

## COMPUTATIONAL THERMODYNAMICS OF A COLLOID OF ISOTROPIC FERROPARTICLES

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*The influence of interparticle magnetic interactions on the aggregate state of the system of isotropic ferrocolloidal particles is investigated. To describe the orientation state and the local structure of a colloid, we use a combined numerical method, including direct modeling of translational Brownian dynamics of an aggregate of particles, and an approximate description of their orientation state by the self-consistent method. To calculate the contribution of magnetic interactions to the thermodynamic properties of a colloid, the thermodynamic process of heating the Brownian ensemble is realized numerically. The magnetic additive to the free energy and the chemical potential of a ferrocolloid have been determined. It has been found that the system of ferrocolloidal particles has critical points of the gas-liquid and gas-solid transitions and can be found in three aggregate states.*

Colloids of ultrasmall ferromagnetic particles have attracted attention because of their unique physicochemical properties. The properties and stability of ferrocolloids are strongly influenced by interparticle magnetic interactions. Stability is provided by the thermal diffusion of particles, and its disturbance can be either local (aggregative instability towards clustering [1]) or global (thermodynamic instability towards colloid splitting into high- and low-concentration phases [2]). Development of a general enough theory of interrelated orientation and aggregative processes in a disperse subsystem of the ferrocolloid with regard for the diversity of properties of particles, liquids, and stabilizing additives entails severe methodological difficulties. The methods of Brownian dynamics have certain prospects. In [3], such an approach was used to study the problem of the existence in the colloid of isotropic single-domain ferroparticles of the orientation state of dipole glass (the state in which the rotational diffusion of individual magnetic moments is frozen by the collective field of interparticle magnetic interactions without the formation of a long-range orientation order). Numerical modeling of small ensembles of particles directly gives information on the orientation properties and local structure of the ferrocolloid [3]. The global structural transformations in the system of colloidal particles can be described in terms of the theory of phase transitions in the real gas whose employment requires determination of the correlation magnetic additive to the thermodynamic potential of the colloid. In the present paper, the method of computing thermodynamic experiment has been used. It has been found that the disperse subsystem of the colloid of single-domain isotropic ferroparticles is characterized by two critical points and, accordingly, by three aggregate states: gas, liquid, and solid.

**Model of the Brownian Dynamics of an Aggregate of Interacting Isotropic Colloid Ferroparticles in the Self-consistent Field Approximation.** Let us formulate the salient points of the model used. We consider a colloid ensemble of  $N$  homogeneously magnetized isotropic ferroparticles of radius  $a$  with magnetization  $I_{sb}$ . The system has two time scales,  $\tau_B$  and  $\tau_0$ , characterizing, respectively, the external (mechanical) and internal (magnetic) rotational diffusion of the particle. The first time scale is determined by the heat-transfer fluid viscosity and is  $10^{-6}$  sec or more, and the second one is determined by the magnetic viscosity of the particle material and is of the order of  $10^{-9}$  sec. The difference between the characteristic times by a few orders of magnitude makes practically impossible direct numerical simulation of combined Brownian dynamics of the particle and the moment, but permits using the local equilibrium hypothesis according to which the magnetic moment of each particle is in thermal equilibrium in the local magnetic field at all times. This assumption leads to the system of algebraic equations relating the effective values of the magnetic moments (averaged on the time interval  $\tau_0 \ll \Delta t \ll \tau_B$ ) to the

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local fields at the particle centers. We use the traditional method for calculating the local field based [4] on the cutting of a Lorentz sphere in the material. The local field acting on the trial dipole at the center of the sphere is the sum of the external field  $\mathbf{H}_0$ , the field established in the nonmagnetic cavity by the homogeneously magnetized material surrounding it  $4\pi\mathbf{I}/3$ , and the field established by the dipoles located inside the sphere. In our model, the particles are inside a sphere whose radius  $R_L$  is determined by the volume concentration of particles  $c$ :  $R_L = \alpha(N/c)^{1/3}$ . The particle  $\alpha$  is characterized by the radius vector of its center  $\mathbf{R}_\alpha$ , the effective moment  $\mathbf{M}_\alpha$ , and the local field at the particle center  $\mathbf{H}_\alpha$ . Let  $\mathbf{H}_{\beta\alpha}$  be the dipole field  $\beta$  at the center of the particle  $\alpha$ . We take into account the mutual influence of the particles located at a distance smaller than a certain radius  $R_i$  (radius of interaction). To decrease the influence of the boundary, we calculate the macroscopic magnetization  $i$  by averaging over the particles whose centers are located in the central region of radius  $R_a \leq R_L - R_i - a$  (averaging radius). Introducing the designations  $\mathbf{m}_\alpha = \mathbf{M}_\alpha/m_0$  ( $m_0 = \nu I_{sb}$ ),  $\mathbf{i} = \mathbf{I}/cI_{sb}$ ,  $\mathbf{h} = \mathbf{H}_\alpha/I_{sb}$ , and  $\mathbf{r}_\alpha = \mathbf{R}_\alpha/2a$ , we write the equations of magnetic state of the system of particles with a given spatial distribution in the following dimensionless form [3]:

$$\mathbf{m}_\alpha = L(\xi_\alpha) \frac{\mathbf{h}_\alpha}{h_\alpha}, \quad \xi_\alpha = \frac{6}{\pi} \lambda h_\alpha, \quad \lambda = \frac{m_0^2}{8a^3 kT}, \quad L(x) = \cot(x) - 1/x, \quad (1)$$

$$\mathbf{h}_\alpha = \mathbf{h}_0 + \frac{4\pi}{3} c \mathbf{i} - \frac{\pi}{6} \sum_{(\beta \neq \alpha)} \frac{1}{r_{\alpha\beta}} [\mathbf{m}_\beta - 3\mathbf{s}_{\alpha\beta} (\mathbf{m}_\beta - \mathbf{s}_{\alpha\beta})], \quad \mathbf{i} = N_a^{-1} \sum_{[\alpha]} \mathbf{m}_\alpha. \quad (2)$$

Here  $N_a$  is the number of particles inside the averaging sphere,  $\mathbf{s}_{\beta\alpha}$  is the unit vector from the center of the particle  $\beta$  to the center of the particle  $\alpha$ ,  $r_{\beta\alpha}$  is the distance between the centers of the particles  $\alpha$  and  $\beta$ , indices enclosed in parentheses and brackets denote the summation over the particles inside the sphere of interaction ( $r_{\beta\alpha} < r_i$ ) and the sphere of averaging ( $r_\alpha < r_a$ ), respectively. The first equation in (1) expresses the Langevin law for the effective value of the moment in the local field and represents the self-consistency condition. The solution of system (1)–(2) can be obtained by organizing an iteration process  $\{\mathbf{m}_\alpha\} \rightarrow \{\mathbf{h}_\alpha\} \rightarrow \{\mathbf{m}_\alpha\}$ .

The Brownian dynamics of particles is described by the system of finite-difference equations

$$\mathbf{R}_\alpha(t + \Delta t) = \mathbf{R}_\alpha(t) + b \mathbf{F}_\alpha(t) \Delta t + (\Delta \mathbf{R})_{\text{ran}}, \quad (3)$$

where  $b = 1/(6\pi\eta a)$  is the particle mobility and  $(\Delta \mathbf{R})_R$  is the random Gaussian shift with a zero mean and dispersion

$$\langle (\Delta \mathbf{R})_{\text{ran}}^2 \rangle = 6D\Delta t, \quad D = kTb = \frac{2a^2}{3\tau_B}.$$

The magnetic force on the particle  $\alpha$  is the sum of the forces of its interaction with neighbors inside the sphere of interaction:

$$\mathbf{F}_\alpha^m = \frac{3m_0^2}{8a^4} \mathbf{f}_\alpha^m, \quad \mathbf{f}_\alpha^m = \sum_{(\beta \neq \alpha)} \mathbf{f}_{\beta\alpha}^m,$$

$$\mathbf{f}_{\beta\alpha}^m = \frac{1}{2r_{\beta\alpha}^4} [\mathbf{s}_{\beta\alpha} (\mathbf{m}_\alpha \mathbf{m}_\beta) + \mathbf{m}_\alpha (\mathbf{s}_{\beta\alpha} \mathbf{m}_\beta) + \mathbf{m}_\beta (\mathbf{s}_{\beta\alpha} \mathbf{m}_\alpha) - 5\mathbf{s}_{\beta\alpha} (\mathbf{s}_{\beta\alpha} \mathbf{m}_\beta) (\mathbf{s}_{\beta\alpha} \mathbf{m}_\alpha)].$$

The mechanical barrier between the particles approaching each other is taken into account by the repulsive force that comes into effect at  $R_{\beta\alpha} < 2a$ , whereas the magnetic interaction between the overlapping particles is calculated at  $R_{\beta\alpha} = 2a$ . We assume

