Shear elasticity of isotropic magnetic gels

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The paper deals with a theoretical study of the effective shear modulus of a magnetic gel, consisting of magnetizable particles randomly and isotropically distributed in an elastic matrix. The effect of an external magnetic field on the composite modulus is the focus of our consideration. We take into account that magnetic interaction between the particles can induce their spatial rearrangement and lead to internal anisotropy of the system. Our results show that, if this magnetically induced anisotropy is insignificant, the applied field reduces the total shear modulus of the composite. Strong anisotropy can qualitatively change the magnetomechanic effect and induce an increase of this modulus with the field.

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I. INTRODUCTION

Composites of fine magnetic particles in soft polymer matrices (e.g., ferrogels, magnetic elastomers, and magnetorheological elastomers) have attracted considerable interest of researchers and engineers because of a rich set of unique physical properties, valuable for many industrial and biomedical applications [1–13]. One of the qualities of these systems, interesting from both scientific and practical points of view, is their ability to change mechanical properties and behavior under the action of an external magnetic field. Uniaxial elongation and magnetostriction of magnetic gels have been studied in many works (see, for example, [13–20]). The shear effects in composites with particles united in linear chainlike aggregates were studied in [21–23]. The general conclusion of these works is that an external magnetic field can significantly increase the shear modulus of these composites.

The chainlike aggregates are created on the stage preceding the composite curing, by application of an external magnetic field (field of polymerization) to the suspension of the magnetic particles in the liquid polymer. At the same time, very often magnetic gels are synthesized without the field. In this case the spatial disposition of the particles is rather random and isotropic (see, for example, [15,17,24]).

Experiments [15,17] have demonstrated that, in soft gels, a magnetic field can induce the spatial rearrangement of the particles and even lead to their unification int heterogeneous structures, aligned along the field. Obviously, these internal transformations can lead to a significant change of the macroscopic properties of the composite materials.

The aim of this work is a theoretical study of the effect of an external magnetic field on the shear elastic modulus of magnetic gels with an initially homogeneous and isotropic distribution of magnetizable spherical particles in a continuous matrix. The field-induced rearrangement of the particles and anisotropy of their dispositions is the focus of our consideration.

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The matrix is taken to be elastic, with the linear law of deformation, and incompressible. It should be noted that the approximation of incompressibility is not fulfilled for all gels. However, it allows us to restrict calculations and to get the final results in quite transparent forms. The analysis of the effects of the composite compressibility can be considered as a natural generalization of this model.

The principal problem of the theory of composite materials is the analysis of cooperative effects of the multiparticle interactions. Usually these effects are taken into account by using various empirical and semiempirical methods, whose accuracy, and even qualitative adequacy, *a priori*, is unknown [25].

In order to achieve a clear understanding of the microscopic nature of the physical properties of magnetic gels as well as their macroscopic behavior, mathematically rigorous models, free from intuitive and heuristic constructions, must be developed. In this work we consider a gel with a low or moderate concentration of spherical particles of the magnetic filler. This allows us to use the regular approximation of the pair interaction between the particles and to avoid a semiempirical intuitive hypothesis with uncontrolled accuracy. We believe that this approach can be considered as a necessary robust background for the development of the models for more concentrated systems where the multiparticle effects are significant.

The paper is organized as follows. In Sec. II we discuss the main points of the physical model. In Secs. III and IV we consider the particles' relative displacements, as consequences of the macroscopic shear of the composite and the action of the applied field. In Sec. V the estimates of the composite shear modulus are presented. We summarize in Sec. VI.

II. PHYSICAL MODEL AND MAIN APPROXIMATIONS

We consider a system of identical spherical non-Brownian magnetizable particles embedded in an elastic continuous medium. For maximal simplification of the mathematics, we restrict ourselves to the case of the moderate field and suppose that the linear law of particle magnetization if fulfilled.

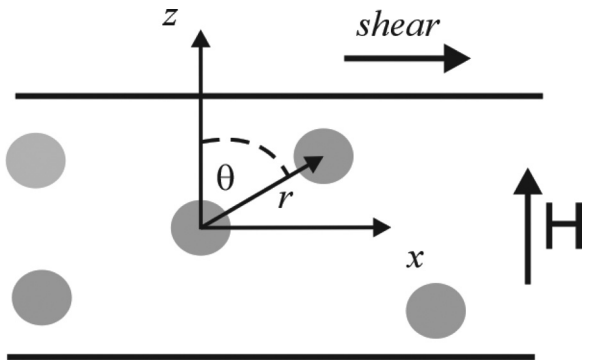

FIG. 1. Illustration of the system under consideration. The gradient of the shear displacement is directed along the axis Oz. The coordinate axis Oy is not shown for simplicity.

