Journal of Engineering Physics and Thermophysics, Vol. 70, No. 2, 1997

THE EFFECT OF THE SURFACE STATE OF PARTICLES ON PAIR INTERACTION IN A MAGNETIC SUSPENSION

B. É. Kashevskii and V. A. Kuz'min

UDC 532.582.7:538.6

The dynamics of a pair of spherical magnetically soft particles suspended in a fluid under the action of a rotating field is studied experimentally and theoretically. Hydrodynamic interaction of the particles and repulsion in the surface layer are taken into consideration in the theory and the magnetic field is described in a dipole-dipole approximation. Experiments confirm the important role of surface roughness, which limits the increase in viscous friction between the particles that are coming closer together. The effect of roughness-induced stochastization of the dynamics of the pair is found in the frequency range near the cutoff frequency of rotation synchronous with the field.

Introduction. Interparticle interactions and structural transformations associated with them in the magnetic disperse phase are important in practical applications of magnetic suspensions. They sometimes have a negative effect, which can result, for example, in aggregate instability or phase stratification of magnetic colloids and impair the quality of the sensitive film of magnetic information carriers. Meanwhile, they are the main channel through which the field affects the properties of the suspensions, primarily, their mechanical properties. Direct computer simulation of interacting particle ensembles can provide useful information about the nature of processes occurring in the disperse phase and their effect on the macroscopic properties of the medium [1].

A very simple case of pair interaction in a rotating field that can be investigated most thoroughly is of great interest. This case has been studied experimentally for nonmagnetic particles in a magnetic fluid [2, 3] and theoretically for magnetic particles in a nonmagnetic fluid [4, 5] and magnetic drops [6]. In the present article, considering pairwise interaction of magnetically soft particles under the action of a rotating field, we concentrated on the role of their hydrodynamic and surface interactions. Surface roughness and the presence of adsorptive surfactant layers have a considerable effect on the behavior of the pair, limiting the growth of viscous friction as the particles approach each other.

Theoretical. Consider a pair of identical spherical magnetically soft particles with radius a suspended in an unbounded Newtonian fluid with viscosity η and subjected to the action of a uniform magnetic field rotating with frequency ω_0 of intensity $\mathbf{H} = h\mathbf{h}$. Magnetic interaction between the particles is described in a dipole approximation ignoring mutual distortion of the uniform magnetization state of the particle $\mathbf{M}$. This assumption is the more correct the higher the intensity of the applied field in comparison with the particle field ($H > M$). It is also assumed that inertial forces and forces of thermal excitation of the particle are low in comparison with viscous forces. This assumption is valid when the following conditions are satisfied:

$$\rho a^2/\eta t^* \ll 1\,, \quad t^*/\tau_B \ll 1\,,$$

where t^* is the characteristic time of the phenomenon: $\tau_B = 4\pi a^2\eta/RT$ is the characteristic time of rotational diffusion. Neglecting hydrodynamic interaction of the particles, with the inverse of the critical frequency of rotation

Academic Scientific Complex "A. V. Luikov Heat and Mass Transfer Institute, Academy of Sciences of Belarus," Minsk, Belarus. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 70, No. 2, pp. 179-183, March-April, 1997. Original article submitted November 29, 1994.

1062-0125/97/7002-0173$18.00

of the pair synchronous with rotation of the field [4] taken as a characteristic time ($t^* = 18\eta/\pi M^2$), we can write these conditions in the form:

$$\frac{\pi\rho}{18}\left(\frac{Ma}{\eta}\right)^2 \ll 1\,, \quad \frac{9kT}{2\pi^2 M^2 a^3} \ll 1\,. \tag{1}$$