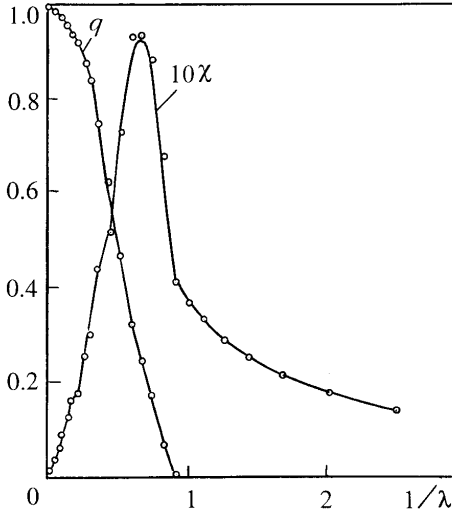


Fig. 1. Temperature dependences of the magnetic susceptibility  $\chi$  and the orientation freezing parameter  $q$  for the 5% ferrocolloidal system.

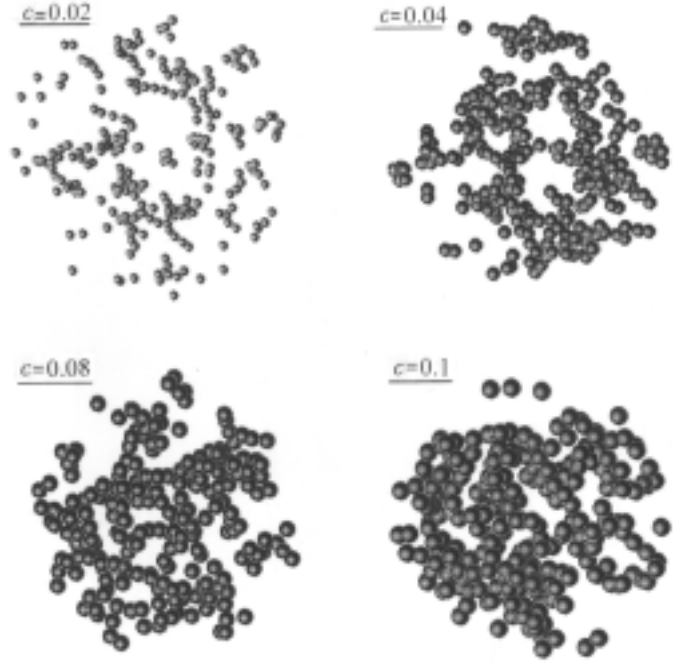


Fig. 2. Influence of the concentration on the character of the local structure of the ferrocolloid in the case of  $\lambda = 3.5$ .

$$\mathbf{f}_{\beta\alpha}^s = F_0^s \mathbf{f}_{\beta\alpha}^s, \quad \mathbf{f}_{\beta\alpha}^s = s_{\beta\alpha} \begin{cases} 0 & (r_{\alpha\beta} > 1), \\ \left( \frac{1 - r_{\beta\alpha}}{\delta} \right)^2 & (r_{\alpha\beta} \leq 1). \end{cases}$$

Using the time scale (see [5])  $t' = 18\eta / (\pi I_{sb}^2)$ , we write Eq. (3) in the dimensionless form ( $\tau = t/t'$ )

$$\mathbf{r}_\alpha(\tau + \Delta\tau) = \mathbf{r}_\alpha(\tau) + \mathbf{f}_\alpha(\tau) \Delta\tau + (\Delta\mathbf{r})_{\text{ran}}, \quad \langle (\Delta\mathbf{r})_{\text{ran}}^2 \rangle = \Delta\tau / \lambda, \quad (4)$$

where

$$\mathbf{f}_\alpha = \mathbf{f}_\alpha^m + \mathbf{f}_\alpha^s, \quad \mathbf{f}_\alpha^s = b_s \sum_{(\beta \neq \alpha)} \mathbf{f}_{\beta\alpha}^s.$$

We consider an ensemble consisting of 500 particles. The system is characterized by the concentration  $c$  and the parameter of the dipole-dipole interaction  $\lambda$ . The quantity  $\lambda^{-1}$  represents the total radiation temperature in units of the characteristic energy of the dipole interaction. In preliminary numerical experiments, the interaction radius was chosen to be equal to the mean interparticle spacing,  $r_i = c^{-1/3}$ , and the averaging radius  $r_a = r_L - r_i - 0.5$ .

