

## Gradient diffusion in concentrated ferrocolloids under the influence of a magnetic field

K. I. Morozov

*Institute of Continuous Media Mechanics, Urals Branch of Russian Academy of Sciences, 1 Korolyov Street, Perm 614061, Russia*

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The effect of interparticle interactions on the gradient diffusion of magnetic grains in a concentrated ferrocolloid under the influence of an external magnetic field is considered. The interparticle interactions are described using the formalism of the direct correlation function, which is related to the value of the thermodynamic force acting on a ferroparticle. The application of a simple representation of the direct correlation function allows one to evaluate the contributions of short- and long-range correlations of the particles to the ferrocolloid gradient diffusion anisotropy. The short-range correlations are negligible in the case of low-concentration fluids. In concentrated ferrocolloids the contributions of short- and long-range correlations to the coefficient of diffusion are of the same order. The theoretical results are compared with the data of a recent experimental study of gradient diffusion in concentrated ferrocolloids.

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### I. INTRODUCTION

A magnetic fluid (ferrocolloid) is a colloidal dispersion of magnetic particles in an ordinary fluid. Due to ferroparticles, magnetic fluids, along with fluidity, acquire pronounced magnetic properties [1,2]. The dependence of the coefficient of gradient translational diffusion on the magnetic field is one of these properties. In our previous paper [3] the case of a low-concentration magnetic fluid was studied. The ferroparticles were considered to be hard spheres. The magnetic interactions typical of ferrocolloids were presented by the interaction of magnetic moments of ferroparticles with an external magnetic field and interparticle dipole-dipole interactions. It was established that in the external field the diffusion coefficient  $D(H)$  of ferroparticles becomes anisotropic, with  $D_{\parallel}(H) > D_{\perp}(H)$ . Physically, the reason of intensification of the diffusion process along the field is clear: the concentration inhomogeneities  $\nabla n$  of particles are accompanied by the appearance of the magnetic force density  $M\nabla H$  ( $M$  and  $H$  being the ferrocolloid magnetization and internal magnetic field, respectively), provoking the reduction in  $\nabla n$ . According to [3], the coefficients of longitudinal  $\Delta D_{\parallel}(H) = D_{\parallel}(H) - D(0)$  and transverse  $\Delta D_{\perp}(H) = D_{\perp}(H) - D(0)$  diffusion satisfy the relation

$$\text{Tr} \Delta D(H) = \Delta D_{\parallel}(H) + 2\Delta D_{\perp}(H) = 0. \quad (1)$$

The experimental study of the gradient diffusion of ferroparticles faces a serious problem: the ferrocolloids are opaque, so the application of standard optical methods is limited to the case of dilute colloids with magnetic phase concentration  $\phi \leq 10^{-4}$ . In such ferrocolloids the interparticle interactions play almost no role.

This problem was overcome in the elegant experiment of Bacri *et al.* [4], in which field dependences of the coefficients of longitudinal and transverse diffusion of concentrated ferrocolloids ( $\phi = 0.1$ ) were determined. Their experimental data confirm qualitatively the predic-

tions of paper [3]; the diffusion of particles strengthens along the field [ $\Delta D_{\parallel}(H) > 0$ ], it weakens in the perpendicular direction [ $\Delta D_{\perp}(H) < 0$ ], and both dependences  $\Delta D_{\parallel}(H)$  and  $\Delta D_{\perp}(H)$  saturate in the strong magnetic fields. However, there is a significant quantitative discrepancy between theory [3] and experiment [4]. According to [3] [see (1)], the ratio  $|\Delta D_{\parallel}(H)|/|\Delta D_{\perp}(H)|$  equals 2 for arbitrary field strength, whereas in experiment [4], this value varied approximately from 1.3 in weak magnetic fields to 3.7 in the saturation region. Presumably this discrepancy resulted from the application of the low-concentration approximation used in [3].

In the present paper we consider magnetic fluids of arbitrary concentration. On the basis of the Lovett-Mou-Buff equation [5], the exact expression relating the thermodynamic force [6] and the direct correlation function is obtained. Next, the well-known Wertheim representation [7] of the direct correlation function is used for determining the thermodynamic forces and diffusion coefficients in two limiting geometries of the problem:  $\nabla n \parallel \mathbf{H}$  and  $\nabla n \perp \mathbf{H}$ . It is shown that the neglect of short-range particle correlations leads to the description of ferrocolloids within the framework of low-concentration and effective field approximations [8–10]. The results obtained for coefficients of longitudinal and transverse diffusion are compared with experimental data [4].