If the conditions are satisfied, motion of the particles is determined by the balance of forces and moments that are exerted on them, and, according to [7], it can be described by a system of linear tensor equations that relate the angular velocities of the particles to external forces and moments (of nonhydrodynamic origin). In formulation of these equations, it will be borne in mind that, first, electrodynamic torque does not act on a magnetically soft particle in the external field and, second, dipole interaction forces, just as surface repulsion forces between the particles, are equal in value and opposite in direction. Consequently, the particles have linear and identical angular velocities equal in magnitude and opposite in sign so that it is sufficient to consider the motion of either of the particles. Using the notation of [8], the appropriate equations are written in the form

$$\eta \mathbf{v} = (\mathbf{a}_{11} - \mathbf{a}_{12})\,\mathbf{F}\,, \quad \eta\,\boldsymbol{\Omega} = (\mathbf{b}_{11} - \mathbf{b}_{12})\,\mathbf{F}\,, \tag{2}$$

where F is the total force exerted on the first particle and a and b are the so-called mobility tensors, that are determined exclusively by a unit vector in the direction from the center of the first to the center of the second particle n with accuracy to scalar functions of the distance R between the particles (mobility functions):

$$a_{ij}^{\alpha\beta} = \frac{1}{6\pi a}\left[x_{\alpha\beta}^{a}\, n_i n_j + y_{\alpha\beta}^{a}\,(\delta_{ij} - n_i n_j)\right]\,, \quad b_{ij}^{\alpha\beta} = \frac{1}{4\pi a^2}\, y_{\alpha\beta}^{b}\, \varepsilon_{ijk}\, n_k\,. \tag{3}$$

The total force exerted on the particles is the sum of the magnetic dipole-dipole force and the surface interaction force. The dipole force exerted on the first particle is given by the relation

$$\mathbf{F} = -\,3m^2 R^{-4}\,(\mathbf{n} + 2\mathbf{h}\,(\mathbf{nh}) - 5\mathbf{n}\,(\mathbf{nh})) \tag{4}$$

and has components along and across the center line. The former is responsible for radial motion of the particle and the latter sets the particles in rotation. According to the second equation in (2) and the expression for the mobility tensor b in (3), the transverse component also brings about angular rotation of the particles different from rotation of the pair. Surface repulsion that is caused by the presence of a surfactant layer or roughness of the surface will be taken into consideration here, and in calculations the distance between the surfaces will be limited to a certain length Δ.

As was shown in [4], for a pair of magnetic particles, ignoring hydrodynamic interaction, the plane of rotation of the field is attracting. It can be demonstrated that this property is also preserved in the present case. Considering plane motion, in accordance with (2) and (3), we find the following dimensionless equations for this motion:

$$\frac{dr}{d\tau} = r^{-4}\,(x_{11}^{a} - x_{12}^{a})\,(1 - 3\cos^2\varphi)\,, \quad \frac{d\varphi}{d\tau} = \nu_0 - r^{-5}\,(y_{11}^{a} - y_{12}^{a})\sin 2\varphi\,. \tag{5}$$

Here ν_0 is the rotation frequency of the field. The distance scale is equal to the particle diameter $2a$ and the time scale is t^*. Equations (5) are solved with the condition $r \leq 1 + \delta$ ($\delta = \Delta/(2a)$). The hydrodynamic functions x and y are defined as functions of r in [8]. Their near asymptotics ($z = 2(r-1) \ll 1$) have the form

$$x_{11}^{a} - x_{12}^{a} = 2z + 1.8z^2 \ln z + O(z^2)\,;$$
$$y_{11}^{a} - y_{12}^{a} = 0.402 - 0.562/\ln z + O(1/\ln^2 z)\,. \tag{6}$$

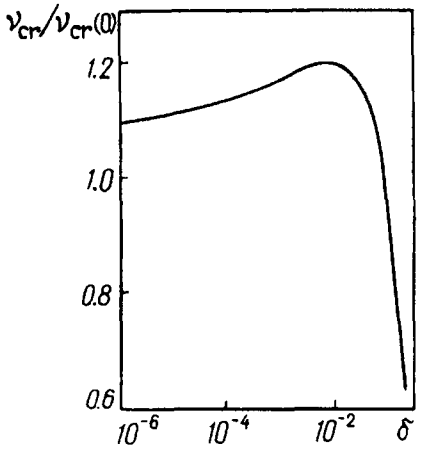

Fig. 1. Plot of critical rotation frequency of pair of particles synchronous with field versus thickness of layer that restricts distance between them.

