties of the arrangement. This implies that not only the domain shape and their surface concentration but also the magnetic particle concentration and the magnetic field strength both inside the domains and in interstices between them have to be simultaneously determined, to incorporate the findings into a complete statistical thermodynamic model of the system under study. Construction of the last model is also by no means an easy task. Although fundamentals of such a model have been recently disclosed in [11], one can hardly hope to overcome all obstacles and to get a complete solution of the whole problem without some decisive simplifications, which we are now going to enumerate.

First of all, we presume the domains to be regular circular cylinders, and their surface concentration (which evidently equals the domain volume concentration within the layer) to be small as compared with unity. Then each domain can be regarded as immersed in a ferrocolloidal medium whose properties, such as concentration of particles by volume \( \phi_1 \), pressure \( p_1 \) and magnetic field strength \( H_1 \) approximately coincide far away from the domain with their actual values which can be got by averaging over merely the interstices. The last assumption is made solely to simplify needed calculation. If it were wrong, an approximation based on the self-consistent field theory could be used, in which case the mentioned quantities should be looked upon as those obtained by averaging over the whole layer plane. Obviously, quantities \( \phi_1, p_1 \) and \( H_1 \) can be regarded as uniform.

Even though the above assumptions hold true, we are again faced with a very difficult problem. A crucial simplification can be attained, nevertheless, by noticing that the magnetic field within a thin cylinder normal to the layer boundaries depends mostly on the field \( H_2 \) near its side surface, and that the demagnetization field \( h \) vanishes as \( a/l \) tends to zero. It means that we are free to take, in the zeroth approximation, the strength of the magnetic field inside a domain to be equal to \( H_2 = H_1 \). This field induces a domain magnetization \( M_d \) that has to be found with the help of some model of macroscopically uniform ferrocolloids (e.g., see [11]).

Now, let us find the demagnetization field \( h \) caused by one domain that can justly be regarded as uniformly magnetized with a specific magnetization \( M_d \). This can be done by summing up field contributions created by infinitesimal parts of the domain. If one neglects effects due to possible refraction of \( h \) at the layer boundaries, which have to be of little significance because of the accepted inequality \( a \ll l \), one gets for any point \( r_0 \) near the domain surface

\[
h_z (z_0, r_0) = \frac{M_d}{\lambda_1} \int_{-l}^{l} \int_{z_0}^{l-z_0} dz \int_{0}^{a} r \, dr \int_{0}^{2\pi} d\theta \left( 3 \frac{z^2}{R^3} - \frac{1}{R^3} \right),
\]

\[
R^2 = r^2 + r_0^2 - 2rr_0 \cos \theta + z^2,
\]  \hspace{1cm} (2.1)

This expression defines a component of \( h \) parallel to the symmetry axis of the domain, and \( z_0 \) and \( r_0 \) are axial and radial (\( r_0 > a \)) coordinates of \( r_0 \) in the cylindrical coordinate system with an origin at the intersection point of the domain symmetry axis and the middle plane of the ferrocolloid layer. Quantity \( \lambda_1 \) is the magnetic permeability of the ambient ferrocolloid. It is easy to show that, at \( a \ll l \), radial component \( h_r \) of the demagnetization field is much smaller than \( h_z \) almost everywhere, so that there is no need to take it into account at all, and vector \( h \) may be regarded as directed normally to the layer plane.

It is convenient to use further, instead of \( h_z (z_0, r_0) \), a value of this quantity obtained by averaging over the layer thickness

\[
h_1 (r_0) = \frac{1}{2l} \int_{-l}^{l} h_z (z_0, r_0) \, dz_0,
\]  \hspace{1cm} (2.2)
without noticeable loss of accuracy. Then one is always able to write
\[ h_1(r_0) = -M_dL(a/l, r_0/l), \]
where \( L \) is a known function that can be readily written out when necessary, in conformity with the definitions in (2.1) and (2.2).