### II. THERMODYNAMIC FORCE AND DIRECT CORRELATION FUNCTION

In the calculation of the thermodynamic force (driving force of diffusion) we use the Batchelor method [6]. This method goes back to Einstein's classical paper [11] and its basic idea is the following. Let us assume that in equilibrium the concentration of particles in the system  $n(\mathbf{r})$  is uniform, i.e.,  $n = \text{const}$ . Deviation of the system from equilibrium ( $\nabla n \neq 0$ ) leads to the appearance of diffusion flow  $\mathbf{j}_{\text{dif}} = -D\nabla n$  ( $D$  being the diffusion coefficient), which tries to restore the initial equilibrium state. Ac-

cording to [11] and [6], this diffusion flow in the nonequilibrium system coincides with diffusion flow  $\mathbf{j}_{\text{eq}}$  in the equilibrium system under a hypothetical one-particle field  $U_h(\mathbf{r})$ , which creates the equivalent concentration distribution  $\nabla n$ . Due to this circumstance we may use the apparatus of equilibrium thermodynamics to calculate the diffusion flows.

Let the magnetic fluid be in a uniform magnetic field and a one-particle external field  $U_h(z)$  that uniquely determines the distribution  $n = n(z)$ . We suppose the form of the ferrocolloid container to be ellipsoidal and  $z$  to be one of the principal axes of the container. When  $U_h = 0$ ,  $n = \text{const}$  and the magnetic field inside the sample is uniform.

Let us consider a ferrocolloid layer, bounded by two parallel planes orthogonal to  $z$  axis. The layer thickness  $l$  is assumed to be macroscopic,  $l \gg d$ , where  $d$  is the diameter of particles, but it is much smaller than the characteristic scale  $l_n$  of concentration variations. The inequality  $l \ll l_n$  means that we limit ourselves to the case of slow changes of the function  $n = n(z)$  or small  $\nabla n$  values. By virtue of this inequality, the magnetic field  $\mathbf{H}$  inside the layer can be regarded as uniform. We will consider two field geometries corresponding to longitudinal ( $\mathbf{H} \parallel z$ ) and transverse ( $\mathbf{H} \perp z$ ) diffusion.

Let  $\rho(1)$  be the one-particle density. Here (1) stands for the coordinate  $\mathbf{r}_1$  of particle 1 in the layer and the unit vector  $\mathbf{e}_1$  of the orientation of its magnetic moment. The Helmholtz free energy of the ferrocolloid layer is a functional of  $\rho(1)$  [5,12,13],

$$F = F_{\text{id}}[\rho(1)] + \Phi[\rho(1)] + \int d(1) U_{\text{ext}}(1) \rho(1). \quad (2)$$

Here  $F_{\text{id}} = kT \int d(1) \rho(1) [\ln \rho(1) - 1]$  and  $\Phi[\rho(1)]$  are ideal and nonideal (that is, related to interparticle interactions) parts of the free energy,  $k$  is the Boltzmann constant,  $T$  is the temperature, and  $d(1) = d\mathbf{r}_1 d\mathbf{e}_1$ . The  $\mathbf{r}$  integral is taken over the layer volume and  $U_{\text{ext}}(1)$  is the one-particle external field equal to the sum of the magnetic potential  $U_m(1) = -m \mathbf{e}_1 \cdot \mathbf{H}_{\text{ext}}$  ( $m$  being the grain magnetic moment) and the hypothetical field  $U_h(z_1)$ :  $U_{\text{ext}}(1) = U_m(1) + U_h(z_1)$ . Let us note that the "external field"  $\mathbf{H}_{\text{ext}}$  here is actually the magnetic field that would exist in the layer *without* the ferrofluid ("cavity field"). In terms of the internal field  $\mathbf{H}$  and the layer magnetization  $\mathbf{M}$  it is given by [14]

$$\mathbf{H}_{\text{ext}} = \begin{cases} \mathbf{B} = \mathbf{H} + 4\pi\mathbf{M}, & \mathbf{H} \parallel z \\ \mathbf{H}, & \mathbf{H} \perp z. \end{cases} \quad (3)$$

The grand thermodynamic potential is

$$\Omega = F - \mu \int d(1) \rho(1), \quad (4)$$

where  $\mu$  is the chemical potential. Setting the functional derivative  $\delta\Omega/\delta\rho(1)$  equal to zero, we find

$$\mu = kT \ln \rho(1) - m \mathbf{e}_1 \cdot \mathbf{H}_{\text{ext}} + U_h(z_1) - kTC(1) \quad (5)$$

for the chemical potential. In the last expression we introduced the one-particle direct correlation function  $C(1) = -(kT)^{-1} \delta\Phi/\delta\rho(1)$  [5,12,13]. The function  $C(1)$

can be interpreted as an effective external potential caused by interparticle interactions only.