In accordance with these relations, the mobility function relative to radial motion tends to zero as the distance between the particles decreases, while the mobility function relative to rotation has a finite value of 0.402 at contact, but its rate of change is infinite there. These peculiarities of the mobility functions of almost contacting particles cause strong sensitivity of the behavior of the pair to the nature of surface interaction between them. The radial component of dipole interaction of a pair of particles averaged over the orientation angle relative to the field corresponds to attraction and, as is shown by calculations ignoring surface repulsion ($\delta = 0$), at all rotation frequencies of the field the particles form a rigid pair (stick together) with time and rotate as a single whole. According to (5) and (6), this rotation is described by the equation $d\varphi/d\tau = \nu_0 - 0.402\sin 2\varphi$. Hence, it follows that up to field frequency $\nu_{cr} = 0.402$, which constitutes 0.402 of the limiting frequency of rotation synchronous with the field ignoring hydrodynamic interaction, the pair rotates synchronously with the field. Asynchronous rotation becomes nonuniform and, following the procedure described in [4], we find for its average velocity

$$\nu = \nu_0 - \sqrt{\nu_0^2 - \nu_{cr}^2}\,, \tag{7}$$

According to (7) the rotation is rapidly damped as the field frequency increases. This can be explained by the fact that unlike its radial component, the average azimuthal component of the dipole force is zero.

The presence of a surface layer brings about drastic changes: the limiting synchronism frequency changes and the pair is no longer rigid. Already in the case of synchronous rotation, rotations of the particles, which partly roll over each other's surfaces are imposed on the rotation of the pair as a single whole. According to (2) and (3), the angular velocity of the particles can be calculated after solution of system (5) from the formula

$$\nu_1 = \frac{3}{2r^4}\,(y_{11}^b - y_{12}^b)\sin 2\varphi\,.$$

When rotation is asynchronous, radial vibrations, studied in [4, 5], are also imposed on rotation of the pair. The limiting synchronism frequency is determined from the second equation of system (2) at $r = 1 - \delta$, $d\varphi/d\tau = 0$, $\sin 2\varphi = 1$ by the formula

$$\nu_{cr}(\delta) = (y_{11}^a(1+\delta) - y_{12}^a(1+\delta))\;(1+\delta)^{-5}\,.$$

Relative changes in the limiting synchronism frequency with increase in δ are plotted in Fig. 1. As can be seen, the increase in ν_{cr} at low δ is followed by an abrupt drop. The increase in the frequency at which the pair rotates synchronously with the field can be explained by a decrease in the viscous resistance to rotation of the pair, since the particles can roll. Moreover, as δ increases, growth of the function $y_{11}^a - y_{12}^a$ becomes slower and the factor of weakening dipole particle interaction starts to prevail, which leads to a drop in ν_{cr}.

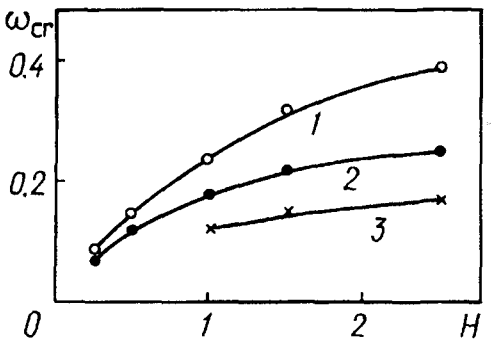

Fig. 2. Plot of critical synchronism frequency versus field intensity: 1-3) initial, glued particles and sand-covered particles. ω_{cr}, sec^{-1}, H, kOe.