Let the composite be placed in a uniform magnetic field **H** and experience small shear deformation in the plane, perpendicular to the field (see Fig. 1). It is convenient to introduce the Cartesian coordinate system with the axis Oz in the field direction and the axis Ox in the direction of the shear. By using the well-known results of the theory of magnetizable media (see, for example, [26,27]), as well as the mathematical similarity between the stationary Navier-Stokes equation at low Reynolds and the Lamé equation of deformation of an elastic poorly compressible medium [25], one can present the needed component of macroscopic (measurable) stress σ in the composite as

$$\sigma = \sigma_{el} + \sigma_m, \tag{1}$$

where $\sigma_{el} = G_{el}\gamma$, $\sigma_m = \frac{1}{2}\varphi\mu_0\langle M_x\rangle > H$, and $\sigma = \sigma_{xz}$. Here σ_{el} is the shear stress in the elastic composite with the hard particles, G_{el} is the corresponding shear modulus of the composite, and σ_m is the part of the total stress provided by the applied magnetic field. The magnitude M_x is the corresponding component of a particle's magnetization; the angular brackets mean averaging over all relative positions of the particles in the composite; $\gamma = \frac{\partial u_x}{\partial z}$; u_x is the component of the macroscopic (measurable) vector $\boldsymbol{u}$ of the composite displacement; φ is volume concentration of the particles; μ_0 is the vacuum magnetic permeability.

By using the Batchelor and Green results [28] of effective viscosity of moderately concentrated suspension, as well as the identity between the Navier-Stokes and Lamé equations, one can estimate the modulus G_{el} as

$$G_{el} = G_0(1 + 2.5\varphi + 5.2\varphi^2). \tag{2}$$

Here G_0 is the shear modulus of the pure host matrix. Usually this formula leads to good agreement with experiments until the concentrations $\varphi \sim 10\%-15\%$.

One needs to note that, in principle, the solid particles can change the conformation of the macromolecules of the host polymer and therefore can change the elastic modulus of the matrix. The possibility of these transformations, induced by the chemical interaction of the ions, dissolved from the particle's surface, and the polymer macromolecules, as well as the effect of this interaction on the mechanic properties of the composites, has been discussed, for example, in [29]. Here we will neglect these effects and focus on the mechanic and magnetic interactions between the particles.

Our main goal now is to determine the component $\langle M_x\rangle$ of the particle magnetization. In order to get the mathematically rigorous results, we will estimate $\langle M_x\rangle$ taking into account interaction only between two particles, ignoring the effect of any third one. It should be noted that the Batchelor-Green formula (2) has been derived in the framework of the pair approximation, taking into account mechanic interaction between the particles through the perturbations of the carrier medium.

Let us consider two particles and put the origin of the Cartesian coordinate system, shown in Fig. 1, in the center of one of them. We will denote the radius vector of the center of the second particle by $\boldsymbol{r}$.

The component M_x of magnetization of each particle, shown in Fig. 1, appears because of mutual magnetization of the particles. The simplest way to take this interaction into account is to use the well-known dipole-dipole approximation. However, this approach describes quite well magnetic interaction between the particles only when they are far from each other and the distance r between their centers significantly exceeds the diameter d of the particle. At the same time, the effects of the mutual magnetization are especially strong at the close dispositions of the particles, where their magnetic interaction is multipolar. We will estimate the energy $U(\boldsymbol{r})$ of the particles' interaction by using the extrapolation formula obtained in [30] from the results of numerical study of the problem on two linearly magnetizable particles:

$$U = -3\mu_0\mu_f H^2 v \sum_{k=3}^{7}\left(\frac{\alpha-1}{\alpha+2}\right)^{p_k} \times\left[\frac{a_k}{(\rho-b_k)^k} + \frac{c_k}{(q-d_k)^k}\cos^2\theta\right]. \tag{3}$$

Here $\rho = 2r/d$; $\alpha = \mu_p/\mu_f$; μ_p and μ_f are the relative magnetic permeabilities of the particle and the host matrix, respectively; $v = \pi d^3/6$ is the particle volume; and $p_k, a_k, \ldots, d_k$ are parameters whose values are tabulated in [30]. For $\rho \gg 1$ the fit formula (3) coincides with the well-known relation for the energy of the dipole-dipole approximation.