When the fluid is in equilibrium  $\mu = \text{const}$  throughout the sample. Differentiation of Eq. (5) with respect to the coordinate  $\mathbf{r}_1$  of particle 1 gives then

$$\nabla_1 [kT \ln \rho(1) + U_h(z_1)] = kT \int d(2) c(1,2) \nabla_2 \rho(2). \quad (6)$$

Here we used the definition of the two-particle direct correlation function  $c(1,2) = \delta C(1)/\delta\rho(2)$  [12,13] and the relation  $\nabla \cdot \mathbf{H}_{\text{ext}} = 0$  [14], valid for both directions of the magnetic field we are considering [see (3)]. Below,  $c(1,2)$  is simply called the direct correlation function, as is customary in the literature [5,7,12,13,15]. Expression (6) is a formally exact relation of the Lovett-Mou-Buff (LMB) type [5], generalized to the case of a spatial and an angular dependence of the distribution function on the external potential  $U_h(z)$ . In the particular case of a system with spatial degrees of freedom only  $\rho(1) = n(z_1)/4\pi$  and the results of [5] follow from (6) after the integration over orientation  $\mathbf{e}_2$ .

In complete analogy with (6), we can obtain the LMB equation for the orientational dependence  $\rho(\mathbf{e})$

$$\mathbf{G}_1 [kT \ln \rho(1) + U_m(\mathbf{e}_1)] = kT \int d(2) c(1,2) \mathbf{G}_2 \rho(2), \quad (7)$$

where  $\mathbf{G}_1 = \mathbf{e}_1 \times \partial/\partial\mathbf{e}_1$  is the operator of infinitesimal rotation. For a homogeneous system with orientational degrees of freedom only where  $\rho(1) = n f(\mathbf{e}_1)$  and  $n = \text{const}$ , Eq. (7) is reduced to the results of [13].

Equation (6) can be considered as the first step in the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy: it will have an ordinary form [15] if we replace

$$-kTc(1,2) \nabla_2 \rho(2) \leftrightarrow (\nabla_1 U_{12}) \rho(2) g(1,2) \quad (8)$$

on the right-hand side. Here  $U_{12}$  is the potential of the interparticle interaction and  $g(1,2)$  denotes the pair distribution function. It is obvious that Eq. (6) and its BBGKY analog are not closed: to define the one-particle density  $\rho(1)$  it is necessary to know the two-particle [direct  $c(1,2)$  or pair  $g(1,2)$ ] distribution function. However, since the classical Ornstein-Zernike paper [16] it is known that the direct correlation function possesses simpler properties than  $g(1,2)$ . This makes it possible to use numerous approximations for  $c(1,2)$ . This circumstance has applications in the statistical theory of simple (see, e.g., [17]) and anisotropic [12,13] fluids. Therefore, below we employ the BBGKY equation in the form (6).

The expression (6) obtained from the thermodynamic equilibrium condition in the sample  $\nabla\mu = 0$  can be interpreted as a relation of a balance of forces, acting on particle 1: the regular external force  $\mathbf{F}_{\text{ext}}(1) = -\nabla_1 U_h(z_1)$  and the thermodynamic [6] force  $\mathbf{F}(1) = -\mathbf{F}_{\text{ext}}(1)$ . Hence, for the thermodynamic force (the driving force of diffusion) we have the exact formula

$$\mathbf{F}(1) = -\nabla_1 [kT \ln \rho(1)] + kT \int d(2) c(1,2) \nabla_2 \rho(2). \quad (9)$$

Two important remarks are in order here. First, as mentioned above, gradients  $\nabla n$  in our diffusion problem

are assumed to be small, so the direct correlation function  $c(1,2)$  in (9) may be calculated to zeroth order in  $\nabla n$ , that is, for a spatially homogeneous case  $U_h(z)=0$ ,  $n=\text{const}$ . Second, from the definitions of the hypothetical field  $U_h(z)$  and  $\mathbf{F}(1)$  it follows that the driving force is a function of the variable  $z$  only and has a single nontrivial component  $F_z$ . This fact would follow from (9) if the direct correlation function were known exactly.