Experimental. For experiments a model system was produced which satisfied the conditions formulated at the beginning of the article and some additional requirements. In particular, for convenient observation and recording of a phenomenon, its characteristic time t^* should be about 1 sec, and to ensure the possibility to surface modification, the particle size should be about 1 mm. In order to exclude the effect of sedimentation, the condition $v_s t^* << a$ (v_s is the velocity of sedimentation) should be satisfied. The necessary conditions were as follows. As a material for model particles, we synthesized a colloid of nanodimensional magnetic particles in an organic liquid that solidifies at temperature $T_m = 39°C$ and demonstrates paramagnetic properties both in liquid and solid states. Its magnetization is described approximately by Langevin's law and reaches a saturation of 49 G in a field of about 2.5 kOe. The particles were produced by slow cooling of a colloid drop squeezed out of a constant-temperature volume ($T = T_m + 1°C$) through a capillary into a water-glycerol mixture with temperature $T = T_m - 1°C$. The particle diameter was 1.7 mm. Because of shrinkage of the colloid under solidification (about 10% v/v), the particle surface had roughnesses that after rolling and application of a varnish layer were about 0.1 mm. According to the presented theory, this roughness is too large to be ideal and since ideal spheres should form a rigid pair, this pair was produced by gluing. In order to study the effect of roughness, a thin layer of particles of sand with a diameter of 0.1 mm was applied to some of the produced particles. Thus, we had three types of particles with different roughnesses: a rigid pair that represented an ideal sphere, initial particles with relative roughness $\delta \approx 0.01$, and particles with $\delta \approx 0.1$ covered by sand. In the experiment the particles were suspended in a Newtonian polymethyloxane liquid with a viscosity of 220 P. The liquid filled a cylindrical vessel with a diameter of 2 cm and a length of 5 cm provided with a temperature-controlling jacket. The particles were in the center and the cell was placed in a uniform field perpendicular to its axis and set in rotation. Motion of the particles was recorded by a video camera.

Without rotation the pair is oriented along the field. At low frequencies it remains stationary, deviating from the direction of the field by a small angle. The angle increases with frequency to 45°, which is followed by cutoff. In the experiments, the field intensity and temperature were varied and the rotation frequency of the cell at which cutoff occurred and the average rotation frequency of the pair after cutoff were measured. Since the inertial forces of the particles are negligible as compared with viscous forces, then considering motion of the pair relative to the rotating liquid, we have a situation identical to the case considered theoretically. In this case the rotation frequency of the cell corresponds to the rotation frequency of the field and the difference between the frequencies of the pair and cell corresponds to the frequency of the pair in a stationary liquid. It is in this way that the experimental results obtained at a fixed temperature of 20°C are presented subsequently.

The limiting synchronism frequency ω_{cr} for the three pairs described above in shown in Fig. 2 as a function of the field intensity. The simple model of surface interaction used in the calculations is certainly too rough an approximation for description of the roughness of the particle surface to expect full agreement with the experiment. However, the theoretical conclusion is verified qualitatively. Indeed, the function $\omega_{cr}(\delta)$ appears nonmonotonic. For the initial particles with a low roughness it is larger in comparison with both the rigid pair and the pair of very rough particles. The rigid pair has a higher limiting frequency than the very rough particles do. It is this conclusion that follows from Fig. 1.

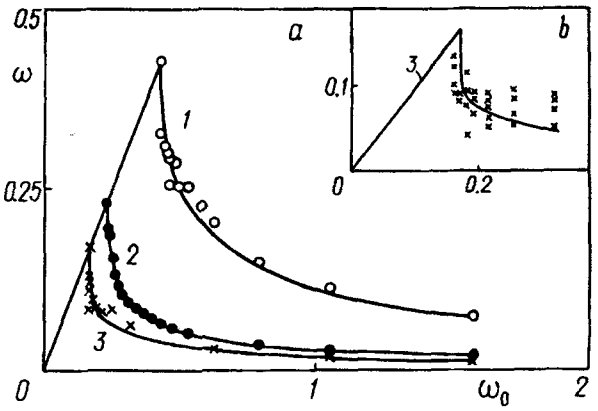

Fig. 3. Average rotation frequency of pair of particles as a function of rotation frequency of field (a) and stochastization of rotation (b, see explanations in text). Designations as in Fig. 1. ω, ω_0, sec.