Consider, next, a cylinder in a field of strength \( H_2 = H_1 + h_1 \) directed along the cylinder axis and introduce \( \phi_2 \) and \( p_2 \) as the particle volume concentration and pressure at the side cylinder surface outside the cylinder. Similar quantities pertaining to the interior of the cylinder are marked with a subscript \( d \). All the thermodynamic potentials of the uniform ferrocolloidal phases are admittedly functions of the above-introduced variables. Furthermore we shall consider chemical potentials \( \mu(p, \phi, H) \) and \( \mu_0(p, \phi, H) \) of the magnetic particles and of molecules of the suspending liquid, respectively.

Conditions of thermodynamic equilibrium require the chemical potentials inside and just outside the cylinder to coincide. Also, mechanical equilibrium demands the pressures at both sides of the cylinder to be distinguished by the surface pressure \( \sigma/a \), where \( \sigma \) is understood as the surface tension coefficient. Thus we have
\[
\begin{align*}
\mu_d &= \mu_2, \quad \mu_{0d} = \mu_{02}, \quad p_d - p_2 = \sigma/a, \\
\mu_j &= (p_j, \phi_j, H_1 + h_1), \quad \mu_{0j} = \mu_0(p_j, \phi_j, H_1 + h_1), \quad j = d, 2.
\end{align*}
\]  
(2.4)

Simple evaluation shows \( p_d - p_2 \) to be relatively small. By accounting for this and for thermodynamic identifies \( \partial \mu/\partial p = v \) and \( \partial \mu_0/\partial p = v_0 \), \( v \) and \( v_0 \) standing for the volumes of a particle and of a molecule, respectively, we get from equation (2.4)
\[
\begin{align*}
\mu_2(p_1, \phi_2, H_1) + g_2h_1 &= \mu(p_1, \phi_2, H_1) + g_2h_1 - \sigma v/a, \\
\mu_0(p_1, \phi_d, H_1) + g_{0d}h_1 &= \mu_0(p_1, \phi_d, H_1) + g_{02}h_1 - \sigma v_0/a, \\
g_j &= \frac{\partial \mu(p_1, \phi_j, H_1)}{\partial H_1}, \quad g_{0j} = \frac{\partial \mu_0(p_1, \phi_j, H_1)}{\partial H_1}, \quad j = d, 2, \quad h_1 \ll H_1.
\end{align*}
\]  
(2.5)

Further, the ambient ferrocolloid phase between the cylinders is at equilibrium if the chemical potentials are uniform throughout interstices. Hence we arrive at new equations yielding necessary conditions of the equilibrium, in much the same manner as when getting equation (2.5),
\[
\begin{align*}
\mu(p_1, \phi_2, H_1) + g_2h_1 &= \mu(p_1, \phi_1, H_1) + v(p_1 - p_2), \\
\mu_0(p_1, \phi_2, H_1) + g_{02}h_1 &= \mu_0(p_1, \phi_1, H_1) + v_0(p_1 - p_2).
\end{align*}
\]  
(2.6)

Equations (2.5) and (2.6) together with that defining the pressure difference in equation (2.4) form a set of five equations to determine \( \phi_d, \phi_2, p_1 - p_2, a \) and \( h_1 \) at any fixed \( \phi_1 \). It can be solved, after which all the indicated variables become known functions, of \( \phi_1 \), within a certain range of the last quantity where a solution exists, if ever. In such a case, \( a \) also changes when \( \phi_1 \) is permitted to vary. The particle chemical potential in the interstitial space depends only on \( \phi_1, p_1 \) and \( H_1 \) and is independent of \( a \), whereas that of the particles inside the domains may now be regarded as a function of \( a \) under otherwise identical conditions.

The situation is schematically illustrated in figure 1. If the domain radius is smaller than \( a_1 \), say, a domain is bound to eventually disappear. If the radius exceeds another critical value, \( a_2 \), the domain also dissolves, but merely down to \( a = a_2 \), when the dissolution ceases. Domains
Fig. 1. — Sketch of dependence of particle chemical potential in both domains and interstices on domain radius. Explanations are given in the text.

where radii lie within the range from \( a_1 \) to \( a_2 \) may either grown but only till the value of \( a_2 \) is reached, or diminish to \( a = a_1 \) and, next, vanish at \( a = 0 \), depending on what phase trajectory corresponds to a monotonous approach of \( \mu_d \) to \( \mu_1 \). Characteristic trends of the development of a single domain are conventionally indicated in figure 1 with arrows, from which it is not difficult to see that the domains under question can be stabilized merely at \( a = a_2 \).