### III. CHOICE OF DIRECT CORRELATION FUNCTION

We write the potential of interparticle interaction  $U_{12}(\mathbf{r}, \mathbf{e}_1, \mathbf{e}_2)$  in the most general form

$$U_{12}(\mathbf{r}, \mathbf{e}_1, \mathbf{e}_2) = U_{\text{HS}}(r) + U_0(r) + U_d(\mathbf{r}, \mathbf{e}_1, \mathbf{e}_2). \quad (10)$$

Here  $\mathbf{r}$  is the vector of the relative position of grains;  $U_{\text{HS}}(r)$  denotes the potential of hard spheres with diameter  $d$ , i.e.,  $U_{\text{HS}}(r < d) = \infty$  and  $U_{\text{HS}}(r > d) = 0$ ;  $U_0(r)$  stands for a spherically symmetric short-range potential describing such a type of ferroparticle interaction as electrostatic and entropic repulsion and van der Waals attraction [1,2];  $U_d(\mathbf{r}, \mathbf{e}_1, \mathbf{e}_2)$  is a dipole-dipole interaction

$$U_d(\mathbf{r}, \mathbf{e}_1, \mathbf{e}_2) = m^2 r^{-3} [\mathbf{e}_1 \cdot \mathbf{e}_2 - 3(\mathbf{r} \cdot \mathbf{e}_1)(\mathbf{r} \cdot \mathbf{e}_2)/r^2]. \quad (11)$$

Let us consider the Wertheim representation for  $c(1,2)$  [7]

$$c(1,2) = c_S(r) + c_\Delta(r)\Delta(1,2) + c_D(r)D(1,2), \quad (12)$$

where  $c_S(r)$ ,  $c_\Delta(r)$ ,  $c_D(r)$  are spherically symmetric functions and  $\Delta(1,2)$  and  $D(1,2)$  designate the orientation-dependent quantities

$$\Delta(1,2) = \mathbf{e}_1 \cdot \mathbf{e}_2, \quad (13)$$

$$D(1,2) = 3(\mathbf{r} \cdot \mathbf{e}_1)(\mathbf{r} \cdot \mathbf{e}_2)/r^2 - \mathbf{e}_1 \cdot \mathbf{e}_2.$$

Expression (12) represents three terms of the expansion of  $c(1,2)$  in terms of spherical harmonic functions of orientations of vectors  $\mathbf{r}$ ,  $\mathbf{e}_1$ , and  $\mathbf{e}_2$  [18]. The number of terms one has to retain in this expansion depends on a dimensionless parameter of dipole-dipole interaction  $\lambda = m^2/d^3 kT$  and grain concentration  $\phi = \pi n d^3/6$  (or their product, the Langevin susceptibility  $\chi_L = nm^2/3kT$ ). For values  $\chi_L < 1$  the approximation (12) is fairly accurate; see [19,20].

The typical values of the Langevin susceptibility of a ferrocolloid are smaller than 1 [1,2]. Therefore, one can expect the representation (12) to be applicable for the description of magnetic fluids. In general, the functions  $c_S(r)$ ,  $c_\Delta(r)$ , and  $c_D(r)$  depend upon the magnetic field strength, which follows from the Ornstein-Zernike equation [15,16]. We approximate them by the values  $c_{S0}(r)$ ,  $c_{\Delta 0}(r)$ , and  $c_{D0}(r)$  in the absence of the magnetic field

$$c(1,2) = c_{S0}(r) + c_{\Delta 0}(r)\Delta(1,2) + c_{D0}(r)D(1,2). \quad (14)$$

The simplest way to get the whole magnetization curve  $M = M(H)$  is to use this relation. The use of Eq. (14) for finding  $M(H)$  [see Eq. (7) for the one-particle density  $\rho(\mathbf{e})$ ] determines the most important initial (linear) section of the curve where the interparticle interactions are

most notable. This is a consequence of the exact Ramshaw formula [21], relating the initial susceptibility  $\chi$  [the slope of  $M(H)$ ] of the dipole fluid and  $c_{\Delta 0}(r)$ :

$$n \int_0^\infty d\mathbf{r} c_{\Delta 0}(r) = 3(1 - \chi_L/\chi - 4\pi\chi_L/3). \quad (15)$$

In a strong magnetic field, magnetization saturates and the interparticle interactions are not important at all. The thermodynamic force  $\mathbf{F}(H)$  is known to vary as  $M^2$  in low-concentration ferrocolloids [3]. So we expect that the approximation (14) will be appropriate when describing the thermodynamic force too.