The measured dependence of the average (in the experiment averaging was performed over five full rotations) rotation frequency ω on the rotation frequency ω_0 of the field (H = 2.5 kOe) is shown in Fig. 3a (dots). In this figure solid curves represent calculation results. In the case of the rigid pair, formula (7) is used. In this case, the frequencies of the field and pair were normalized to the measured critical synchronism frequency. It can be stated that the theory almost fully agrees with experiment. In the two other cases the average frequency (which was also normalized to measured values of ω_{cr}) was calculated from equation (5) with δ = 0.01 (curve 1) and δ = 0.1 (curve 3). As can be seen, the calculations agree well with the measured trends, in particular, reflecting the fact that in the case of a thin surface layer (δ = 0.01) after synchronism cutoff, the rotation frequency falls more smoothly in comparison with the rigid pair, while in the case of a thick layer (δ = 0.1) it falls abruptly.

It is worth noting that for the particles with a rough surface, the scatter of points is significant, while for the glued particles it is almost unnoticeable. This fact demonstrates the high sensitivity of the pair to the quality of the particle surface in the region of synchronism cutoff. Additional measurements have shown that there stochastization of rotation takes place, which is recorded by several measurements of the average frequency for half of a full rotation (Fig. 3b, data for the sand-covered particles). As can be seen, the rotation frequency experiences greater random deviations in different half-periods.

Conclusions. Interparticle interactions in disperse liquids are very sensitive to the mechanical state of the particle surface and the mechanical properties of adsorption layers. This sensitivity is the more noticeable, the closer the surface to a perfectly smooth one, which is explained by the unlimited increase in viscous forces when the distance between smooth surfaces decreases. It can be concluded that use of surfactants in the dispersions has a positive effect as regards not only the decrease in the surface energy of particles and the preservation of thermodynamic stability of the dispersion, but also the prevention of viscous sticking. In the case of magnetorheological dispersions there is an optimal thickness of the surface layer, since an increase in it results in weaker magnetic interaction.

The authors wish to express their gratitude to O. K. Safonenko for production of the magnetic colloid.

The study is financed by the Fundamental Research Fund of the Republic of Belarus.

NOTATION

a, radius of particle; Δ, δ, roughness, relative roughness of surface; η, viscosity, ρ, density; ω, ν, frequency, relative frequency; H, field intensity; M, magnetization; m, magnetic moment of particle; n, unit orientation vector ot pair of particles; φ, orientation angle of field relative to pair; R, r, distance, relative distance between centers of particles; k, Boltzmann constant; T, temperature; t, τ, time, dimensionless time. Subscripts: B, Brownian time; cr, critical value; m, melting.

REFERENCES

1. B. E. Kashevsky, JMMM, **122**, 34-36 (1993).
2. A. T. Skjeltorp, JMMM, **65**, 195-203 (1987).
3. G. Helgesen, P. Pieranski, and A. T. Skjeltorp, Phys. Rev. Lett., **64**, 1426-1428 (1990).
4. B. E. Kashevskii and A. L. Novikova, Magnit. Gidrodinamika, No. 3, 33-38 (1989).
5. B. E. Kashevskii and V. I. Kordonskii, Izv. Akad. Nauk, SSSR, Ser. Fiz, **56**, 1110-1119 (1991).
6. B. E. Kashevskii, Inzh.-Fiz. Zh., **69**, No. 1, 98-102 (1996).
7. G. K. Batchelor, J. Fluid Mech., **74**, Pt. 1, pp. 1-29 (1976).
8. D. J. Jeffrey and Y. Onishi, J. Fluid Mech., **139**, 261-290 (1984).