Spontaneous fluctuational origination of new domains results inevitably in a decrease in the particle concentration within the interstitial space and, consequently, in a fall of \( \mu_1 \). This is why the whole system evolution causes a line \( \mu = \mu_1 = \text{Cte.} \) to come gradually downward, until the line touches the curve of \( \mu = \mu_d(a) \) at a point \( a = a_e \) where \( \mu_1 = \mu_d = \mu_e \). The last equation determines also a critical concentration \( \phi_{1e} \) of particles outside the domains. The state that corresponds to this critical point can be shown to be stable since a further increase in the total amount of magnetic particles within the domains reduces \( \phi_1 \) below \( \phi_{1e} \), and so the whole line \( \mu = \mu_1 = \text{Cte.} \) is displaced down with respect to \( \mu = \mu_d(a) \). It compels, in its turn, an excessive amount of the domain phase to dissolve and, thereby, leads to reestablishing of the critical particle concentration specific to the stable equilibrium situation. This concentration has to be found, in compliance with the above arguments, from an equation

\[
\frac{\partial \mu_d(a)}{\partial a} = 0. \tag{2.7}
\]

Equations (2.5) and (2.6) supplemented with equation (2.7) serve now to find \( \phi_d, \phi_2, \phi_{1e}, p_1 - p_2, a_e \) and \( h_1 \). In order to close the formulation, however, we need a relationship defining \( H_1 \) in terms of the other variables. An evident relation can be put forward

\[
H_0 = (1 - s)\lambda_1 H_1 + s\lambda_d (H_1 + h), \tag{2.8}
\]

in which \( \lambda_d \) is the magnetic permeability of the domains, the surface (or volume within the layer) domain concentration to be derived from a condition of conservation of the overall
number of the magnetic particles which is certainly not affected by the domain formation. Hence
\[ s = \frac{\phi_0 - \phi_{1e}}{\phi_d - \phi_{1e}}, \]  
where \( \phi_0 \) stands for an initial particle volume concentration in the same ferrocolloid without domains.

Thus all the equations necessary to resolve the problem are stated. They suffice, in principle, to determine all equilibrium properties of a ferrocolloid layer with domains at arbitrary \( \phi_0, \ l \) and \( H_0 \). What solely remains to be done in order to bring the analysis to a completion consists in specifying expressions for both magnetostatic properties and chemical potentials on the basis of some reliable model of ferrocolloids. Judging by a good agreement with experiments, the model of [11] can be successfully used in such a capacity. Then
\[ M = \frac{m\phi}{v} \left( \cosh \alpha - \frac{1}{\alpha} \right) \left[ 1 + 8\gamma \phi \left( \frac{1}{\alpha^2} - \frac{1}{\sinh^2 \alpha} \right) \right], \]  
\[ \lambda = 1 + \frac{4\pi M}{H}, \quad \alpha = \frac{mH}{kT}, \quad \gamma = \frac{\pi m^2}{6v_kT}, \]  
and, further,
\[ \mu(p, \phi, H) = \mu^0(p) + \nu(\phi, H), \quad \mu_0(p, \phi, H) = \mu_0^0(p) - \left( \frac{\nu_0}{v} \right) \nu_0(\phi, H), \]  
\[ \nu(\phi, H) = kT \phi \left[ \ln \phi - \phi - \ln (\sinh \alpha/\alpha) + \phi(8 - 5\phi)(1 - \phi)^{-2} - (2 - \phi)G(T, H) \right], \]  
\[ \nu_0(\phi, H) = kT \phi \left[ (1 + \phi + \phi^2 - \phi^3) (1 - \phi)^{-3} - \phi G(T, H) \right], \]  
\[ G(T, H) = 4\gamma (\cosh \alpha - 1/\alpha)^2 + (4/3)\gamma^2. \]  

Here \( \mu^0 \) and \( \mu_0^0 \) are the standard chemical potentials of particles and molecules, respectively, \( m \) is the particle dipole magnetic moment and \( kT \) is the temperature in energy units.