Below we use the representation (14) and the following rigorous properties of the components of the direct correlation function  $c(1,2)$  of the dipole system with an arbitrary, spherically symmetric, short-range potential  $U_0(r)$  decaying for large  $r$  as  $r^{-\alpha}$ , where  $\alpha > 4$  [22]: (i) functions  $c_{S0}(r)$  and  $c_{\Delta 0}(r)$  are short range; (ii)  $c_{D0}(r > d) = m^2 r^{-3}/kT + \xi(r)$ , where  $\xi(r)$  is a short-range function; and (iii)  $c_{D0}(r < d)$  is finite.

### IV. CALCULATION OF THERMODYNAMIC FORCES

The calculation of the thermodynamic force is fulfilled by means of formula (9). The integration is carried out over the layer of magnetic fluid. Since the layer is assumed to be thin, the particle concentrations  $n(z_1)$  and  $n(z_2)$  at points 1 and 2 satisfy the equality  $\nabla_2 n(z_2) = \nabla_1 n(z_1) \equiv \nabla n$ . For this reason we omit the subscripts of differentiation operators.

Further calculations in (9) are fulfilled by taking into account properties (i)–(iii), the explicit form of one-particle density  $\rho(1)$

$$\rho(1) = n(z_1) f(\mathbf{e}_1), \quad (16)$$

where  $f(\mathbf{e}_1)$  is the orientational part of  $\rho(1)$ , and the obvious equalities

$$\int \nabla f(\mathbf{e}) d\mathbf{e} = \nabla \int f(\mathbf{e}) d\mathbf{e} = \mathbf{0}, \quad (17)$$

$$\int \mathbf{e} \nabla f(\mathbf{e}) d\mathbf{e} = \nabla \int \mathbf{e} f(\mathbf{e}) d\mathbf{e} = \nabla(\mathbf{M}/nm) = \mathbf{h} \nabla(M/nm). \quad (18)$$

Here  $\mathbf{h} = \mathbf{H}/H$  is the unit vector along the field direction and  $\mathbf{h} \nabla$  and the other analogous quantities in (18) denote the dyads.

The second term in the expression for the thermodynamic force (9), which we denote as  $\mathbf{F}_c(1)$ , is due to the direct correlation function. We divide it into three terms

$$\mathbf{F}_c(1) = \mathbf{F}_S(z) + \mathbf{F}_\Delta(1) + \mathbf{F}_D(1), \quad (19)$$

$$\mathbf{F}_S(z) = (\nabla n) kT \int c_{S0}(r) d\mathbf{r} = kT(1 - \omega) \nabla n / n, \quad (20)$$

$$\mathbf{F}_\Delta(1) = (\chi_L^{-1} - \chi^{-1} - 4\pi/3)(\mathbf{e}_1 \cdot \mathbf{h}) m \nabla M, \quad (21)$$

$$\mathbf{F}_D(1) = 4\pi(\frac{1}{3} - n_d)(\mathbf{e}_1 \cdot \mathbf{h}) m \nabla M, \quad (22)$$

where  $\omega = (\partial P / \partial n) / kT$  is the inverse compressibility in the case of dielectric fluid in the absence of an external field (for ferrocolloids  $P$  means the osmotic pressure of ferroparticles) and  $n_d$  stands for the demagnetizing factor

of the layer. When deriving Eq. (20), we used the equation of state of the multicomponent system in terms of the direct correlation function [23], because a ferrocolloid can be considered as a mixture of particles of the same size but differing in their magnetic moment orientations. In writing (21) we have applied the Ramshaw formula (15).

We note that the value  $\mathbf{F}_D(1)$  is due to the long-range term only [see (ii)]. The magnitude of  $\mathbf{F}_D(1)$  depends on the field direction in relation to the layer plane. If the field is normal to layer ( $\mathbf{H} \parallel z$ ), then  $n_d = 1$ ; when the field lies in the plane,  $n_d = 0$  [14]. The term  $\mathbf{F}_D(1)$  can be written in a unified form for both geometries considered. Indeed, the condition  $\nabla \cdot \mathbf{H}_{\text{ext}} = 0$  (see Sec. II) and the relations (3) give  $\nabla H + 4\pi n_d \nabla M = 0$ . Hence

$$\mathbf{F}_D(1) = (\mathbf{e}_1 \cdot \mathbf{h}) m (\nabla H + 4\pi \nabla M / 3). \quad (23)$$