The y component of the torque Γ, acting on the cluster of the particles, can be calculated from two general relations. On the one hand, $\Gamma_y = -\frac{\partial U}{\partial\theta}\cos\phi$ [30,31] (ϕ is the azimuthal angle, not shown in Fig. 1 for brevity); on the other hand, $\Gamma_y = -2\mu_0 v M_x H$ [27] (the multiplier 2 appears here because we are dealing with a cluster consisting of two particles). Equating these relations and taking into account the relations $\mu_f = 1$ and $\alpha \gg 1$, fulfilled for typical magnetic gels and elastomers, we find M_x for the given relative disposition of the particles:

$$M_x = 3H\sum_{k=3}^{7}\frac{c_k}{(\rho-d_k)^k}\sin\theta\cos\theta\cos\phi. \tag{4}$$

Let $g(\boldsymbol{r})$ be the pair distribution function over relative positions of the particles. For convenience we suppose that the normalization condition $g \to 1$ when $r \to \infty$ is held. In the frame of the pair approximation, the average magnetization

of a particle can be presented as

$$\langle M_x\rangle = n\int M_x(\boldsymbol{r})g(\boldsymbol{r})d\boldsymbol{r}, \quad n=\frac{\varphi}{v}.$$

Here n is number of particles in a unit volume of the composite and v, again, is the volume of the particle. The distribution function g can be presented as $g = g_0 + \delta g$, where g_0 corresponds to the isotropic nondeformed composite before the field application and δg reflects the change of the function because of the particles' rearrangement and the sample deformation. In the isotropic composite, where g_0 depends only on the absolute value r of the radius vector $\boldsymbol{r}$, the equality $\int M_x(\boldsymbol{r})g_0(\boldsymbol{r})d\boldsymbol{r} = 0$ is held. Therefore,

$$\langle M_x\rangle = \frac{\varphi}{v}\int M_x(\boldsymbol{r})\delta g(\boldsymbol{r})d\boldsymbol{r}. \tag{5}$$

The function δg can be determined from the following equation [32]:

$$\delta g = -\mathrm{div}(g\boldsymbol{w}). \tag{6}$$

Here $\boldsymbol{w}$ is the vector of the relative displacement of the particles, which is determined by two factors: the particles' rearrangement under magnetic interaction between them and the macroscopic shear of the composite as well. We will consider separately these displacements and the corresponding changes δg of the distribution function g.

III. MAGNETICALLY INDUCED DISPLACEMENT OF THE PARTICLES

Let us suppose that the sample does not undergo macroscopic deformation and the particles' rearrangement takes place because of their magnetic interaction. By using (3), we determine the components of the force $\boldsymbol{F} = -\nabla U$ of magnetic interaction between two particles. The vector of their relative displacement $\boldsymbol{w}_m$, induced by this interaction, can be determined from the theory [33] of mutual motion of two particles in a suspension combined with the mathematical identity of the Navier-Stokes and Lamé equations:

$$\boldsymbol{w}_m = \hat{\beta}\cdot\boldsymbol{F}. \tag{7}$$

Here $\hat{\beta}$ is tensor of the particles' displacement. According to [33], the Cartesian components of this tensor can be presented as

$$\begin{aligned}\beta_{ii} &= \beta_0\left[(G_B - H_B)\frac{x_i^2}{r^2} + H_B\right],\\ \beta_{ij} &= \beta_0(G_B - H_B)\frac{x_i x_j}{r^2}\\ \beta_0 &= \frac{2}{3\pi G_0 d},\end{aligned} \tag{8}$$

where G_0 again is the shear modulus of the host elastic matrix, $i,j = x,y,z$, and $G_B(r)$ and $H_B(r)$ are functions of the distance r between centers of the particles. Explicit forms of these functions, valid for all values of r, are unknown. Their asymptotic approximations are given in [33]:

$$\begin{aligned}&G_B \approx 2(\rho-2), \quad H_B \approx 0.401 \quad \text{for} \quad \rho\to 2,\\ &G_B \approx 1 - \tfrac{3}{2}\rho^{-1} + \rho^{-3} - \tfrac{15}{4}\rho^{-4} + O(\rho^{-6}),\\ &H_B \approx 1 - \tfrac{3}{4}\rho^{-1} - \tfrac{1}{2}\rho^{-3} + O(\rho^{-6}) \quad \text{for} \quad \rho\to\infty.\end{aligned} \tag{9}$$

The dimensionless distance ρ between the particles is defined in (4). Numerical dates for $G_B(\rho)$ and $H_B(\rho)$ are tabulated in [33].