Although the relations in equations (2.10) and (2.11) have been meticulously discussed in [11], it would be worth while, perhaps, to give a short explanation of their origin. Equations (2.10) were obtained on the basis of an approximate version of the hard sphere perturbation theory which happened to describe experimental data by various authors in quite an excellent way. The second contribution within the brackets in equation (2.10) is called to allow for an effect of the interparticle dipole interaction on the equilibrium magnetization of a crowded assemblage of magnetic particles being subject to a constant external magnetic field. In the dilute limit \( (\phi \ll 1) \), this specific magnetization turns to that by Langevin of an ideal superparamagnetic gas. Parameters \( \alpha \) and \( \gamma \) reflect the interaction of the particles with the external field and between themselves, respectively.

The sum of the first three addendumps in the expression of \( \nu \) in equation (2.11) presents the chemical potential of particles of an ideal paramagnetic gas in an external field of constant strength \( H \). The forth addendum takes into account the steric interaction of hard spheres. It has been evaluated with the help of the equation of state of a gas of hard spheres suggested by Carnahan and Starling [16]. The fifth addendum takes care of the dipole – dipole interaction between the particles in the external field which is estimated by means of the method proposed previously by Brout [17]. It can be seen, by the way, that interaction parameter \( G \) increases with \( H \), what is indicative of an intensification of the interparticle attraction due to the magnetic interaction between the particles when an external magnetic field is present.

Quantity \( \nu_0 \) coincide with the pressure of a dense gas of hard magnetic spheres evaluated within the frames of the method of [11], a deviation of the first term within the brackets
from unity being caused by the steric component of the interparticle interaction, whereas the emergence of the second term is due to the dipole – dipole part of the interaction. It is worth noting that equations (2.10) and (2.11) have been derived in [11] by perturbation theory methods which ought to be adequate if $\gamma \phi$ is of the order of unity or smaller. In an opposite case of large $\gamma \phi$, equations (2.10) and (2.11) have to be thought of as estimates in an order of magnitude of thermodynamic properties of a highly concentrated ferrocolloid. Such estimates are proved in [11], nevertheless, to be sufficiently accurate.

Conditions at which the ferrocolloid under consideration loses its thermodynamic stability in the bulk and ought to undergo phase separation have also been investigated in [11] at some length on the basis of equations (2.10) and (2.11). The same conditions pertain to a domain arrangement beginning to occur in a thin layer of the ferrocolloid as well. Equations (2.4) and (2.5) supplied with expressions (2.8–2.11) make sense, of course, if the point that specifies an actual state of the ferrocolloid in the parametrical space before separation lies within the instability region, that is, above the phase diagram curve obtained in [11], in which case those equations can well be solved to yield all the desired equilibrium characteristics of the ferrocolloid displaying the domains.

Calculation of dimensionless radius and surface (volume concentration of the domains with allowance for formulae (2.10) and (2.11) is quite straightforward, however tedious, and so hardly merits a detailed discussion. Its results are illustrated in figure 2. The surface tension coefficient has been evaluated with the help of a special model developed in [18], according to which

$$\sigma \sim \gamma^2 (\phi_d - \phi_i)^2 v^{-2/3} kT.$$  \hspace{1cm} (2.12)

The radius of stable domains decreases and the concentration of domains increases when either the external field strength or the particle magnetic moment grows, in a fair agreement with the experimental conclusions in [1-6].

![Fig. 2. Dependence of dimensionless radius (a) and of number concentration (b) of domains on dimensionless external magnetic field strength. Figures at curves on b give values of $\phi_0$.](image-url)
3. Ordered arrangements.