In [3], the model presented was used to study the orientation state and the local structure of a colloid. Equations (1)–(2) for the orientation variables have in the zero external field a trivial solution with zero values of the effective magnetic moments. Apparently, this solution describes the paramagnetic state. As established in [3], on cooling to a certain temperature the trivial solution turns out to be unstable and the effective magnetic moments of particles acquire in the zero external field values other than zero, i.e., the effect of collective orientation freezing arises. As a quantitative characteristic of this phenomenon, the root-mean-square value of the effective magnetic moments  $q$  serves. With further cooling the freezing monotonically progresses and leads to the appearance of a peak on the temperature curve of the initial magnetic susceptibility  $\chi$ , which serves for molecular systems as

a characteristic indication of the transition to the state of spin glass. The dependences  $\chi(T)$  and  $q(T)$  calculated for the case of  $c=0.05$  are given in Fig. 1. The change in the local structure of the colloid with increasing concentration of particles for the case of  $\lambda=3.5$  is illustrated in Fig. 2.

**Computer Thermodynamic Experiment. Phase Transitions in the System of Colloid Particles.** The phase portrait of the system of colloid particles in an incompressible liquid can be given by a set of isotherms  $p(c)$  for the partial pressure or  $\varphi(c)$  for the chemical potential. Exactly these thermodynamic functions in the case of division of the system into macroscopic regions with a different concentration that are at equilibrium with one another hold the values constant along the system. The onset of instability of the homogeneous state is due to the appearance of the dependence  $\varphi(c)$  maximum, and the colloid splits into phases corresponding to the thermodynamically stable branches ( $(\partial\varphi/\partial c)_T > 0$ ) of this dependence. The critical temperature and concentration values at which separation begins are determined from the conditions

$$\left(\frac{\partial\varphi}{\partial c}\right)_T = 0, \quad \left(\frac{\partial^2\varphi}{\partial c^2}\right)_T = 0. \quad (5)$$

In the case of numerical simulation of an ensemble of particles, one can directly calculate the correlation magnetic addition to the internal energy  $E'$  at given values of  $T$ ,  $V$ , and  $N$ . This addition, however, is not a thermodynamic potential, since for this the internal energy should be known as a function of entropy. This method is based on the relation [6]

$$E = -T^2 \frac{\partial}{\partial T} \left( \frac{F}{T} \right)_n,$$

where  $n=N/V$ . Using the assumption of additivity of the magnetic addition and ignoring this relation in terms of temperature at fixed  $n$ , we find

$$F'(T, n) = T \int_{\infty}^T \frac{E'(T, n)}{T^2} dT. \quad (6)$$

With the aid of (6), calculating in the computer experiment the value of  $E'$  for various temperatures and fixed  $V$  and  $N$ , one can determine the addition to the free energy.

The quantity  $E'$  represents the total energy of interparticle magnetic interactions in the colloid in the state of statistical equilibrium related to the volume  $V$ . The  $E'(T, n)$  algorithm is as follows. For the spatial and orientation configurations of an ensemble of particles with given  $n$  and  $T$  existing at a certain instant of time, we find the mean value of the interaction energy of dipoles on a per-particle basis  $U_1(t)$ . Then, using the successive configurations arising in the process of Brownian motion in a fairly long time interval, we find the time average of this quantity and calculate  $E'$  according to  $E' = n\overline{U_1}$ . Iteration of this procedure with a gradual decrease in the temperature permits obtaining a table of  $E'(T)$  values and determining the function  $F(T)$  for a given value of  $n$  by numerical integration of relation (6). Using various values of  $n$ , we find a table of values of the function  $F(n, T)$ .

The magnetic interaction energy of particles  $\alpha$  and  $\beta$  from the viewpoint of the self-consistent field model is given by the relation

$$U_{\alpha\beta} = U_0 u_{\alpha\beta}, \quad u_{\alpha\beta} = \frac{m_{\Gamma}^{\alpha} m_{\Gamma}^{\beta}}{r_{\alpha\beta}^3} [\mathbf{e}_{\alpha} \mathbf{e}_{\beta} - 3 (\mathbf{e}_{\alpha} \mathbf{s}_{\alpha\beta}) (\mathbf{e}_{\beta} \mathbf{s}_{\alpha\beta})], \quad U_0 = \frac{m_0^2}{8a^3} = \frac{\pi c I_{\text{sb}}^2}{6n}.$$

We determine the value of  $U_1$  by the relation

TABLE 1. Relative Magnetic Correlation Addition ( $-F_r'$ ) to the Free Energy of the Colloid of Isotropic Ferroparticles