Expressing the orientation distribution  $f(\mathbf{e})$  as

$$f(\mathbf{e}) = \frac{\xi}{4\pi \sinh \xi} \exp(\xi \mathbf{e} \cdot \mathbf{h}), \quad (24)$$

where  $\xi$  is a dimensionless parameter playing the role of an effective field acting on magnetic moment of a particle, and taking into account relations (19)–(21) and (23) we obtain, for the thermodynamic force,

$$\mathbf{F}(1) = -kT \left[ \omega \frac{\nabla n}{n} + \frac{M}{nm} \nabla \xi \right] + \mathbf{e}_1 \cdot \mathbf{h} [\nabla \xi + m \nabla H + (\chi_L^{-1} - \chi^{-1}) m \nabla M]. \quad (25)$$

As mentioned above (see Sec. II), the force  $\mathbf{F}$  is a function of the variable  $z$  only. Therefore, the coefficient at  $\mathbf{e}_1 \cdot \mathbf{h}$  must be equal to zero. Finally, we find, for the thermodynamic force  $\mathbf{F}$ ,

$$\mathbf{F} = -kT \omega \nabla n / n + (M/n) [\nabla H + (\chi_L^{-1} - \chi^{-1}) \nabla M]. \quad (26)$$

This expression can be obtained also by averaging (25) with the orientational distribution  $f(\mathbf{e}_1)$ .

The most interesting part of  $\mathbf{F}$  is the field-dependent term. We write it for two field directions with respect to the layer normal [see Eq. (3)]

$$\mathbf{F}_{\parallel}(H) = -\frac{\nabla n}{n} [4\pi + \chi^{-1} - \chi_L^{-1}] M \left[ \frac{\partial M}{\partial n} \right]_B, \quad (27)$$

$$\mathbf{F}_{\perp}(H) = -\frac{\nabla n}{n} [\chi^{-1} - \chi_L^{-1}] M \left[ \frac{\partial M}{\partial n} \right]_H. \quad (28)$$

Here the derivatives are taken under constant values of the induction  $B$  and the internal field  $\mathbf{H}$  in accordance with the condition of their continuity  $\partial H_{\text{ext}} / \partial z = 0$ .

It is obvious from the above calculations that the values  $\mathbf{F}_{\parallel}(H)$  and  $\mathbf{F}_{\perp}(H)$  are determined by both the short- and long-range terms of the direct correlation function (14). If the short-range particle correlations are neglected, which is equivalent to setting  $c_{\Delta 0}(r) = 0$  or replacing  $\chi_L^{-1} - \chi^{-1} \rightarrow 4\pi/3$  according to (21), then (27) and (28) give the results of the low-concentration [3] and

effective field approximations [4,9,10]. These approximations differ only by the fact that within the framework of the former the derivatives in (27) and (28) are supposed to be equal to each other:  $(\partial M / \partial n)_B \cong (\partial M / \partial n)_H \cong M/n$  [3]. Since this relation is also applicable in strong magnetic fields ( $H \gg M$ ) for the effective field approximation ( $H_{\text{eff}} = H + 4\pi M/3 \cong H$ ), both theories give identical results in the saturation region

$$\mathbf{F}_{\parallel}(H) = -2\mathbf{F}_{\perp}(H) = -(8\pi/3)m^2 \nabla n. \quad (29)$$

In turn, Eq. (29) is reduced to the diffusion coefficients relation (1) (see below) contradicting the experiment [4].

The role of the short-range correlations must increase with the growth of the magnetic fluid concentration. This follows from the formally exact expansion of the inverse susceptibility in powers of the concentration [7,19,20]:  $\chi^{-1} = \chi_L^{-1} + 4\pi/3 + O(\chi_L)$ . Here  $O(\chi_L)$  denotes a function containing all positive powers of the concentration.

## V. CALCULATION OF DIFFUSION COEFFICIENTS

We define a tensor of the gradient diffusion as the coefficient of proportionality between the diffusion flow and the concentration gradient

$$\mathbf{j}_{\text{dif}} = -\mathbf{D} \cdot \nabla n. \quad (30)$$

The analogous definition of  $\mathbf{D}$  was employed in [3,4,6]. In the Stokes approximation, the diffusion flow is expressed in terms of thermodynamic force  $\mathbf{F}$  and the particle mobility  $\mathbf{b}$  [6]:

$$\mathbf{j}_{\text{dif}} = n \mathbf{b} \cdot \mathbf{F}. \quad (31)$$

In general, the mobility of spherical ferrocolloid particles in an external magnetic field is a tensor quantity. This fact is connected with the nonspherical symmetry of interparticle (dipole-dipole) interactions [24]. For simplicity, however, we regard the particle mobility as a scalar quantity equal to its value  $b$  in the absence of the field.