Chaotic domain structures commonly arise in ferrocolloid layers in comparatively weak or moderately intensive magnetic fields. When the field strength increases, a transition to an ordered hexagonal arrangement of the domains can be foreseen, which reminds us, in its outward appearances, of a disorder - order phase transition. Such a transition has been actually observed in [4]. An elementary cell of the hexagonal arrangement is shown in figure 3. Below we are going to demonstrate how the theory developed for chaotic structures is to be generalized to include ordered structures. It should be pointed out that experiments of [1-6] confirm the concept of the ordered domain arrangements corresponding to a regular hexagonal two-dimensional lattice.

![Hexagonal arrangement diagram](image)

Fig. 3. — Representative cell of hexagonal arrangement.

Particle concentration, pressure and strength of the external magnetic field, $\phi_1$, $p_1$ and $H_1$, in the interstitial space can be presented as Fourier transformations with respect to coordinates $x$ and $y$ chosen in the layer plane. Since the harmonic that possess the symmetry of a hexagonal lattice under study must be of maximal amplitude, we are free to take, as a first approximation,

$$
\phi_1 = \phi_1^0 + \phi_k \sum_{n=0}^2 \cos (k_n r),
$$

$$
p_1 = p_1^0 + p_k \sum_{n=0}^2 \cos (k_n r),
$$

$$
H_1 = H_1^0 + h_k \sum_{n=0}^2 \cos (k_n r),
$$

where quantities marked with a degree as well as amplitudes $\phi_k$, $p_k$ and $h_k$ are so far unknown. Let us suppose that

$$
\phi_1^0 \gg \phi_k, \quad p_1^0 \gg p_k, \quad H_1^0 \gg h_k.
$$
The validity of these strong inequalities can be checked later on. It should also be noted that this assumption is not of principal significance and can be avoided at the cost of making calculation somewhat more cumbersome and unwieldy.

The chemical potentials of both particles and molecules must be uniform throughout the interstices. By using equation (3.2) and all the former considerations we can consequently write out

\[
\mu = \mu_0^\ast (p_1^\ast) + kT \nu (\phi_1^\ast, H_1^\ast) + kT (v_p k + \nu_h h_k + \nu_\phi \phi_k) \sum_{n=0}^2 \cos (k_n r) = \text{Cte.}
\]

\[
\mu_0 = \mu_0^\ast (p_1^\ast) - kT (v_0 / v) \nu_0 (\phi_1^\ast, H_1^\ast) - kT (v_0 / v) (v_0 p_k + \nu_0 h_k + \nu_0 \phi_k) \times \sum_{n=0}^2 \cos (k_n r) = \text{Cte.}, \quad (3.3)
\]

where derivatives

\[
\nu_h = \frac{\partial \nu}{\partial H}, \quad \nu_\phi = \frac{\partial \nu}{\partial \phi}, \quad \nu_0 h = \frac{\partial \nu_0}{\partial H}, \quad \nu_0 \phi = \frac{\partial \nu_0}{\partial \phi} \quad (3.4)
\]

are evaluated at \( \phi = \phi_1^\ast \) and \( H = H_1^\ast \) and functions \( \nu \) and \( \nu_0 \) are specified in equation (2.11).

A necessary condition of equations (3.3) holding true requires

\[
v_p k + \nu_h h_k + \nu_\phi \phi_k = 0, \quad v_0 p_k + \nu_0 h_k + \nu_0 \phi_k = 0. \quad (3.5)
\]