In the spherical coordinate system, with the radius r and polar and azimuth angles θ and ϕ, respectively ($x = r\sin\theta\cos\phi$; $y = r\sin\theta\sin\phi$; $z = r\cos\theta$), after simple, but cumbersome calculations, we get the following relations for the components of the displacement vector $\boldsymbol{w}_m$:

$$\begin{aligned}w_{mr} &= \kappa\beta_0\mu'(r)G_B(r)(3\cos^2\theta - 1),\\ w_{m\theta} &= -6\kappa\beta_0\frac{\mu(r)}{r}H_B(r)\sin\theta\cos\theta,\\ w_{m\phi} &= 0.\end{aligned} \tag{10}$$

Here

$$\mu(r) = \sum_{k=3}^{7}\frac{c_k}{(\rho - d_k)^k}, \quad \mu'(r) = \frac{d\mu}{dr}, \quad \kappa = 3\mu_0 H^2 v.$$

By using (6), in the first approximation with respect to the displacement $\boldsymbol{w}_m$, the change δg_m of the distribution function can be determined as

$$\delta g_m = -\mathrm{div}(g_0\boldsymbol{w}_m). \tag{11}$$

Combining (10) and (11), one can obtain, after calculations,

$$\begin{aligned}\delta g_m &= -\kappa\beta_0 f(r)(3\cos^2\theta - 1),\\ f(r) &= \frac{1}{r^2}\frac{d}{dr}(r^2 g_0 G_B\mu') - 6g_0\frac{\mu}{r^2}H_B.\end{aligned} \tag{12}$$

The function δg_m describes the structural anisotropy that appears in the nondeformed composite under the action of the applied field.

IV. PARTICLE DISPLACEMENT DUE TO THE COMPOSITE SHEAR

Let us suppose now that the sample experiences macroscopic shear in the direction Ox and the gradient of the sample displacement is directed along Oz. The vector $\boldsymbol{w}_\gamma$ of the corresponding relative displacement of the particles again can be determined by using the identity of the Navier-Stokes and Lamé equations [25], as well as the relation [28] for the relative motion of two particles in a suspension. In the spherical coordinate system the result reads

$$\begin{aligned}w_{\gamma r} &= \gamma r(1 - A_B)\sin\theta\cos\theta\cos\phi,\\ w_{\gamma\theta} &= \gamma r\left[\cos^2\theta + \tfrac{1}{2}B_B(\sin^2\theta - \cos^2\theta)\right]\cos\phi,\\ w_{\gamma\phi} &= -\gamma r\left(1 - \tfrac{1}{2}B_B\right)\cos\theta\sin\phi.\end{aligned} \tag{13}$$

Here γ is the macroscopic dimensionless shear of the sample and $A_B(r)$ and $B_B(r)$ are functions of r. Their explicit forms for the whole range of r have not been determined in the literature; asymptotic relations are given in [28] as

$$\begin{aligned}&A_B \approx 1 - 4.077(\rho-2), \quad B_B \approx 0.406 \quad \text{for} \quad \rho\to 2,\\ &A_B \approx 5\rho^{-3} - \tfrac{40}{3}\rho^{-5} + 25\rho^{-6},\\ &B_B \approx \tfrac{16}{3}\rho^{-5} \quad \text{for} \quad \rho\to\infty.\end{aligned} \tag{14}$$

In the range $2 < \rho < 20$, the numerical values of A_B and B_B are tabulated in [28].

Note that the equality $A_B(r) = 1$ is held at $r = d$ (i.e., at $\rho = 2$). Thus the condition $w_{\gamma r}(r = d) = 0$ of the particles' nonintersection is fulfilled in (13). At the same time the components $w_{\gamma\theta}$ and $w_{\gamma\phi}$ are not zero at d, i.e., $\rho = 2$. This means that the particles can slip over each other, being in physical contact.