$\lambda$	$c$								
	0.01	0.02	0.03	0.04	0.06	0.08	0.10	0.15	0.20
1.0	0	0	0	0	0	$4.2 \cdot 10^{-5}$	$5.1 \cdot 10^{-4}$	$3.3 \cdot 10^{-3}$	0.012
1.5	0	$6.2 \cdot 10^{-4}$	0.002	0.005	0.015	0.029	0.045	0.088	0.118
2.0	$1.4 \cdot 10^{-3}$	0.007	0.022	0.040	0.075	0.105	0.133	0.200	0.243
2.5	0.009	0.036	0.066	0.100	0.158	0.203	0.243	0.308	0.348
3.0	0.040	0.084	0.127	0.169	0.230	0.275	0.312	0.392	0.438
3.5	0.057	0.140	0.205	0.256	0.320	0.360	0.390	0.460	0.516
4.0	0.110	0.220	0.300	0.347	0.390	0.424	0.456	0.529	0.588

$$U_1 = U_0 u_1, \quad u_1 = \frac{1}{N_a} \sum_{[\alpha]} \left( \frac{1}{2} \sum_{(\beta \neq \alpha)} u_{\alpha\beta} + \sum_{)\beta(} u_{\alpha\beta} \right), \quad (7)$$

where the symbol between square brackets denotes, as before, the summation over the particles in the sphere of averaging, the symbol in parentheses ( ) — the summation over the particles falling within both the interaction sphere of the particle  $\alpha$  and the averaging sphere (the factor 1/2 takes into account that the interaction of such particles in (7) is taken twice), and the symbol in parentheses )( determines the summation over the particles located inside the interaction sphere of the particle  $\alpha$  but outside the averaging sphere. For the internal energy density we have

$$E' = c I_{sb}^2 E_r', \quad E_r' = \frac{\pi}{6} \bar{u}_1,$$

the correlation addition to the free energy is reduced to

$$F' = c I_{sb}^2 F_r', \quad F_r' = \frac{1}{\lambda} \int_0^\lambda E_r' d\lambda,$$

and the addition to the chemical potential of the colloid on a per-particle basis is

$$\phi' = \left( \frac{\partial F'}{\partial n} \right)_T = \frac{6}{\pi} \lambda k T \left( F_r' + c \frac{\partial F_r'}{\partial c} \right). \quad (8)$$

The results of the calculation of the value of  $F_r'$  are reported in Table 1. The concentration dependence  $\phi'(c)$  for each value of  $\lambda$  was found from Eq. (8) numerically, for which the continuous function  $F_r'(c)$  was obtained by means of cubic spline interpolation of the table values (with the addition of the value of  $F_r'(c=0)=0$ ). We determine the total chemical potential density of the colloid on a per-particle basis as the sum  $\phi = \phi_0 + \phi'$ , where  $\phi_0$  is the chemical potential at eliminated magnetic interaction of particles for which we make use of the equation of the gas state of Carnahan–Starling solid spheres [7] in the form

$$\phi_0 = kT \left[ \ln c + \frac{4 - 4c + 3c^2 - c^3}{(1-c)^3} \right] + \text{const}. \quad (9)$$

The thus-found aggregate of isotherms  $\phi(c)$  (up to the constant in (9)) is depicted in Fig. 3. The data obtained make it possible to draw several important conclusions about the state of the disperse system of the ferrocolloid. Note, first of all, the simultaneous existence of two critical points at which the first and second derivatives of the chemical potential with respect to the concentration go to zero simultaneously. This means that the system of particles under con-

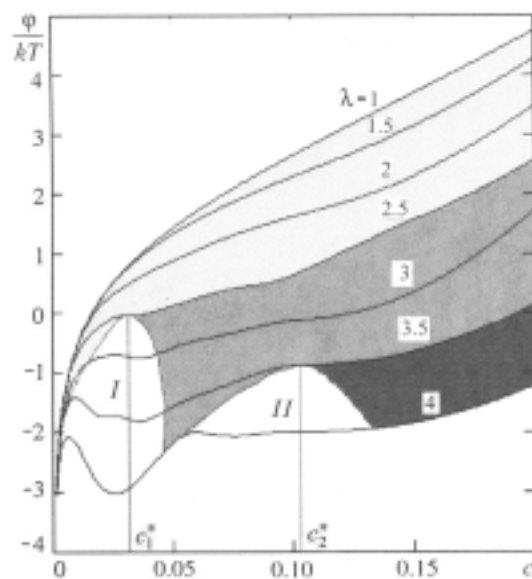


Fig. 3. Diagram of the state of the colloid of isotropic ferroparticles: curves  $\lambda = 1, 1.5, \dots$  are the chemical potential isotherms;  $c_1^*$  and  $c_2^*$  are the critical points of phase transitions; *I* and *II* are the instability regions of the homogeneous state; the light region shows the gaseous state, the intermediate region — the liquid state, and the dark region — the solid state.