We find the coefficients of longitudinal  $D_{\parallel}$  and transverse  $D_{\perp}$  diffusion from the comparison of Eqs. (26)–(28), (30), and (31),

$$D_{\parallel} = bkT\omega + b [4\pi + \chi^{-1} - \chi_L^{-1}] M \left[ \frac{\partial M}{\partial n} \right]_B, \quad (32)$$

$$D_{\perp} = bkT\omega + b [\chi^{-1} - \chi_L^{-1}] M \left[ \frac{\partial M}{\partial n} \right]_H. \quad (33)$$

It is clear that each of the diffusion coefficients  $D_{\parallel}$  and  $D_{\perp}$  is equal to the sum of the diffusion coefficient  $D_0 = bkT\omega$  and the field-dependent part  $\Delta D(H) = D - D_0$  determined by the magnetic properties of the ferrocolloid. We notice that  $\Delta D_{\parallel}(H) > 0$  and  $\Delta D_{\perp}(H) < 0$ .

The anisotropic character of diffusion in an external field can be described by the ratio  $\Delta D_{\parallel}(H) / |\Delta D_{\perp}(H)|$  used for the limiting cases of weak ( $M \approx \chi H$ ) and strong ( $M \approx nm$ ) magnetic fields

$$\frac{\Delta D_{\parallel}(H)}{\Delta D_{\perp}(H)} = \begin{cases} (\mu_m^{-1} + \mu_L - 2)/(\mu_m - \mu_L), & H \rightarrow 0 \\ \mu_m(\mu_m^{-1} + \mu_L - 2)/(\mu_m - \mu_L), & H \rightarrow \infty \end{cases} \quad (34)$$

Here  $\mu_m = 1 + 4\pi\chi$  is the magnetic permeability of the ferrocolloid and  $\mu_L = 1 + 4\pi\chi_L$ .

To plot the theoretical curves corresponding to formulas (32) and (33) it is necessary to know the magnetization curve  $M = M(H)$  for a homogeneous system and the value of  $\omega$ . We find  $M$  by solving the LMB equation (7) for the orientational distribution function  $f(\mathbf{e}_1) = \rho(1)/n$  with the same representation (14) of the direct correlation function as before. After analogous calculations, we obtain a pair of self-consistent equations determining  $M$ ,

$$M = nmL(\xi), \quad \xi = m[H + (\chi_L^{-1} - \chi^{-1})M]/kT. \quad (35)$$

Here  $L(\xi) = \coth(\xi) - 1/\xi$  is the Langevin function.

The value of "inverse compressibility"  $\omega$  is estimated in the following way. From the data of independent experiments on small-angle x-ray [4] and neutron [25] scatterings in an ionic ferrocolloid with concentrations  $\phi \leq 0.084$  in the absence of the field, the simple relation  $\omega(\phi) = 1 + 20\phi$  was established. Applying this result to our case, we have  $\omega = \omega(0.1) = 3$ .

The experimental data in [4] are given in terms of the reduced variations  $\Delta D_{\parallel}(H)/D_0$  and  $\Delta D_{\perp}(H)/D_0$  as functions of the strength of the magnetic field. We obtain for these quantities from (32) and (33),

$$\frac{\Delta D_{\parallel}(H)}{D_0} = (kT\omega)^{-1} [4\pi + \chi^{-1} - \chi_L^{-1}] M \left[ \frac{\partial M}{\partial n} \right]_B, \quad (36)$$

$$\frac{\Delta D_{\perp}(H)}{D_0} = (kT\omega)^{-1} [\chi^{-1} - \chi_L^{-1}] M \left[ \frac{\partial M}{\partial n} \right]_H. \quad (37)$$

In calculations based on formulas (35)–(37) we used the following experimental data [4]:  $d = 12 \times 10^{-7}$  cm is the magnetic diameter of the grains,  $M_S = 400$  G is the bulk magnetization,  $\chi = 0.143$ , and  $\chi_L = 0.109$ . The temperature was taken to be equal to 296 K. From the experimental dependence  $\chi = \chi(n)$  no well-defined slope  $\partial\chi/\partial n$  can be found. This derivative was computed within the framework of the mean spherical model [7] from the value  $\chi$  and proved to be equal to  $\partial\chi/\partial n = 1.29\chi/n$ . The influence of the derivative on the final result, however, is insignificant, because even a crude estimate  $\partial\chi/\partial n \approx \chi/n$  changes the reduced diffusion coefficients slightly—by less than 10%—already in the region of weak magnetic fields  $H \geq 15$  kA/m (the magnetic field strength in the experiment [4] ranged from 0 to 120 kA/m).