Further, the magnetic field strength at the side surface of a domain can be expressed as

\[
H_s = H_1^\ast + h_k \sum_{n=0}^2 \cos [a(\theta) k \cos(\theta - \pi n / 3)], \quad (3.6)
\]

where \( \theta \) is an angular coordinate of the cylindrical coordinate system with an origin in the centre of symmetry and \( a(\theta) \) means the distance from this centre to the domain boundary along the line drawn at angle \( \theta \). Dependence of \( H_s \) on \( \theta \) through \( \cos(\theta - \pi n / 3) \) and \( a(\theta) \) violates the cylindrical symmetry of any domain in favour of the hexagonal symmetry, and this fact makes calculation extremely complicated. In order to simplify the matter, in what follows we shall make use of a quantity

\[
\hat{H} = H_1^\ast + h_k f, \quad f = \frac{1}{2\pi} \sum_{n=0}^2 \int_0^2 \cos \left[ a(\theta) k \cos \left( \theta - \frac{\pi n}{3} \right) \right] d\theta, \quad (3.7)
\]

in the capacity of an effective field strength at the domain surface. This amounts to neglect of deviations of the actual domain form from that of a circular cylinder. Within the scope of the same approximation, we are now able to use an averaged domain radius a instead of \( a(\theta) \). It is worth noting right away that if equation (3.6) were used but not its angle-averaged version (3.7), we should infer domain cross-sections to be hexagonal. This inference agrees with the findings of [4].

It has also to be underlined that we have used in the above consideration a conclusion that \( h_k \) is almost normal to the layer plane, and thus have not retained vector notation while dealing with this and other vector quantities.

The period of the hexagonal lattice cannot apparently be smaller than the domain radius (see Fig. 3), so that surely \( a k < \pi \). This inequality becomes stronger when the concentration
decreases. When expanding the integrands of equation (3.7) into a Taylor series in powers of \( ak \), we obtain

\[
f = \sum_{q=0}^{\infty} (-1)^q C_{2q} (ak)^{2q} \left( \frac{2q}{(2q)!} \right), \quad C_{2q} = \frac{1}{2\pi} \sum_{n=0}^{2q} \int_0^\pi \cos^{2q} \left( \theta - \frac{\pi n}{3} \right) \text{d}\theta. \tag{3.8}
\]

If \( a \ll l \), a variation of the field strength inside a domain can be neglected, and \( \tilde{H} \) of equation (3.7) with \( f \) from equation (3.8) can be identified with the strength of an approximately uniform magnetic field \( H_d \) inside the domains.

The chemical potentials of particles and fluid molecules in the domain interior are now to be expressed as

\[
\mu_d = \mu_0 (p_d^0) + v (p_d - p_h^0) + kT [\nu (p_d, H_d^0) + \nu_h h_k f], \\
\mu_{od} = \mu_0 (p_d^0) + v_0 (p_d - p_h^0) - (v_0 / v) kT [\nu_0 (p_d, H_d^0) + \nu_{oh} h_k f]. \tag{3.9}
\]

By equating these potentials to those in equation (3.3) we get in an equilibrium state, after averaging over the domain side surface,

\[
v (p_d - p_h^0 - p_k f) + kT [\nu (p_d, H_d^0) + \nu_h h_k f] = kT [\nu (\phi_d, H_1^0) + \nu_{h1} h_k f], \\
v_0 (p_d - p_h^0 - p_k f) - (v_0 / v) kT [\nu_0 (p_d, H_d^0) + \nu_{oh} h_k f] = - (v_0 / v) kT [\nu_0 (\phi_d, H_1^0) + \nu_{oh1} h_k f]. \tag{3.10}
\]

Here additional subscripts \( d \) and \( 1 \) at \( \nu_h \) and \( \nu_{oh} \) signify that the derivatives with respect to \( H \) in equations (3.4) have to be estimated at \( \phi = \phi_d \) and \( \phi = \phi_1 \), respectively.

Thus we have arrived at four equilibrium equations (3.5) and (3.10) to be employed when determining nine unknown variables: \( k, p_d - p_h^0, p_k, H_d^0, h_k, \phi_d, \phi_1, \phi_k, \) and \( a \). The physical meaning of these equations is entirely similar to that of equations (2.5) and (2.6), so that there is no need to dwell upon it in more detail. It is evident that five supplementary equations must be brought into action for the purpose of completely defining the mentioned variables, much in the same way as equations (2.7-2.9) have been put forward in the preceding section.