sideration can be found in three aggregate states. The critical isotherm of the gas–liquid phase transition is (approximately) the isotherm  $\lambda = 2.5$ , and that of the liquid–solid phase transition is the isotherm  $\lambda = 3.5$ . The corresponding critical concentrations are  $c_1^* \approx 0.03$  and  $c_2^* \approx 0.1$ . In the critical regions *I* and *II*, the homogeneous state of the system of particles is unstable, and it breaks down into regions with a different concentration and different aggregate states.

The stability of the gas state of the system of interacting dipoles is explained by the high probability of thermofluctuation disintegration of simple particle associations in the characteristic time of the addition of a new particle. In the liquid aggregate state, as computer visualization shows, is the system of ferroparticles largely associated as is the system of molecules of normal liquids. Under overcooling the liquid phase condenses, leading to a macroscopic breakdown of the colloid into regions of higher and lower concentrations that are at equilibrium with one another. Using the Maxwell rule, we find that these concentrations are equal to 0.0045 and 0.044 for the isotherm  $\lambda = 3.5$  and 0.0016 and 0.038 for  $\lambda = 4$ . In the solid state, instead of the temporary particle associations their stable spatial structure arises. Figure 2 gives a visual image on the colloid structure in different aggregate states. In this figure, the concentration  $c = 0.02$  corresponds to the region of instability *I*, the concentration  $c = 0.04$  approximately corresponds to the liquid-phase concentration (0.044) in the region of its equilibrium with the particle gas, the concentration  $c = 0.08$  corresponds to the liquid state in the region beyond the critical one, and the concentration  $c = 0.1$  corresponds to the critical concentration of the liquid–solid transition. As we see, in the instability region *I*, fairly large but isolated particle associations arise, and their integration leads to macroscopic breakdown of the colloid. The structure of the liquid phase is characterized by a practically continuous net in which simple chains dominate, and on going to the solid state the chain structure gives way to the braid structure. Throughout the temperature range under consideration the aggregate state of the carrier liquid is thought of as being unaltered, the colloid as a whole remains liquid, and its physical properties sensitive to the state of the disperse subsystem undergo changes. In particular, depending on the aggregate state of the disperse subsystem, the colloid should exhibit Newton (gas state), nonlinear-viscous (liquid state) or viscoelastic properties, and thixotropy (solid state). Exactly such types of rheological behavior were observed in the absence of an external field in the "magnetite in kerosene" colloidal system when its concentration was changed by diluting it with the carrier liquid [8]. Taking into account the results of the investigation of the dipole-glassy transition in [3], we arrive at the conclusion that the critical points of phase transformations lie in the region of the dipole-glassy state and the liquid and solid systems are dipole glasses. The gas of the ferrocolloidal particles above the critical isotherm can be both

paramagnetic and dipole-glassy and below the critical isotherm, in equilibrium with the liquid phase, it can be only paramagnetic.

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## NOTATION

$t$ , time;  $\tau$ , dimensionless time;  $\mathbf{I}$ , magnetization;  $m_0$ , value of the magnetic moment of the particle;  $N_a$ , number of particles in the averaging sphere;  $\mathbf{s}_{\alpha\beta}$ , unit vector from the center of particle  $\alpha$  to the center of particle  $\beta$ ;  $R_{\alpha\beta}$ , distance between the centers of the particles  $\alpha$  and  $\beta$ ;  $\mathbf{F}_\alpha$ , force acting on the particle  $\alpha$ ;  $\eta$ , viscosity;  $D$ , diffusion coefficient;  $n$ , numerical concentration of particles;  $c$ , volume concentration;  $V$ , volume of the system;  $v$ , particle volume;  $k$ , Boltzmann constant;  $T$ , temperature;  $E$ , internal energy;  $F$ , free energy;  $\varphi$ , chemical potential;  $\dot{E}$ ,  $\dot{F}$ ,  $\dot{\varphi}$ , magnetic correlation additions. Subscripts: sb, solid body; L, Lorentz; i, interaction; a, averaging; m, magnetic; r, relative; B, Brownian; s, surface; ran, random value.

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