Solid lines in Fig. 1 show the calculated values of the reduced variations of the diffusion coefficients as functions of the strength of the external field. The values of longitudinal and transverse diffusion lie higher and lower than the abscissa axis, respectively. The dots mark the experimental data [4].

## VI. DISCUSSION

As follows from the analysis of Fig. 1, our model describes the field dependence of the diffusion coefficients

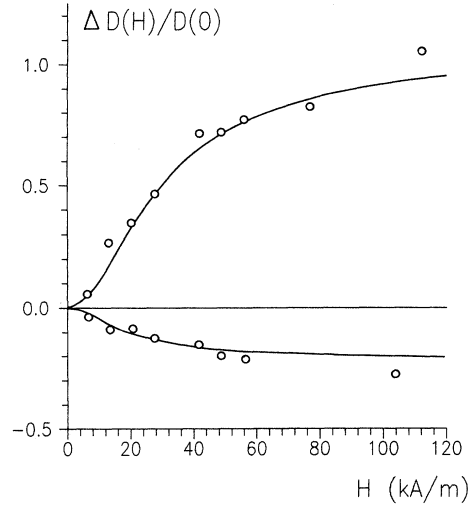


FIG. 1. Reduced variations of  $D(H)$  as a function of the strength of the magnetic field. The solid line is obtained from Eqs. (35)–(37) with  $\chi = 0.143$ ,  $\chi_L = 0.109$ , and  $\omega = 3$ . The upper and lower curves represent the longitudinal and the transverse diffusion, respectively. The dots mark the experimental data from [4].

surprisingly well. A deviation from the experiment takes place for the coefficient of transverse diffusion in the region of the strong magnetic fields only. This fact may be connected with the field dependence of the particle mobility, which was neglected in the present investigation. However, if this is so, this dependence cannot be strong, as is obvious from Fig. 1.

For the parameter of asymmetry  $|\Delta D_{\parallel}(H)/\Delta D_{\perp}(H)|$  of the diffusion curve, the substitution in (34) of the experimental data  $\mu_m = 2.8$  and  $\mu_L = 2.37$  gives the interval of values from 1.7 to 4.8. This is consistent with the measured values 1.3–3.7. Within the framework of the low-concentration approximation [3], this parameter is equal to 2 for any field strength; in the effective field model [8–10] it ranges from  $2/\mu_m$  to 2, i.e., from 0.7 to 2. The analysis of these results shows that the inadequacy of the low-concentration and effective field approximations is caused by neglecting short-range particle correlations.

The meaning of the short-range correlations is easily seen from the following. The result (35) for the magnetization law is very similar to that of the effective field model [8–10]. The only difference is that the role of the Lorentz constant  $4\pi/3$  in the latter theory is played by the quantity  $\chi_L^{-1} - \chi^{-1}$  in our consideration. This conclusion also follows from the analysis of Eqs. (27) and (28). Thus, taking into account the short-range correlations, that is, the term  $c_{\Delta 0}(r)\Delta(1,2)$  in expression (14), leads to the "renormalization" of the Lorentz constant

$$4\pi/3 \rightarrow \chi_L^{-1} - \chi^{-1}. \quad (38)$$

The importance of the short-range correlations can be estimated by forming the ratio of the left- (the short-range correlations are neglected) and right- (the correlations of

both type are taken into account) hand sides of (38). In the problem under consideration this ratio is equal to 1.9, so that the contributions to the diffusion coefficient of the short- and long-range correlations are of the same order.

## VII. CONCLUSIONS

The problem of the effect of interparticle interactions on the gradient diffusion in the concentrated ferrocolloids under external magnetic fields is considered. The thermodynamic force acting on magnetic grains is found on the basis of an exact equation relating the force to the direct correlation function. The latter is approximated by its value in the absence of the field. The thermodynamic forces and the diffusion coefficients are obtained for two directions of the magnetic field direction with respect to the concentration gradient. It is shown that the anisotropy of diffusion arising in a magnetic field is the result of the short- and long-range correlations of ferro-particles. The role of the short-range correlations grows with an increase in concentration. In concentrated

ferrocolloids, the contributions of correlations of both type are of the same order.

The ratio of the field-dependent parts of the longitudinal and transverse diffusion in the regions of weak and strong fields is determined by two well-defined parameters. They are the initial ferrocolloid susceptibility and its Langevin value. The magnetization law obtained from Lovett-Mou-Buff equation and the same representation of the direct correlation function as for the thermodynamic force is applied in intermediate fields. The theoretical results for diffusion anisotropy are in good agreement with the data of recent experiments [4].

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