One supplementary equation immediately follows from a usual condition of mechanical equilibrium imposed upon a pressure jump at the domain surface. We get

\[
p_d - p_h^0 - p_k f = \sigma / a, \tag{3.11}
\]

which is nothing more than another representation of the similar equation in equation (2.4).

A requirement of conservation of the total number of magnetic particles leads to an equation

\[
s = (\phi_0 - \phi_1^0) (\phi_d - \phi_1^0)^{-1}, \tag{3.12}
\]

whose meaning entirely coincides with that of equation (2.9).

On the other hand, we can derive an expression for \( s \) from considering the unit hexagonal cell of figure 3. The whole area that is occupied by cross-sections of the central domain and of the other domains with centres at apexes of the hexagon which fall inside the cell equals \( 3\pi a^2 \).

It means that \( s = 3\pi a^2 / S, \quad S = \left( 3\sqrt{3}/2 \right) r_c^2 \) being the total area of the cell. By definition, \( r_c = 2\pi / k \) whence \( s = \left( 2\sqrt{3}\pi \right)^{-1} (ak)^2. \) By comparing this with equation (3.12) we get

\[
(ak)^2 = 2\sqrt{3}\pi \frac{\phi_0 - \phi_1^0}{\phi_d - \phi_1^0}. \tag{3.13}
\]
To derive other relevant equations, let us present the specific magnetization \( M_d \) inside a domain in the form
\[
M_d (\phi_d, H_1^1 + h_k f) = M (\phi_d, H_1^1) + (\partial M / \partial H_1^1) h_k f. \tag{3.14}
\]
Now, by using equations (2.1-3.3) that define the domain demagnetization field, we arrive next at a formula
\[
h_1 = -M_d L(r), \quad L(r) = (\pi / 8) (a^2 / l) . \tag{3.15}
\]
Furthermore, the nearest neighbour approximation appears to be applicable since the domain arrangement is two-dimensional. Then the field at the domain surface is a vector sum of the inner field \( H_1^1 \), that is directed normally to the layer plane, the own field \( h_1 \) of the domain and a field \( h_1' \) caused by its nearest neighbours. It is not difficult to evaluate the latter field in a general case. Within the accepted accuracy of the approximation being used, however, it suffices to replace the strength of this field by that of the same field at the symmetry axis of the central domain, that is also normal to the layer plane due to symmetry. In this case,
\[
h_1' = -6 M_d L(r_c) , \tag{3.16}
\]
\( r_c \) being identified in figure 3, whence, with allowance for equation (3.7),
\[
h_k f = -M_d [L(a) + 6 L (r_c)] , \tag{3.17}
\]
what defines \( M_d \) in accordance with equation (3.14) and leads, next, to an equation
\[
h_k f = - \frac{L(a) + 6 L (r_c)}{1 + (\partial M / \partial H_1^1) [L(a) + 6 L (r_c)]} M (\phi_d, H_1^1) . \tag{3.18}
\]
A further equation is to be deduced from a continuity condition of the magnetic induction at the boundaries of a domain with the layer plates. It resembles equation (2.8) and is of the form
\[
H_0 = (1 - s) \lambda_1 H_1^1 + s \lambda_d (H_1^d + h_1 + h_k f) , \tag{3.19}
\]
h_1, h_k and f being defined by equation (3.15, 3.16 and 3.7), respectively.
Thus we have succeeded in deriving additional equations which are necessary to supplement equations (3.5) and (3.10) stemming from the thermodynamic equilibrium conditions. All these equations when being closed with the aid of equations (2.10) and (2.11) enable us to express variables \( k, p_d - p_1^1, p_k, H_1^1, h_k, \phi_d, \phi_1^1 \) and \( \phi_k \) as functions of averaged domain radius \( a \). After that, the last variable that only remains unknown can be found without much ado, from equation (2.7).
The set of equations (3.5) and (3.10-3.19) can be greatly simplified in view of the fact that normally \( H_0 \) considerably exceeds fields caused by the magnetic particles, so that \( H_1^1 \approx H_0 \). Further, concentrations \( \phi_1 \) and \( \phi_d \) may also justly be looked upon as quantities which insignificantly differ from their equilibrium values which have to be established at a plane phase boundary, that is, with no account for the domain side surface curvature. Besides, by virtue of \( f \) deviating from unity only slightly, it may be taken \( f \approx 1 \). As a result, we obtain a simplified version of the equations which can be resolved even in an analytical form. It is not our intention, however, to write out either the simplified set or its solution in an explicit form because of them being rather unwieldy. Suffice it to say that results concerning properties of equilibrium states with hexagonal domain arrangements, which can be got from this set when making use of the equations (2.10) and (2.11), are basically of the same kind as those derived in the case of chaotic domain structures.

Because of a number of comparatively bold assumptions made while evaluating properties of the equilibrium system under study, the above results should be ultimately regarded as substantially approximate, pertaining to rather a crude attempt to theoretically describe those properties. The assumptions help, nevertheless, to avoid inessential calculation difficulties and are surely not of a principal nature, whereas the said attempt to explain the very existence of stable domains in thin ferrocolloid layers is seemingly the first one, not to mention that all the results can readily be improved at the expense of making calculation more tedious. At any rate, these assumptions do not violate in the least the principal conclusions that have to be drawn from the above treatment.

The main inference consists in that the phase separation of a ferrocolloid or of a magnetic fluid does not necessarily imply the terminal occurrence of two massive colloidal phases, as it is commonly specific to most of colloidal systems, but leads to establishing a stable state with domains of finite size. Moreover, this has been proved to occur, due exclusively to a peculiar scaling effect that is caused by the finite distance between the layer boundaries. It is just this effect that is evidently responsible for the indicated deviation of phase separation patterns in thin layers of a ferrocolloid from those observed in unbounded systems.

It appears to be important for generation of the stable domain arrangements that growing droplets of the new ferrocolloidal phase must be noticeably elongated in the direction normal to the layer plane. This happens in a system of dipole particles under action of a corresponding normal external field, no matter whether the dipoles are of magnetic or electric origin. Such a point of view is surely confirmed by the mere fact that stable domain structures establish themselves not only in thin layers of ferrocolloids with permanent particulate magnetic moments but also in layers of electrocolloids when particle dipoles are induced by an externally applied normal electric field [6]. For the same reasons, the occurrence of similar domain patterns ought to be expected in various other dispersions in which dipole interactions prove to be significant, such as new ferrosmectics recently synthesized in [19]. It should be noted that, if the layer boundaries are pliant, the formation of domains of particles with either permanent or induced dipole moments have to be accompanied by distortions of the form of these boundaries.

However, if would be unreasonable and, perhaps, somewhat preposterous to envisage the emergence of domain arrangements of the discussed type in diverse latex layers and in thin colloidal films of different origins in cases when there are no particulate dipoles. Domain patterns in such layers and films, if any, are hardly unlikely to be explained on the basis of the same considerations as those exploited above.

In conclusion, we have to emphasize that, while key reasons of formation and main properties of both chaotic and ordered domain arrangements can be understood and evaluated with sufficient accuracy, a crucial question of why and at what exact condition an ordered structure suddenly replaces a chaotic one remains obscure. Similarly, there is no answer to a question: why the ordered structure corresponds to a hexagonal lattice?

This phenomenon of disorder-order transition in a two-dimensional system of domains is certainly not of the type of a liquid-crystal phase transition in a system of attracting molecules or particles. It is far more likely to resemble generation of the particle packing with a long-range order in a system of identical hard spheres of high concentration due to purely geometrical reasons [20]. The ordering of the domains really seems to be caused by domain repulsion at a condition of the overall volume accessible to the ferrocolloid under consideration being limited. In contrast to [20], however, both size and interaction potential of the domains that are going to form an ordered lattice are unknown, and this hampers to a great extent the development of an analysis to describe the phenomenon. It may be expected, nonetheless, that a domain structure
is likely to be chaotic if the mean distance between the symmetry axes of two neighbouring domains happens to considerably exceed the domain diameter, and to be ordered otherwise.

References

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*Proof not corrected by the authors*