By using Eq. (7), in the first approximation with respect to γ, one can present the change δg_γ of the distribution function, produced by the macroscopic shear, as

$$\delta g_\gamma = -\mathrm{div}[(g_0 + \delta g_m)\boldsymbol{w}_\gamma]. \tag{15}$$

Combining (12), (13), and (15), after some transformations we get

$$\begin{aligned}
\delta g_\gamma &= \delta g_\gamma^{(1)} + \delta g_\gamma^{(2)},\\
\delta g_\gamma^{(1)} &= -\mathrm{div}(g_0\boldsymbol{w}_\gamma) = -\gamma\left[\frac{1}{r^2}\frac{d}{dr}[r^3(1-A_B)g_0]\right.\\
&\quad \left. - 3g_0(1-B_B)\right]\sin\theta\cos\theta\cos\phi,\\
\delta g_\gamma^{(2)} &= -\mathrm{div}(g_m\boldsymbol{w}_\gamma) = \kappa\beta_0\gamma\left[\frac{1}{r^2}\frac{d}{dr}[r^3(1-A_B)f]\right.\\
&\quad \times(3\cos^2\theta - 1) + 3f(1 - 5\cos^2\theta\\
&\quad \left. - B_B(2 - 5\cos^2\theta))\right]\sin\theta\cos\theta\cos\phi.
\end{aligned} \tag{16}$$

The function $f(r)$ is defined in Eq. (12). The term $\delta g_\gamma^{(1)}$ corresponds to mutual rearrangement of the particles due to the macroscopic shear of the composite and the term $\delta g_\gamma^{(2)}$ is due to the combination of the shear and magnetic interaction between the particles. Substituting $\delta g = \delta g_m + \delta g_\gamma$ into (5) and taking into account (4) and the equality $\frac{\varphi}{v}\int M_x(\boldsymbol{r})\delta g_m(\boldsymbol{r})d\boldsymbol{r} = 0$,we arrive at the relations

$$\begin{aligned}
\langle M_x\rangle &= \langle M_x\rangle^{(1)} + \langle M_x\rangle^{(2)},\\
\langle M_x\rangle^{(1)} &= \frac{\varphi}{v}\int M_x(\boldsymbol{r})\delta g_\gamma^{(1)}(\boldsymbol{r})d\boldsymbol{r},\\
\langle M_x\rangle^{(2)} &= \frac{\varphi}{v}\int M_x(\boldsymbol{r})\delta g_\gamma^{(2)}(\boldsymbol{r})d\boldsymbol{r}.
\end{aligned} \tag{17}$$

By using (16) in (17), one can get, after some transformations,

$$\langle M_x\rangle^{(1)} = -\tfrac{3}{5}\gamma H\varphi J, \tag{18}$$

where

$$\begin{aligned}
J = \int_0^\infty \mu(\rho)\left[\frac{d}{d\rho}\{g_0\rho^3[1-A_B(\rho)]\}\right.\\
\left. - 3\rho^2[1-B_B(\rho)]\right]d\rho,
\end{aligned}$$

and

$$\langle M_x\rangle^{(2)} = -\frac{3}{35}\gamma H\varphi\frac{\kappa\beta_0}{a^2}\int_0^\infty f(\rho)q(\rho)\rho^2 d\rho, \tag{19}$$

where $q(\rho) = 2\mu'(1-A_B)\rho + 3\mu(8-B_B)$. The function $f(\rho)$ represents the function (r), defined in (13), after substituting r for ρ. A prime here and in the following means derivation over ρ.

By using the explicit form (13) for the function f, integrating by part in (18) and (19), and taking into account that

$$\begin{aligned}
&g_0 = 0 \quad \text{for} \quad \rho < 2, \quad \mu \to \frac{3}{\rho^3},\\
&g_0 \to 1, \quad A_B \to 0, \quad f(\rho) \to 0 \quad \text{for} \quad \rho \to \infty.
\end{aligned}$$

we arrive at the relations

$$J = 3 - \int_2^\infty g_0\{\rho^3(1-A_B)\mu' + 3\rho^2[1-B_B(\rho)]\mu\}d\rho \tag{20}$$

and

$$\begin{aligned}
\langle M_x\rangle^{(2)} &= \frac{4}{35}\mu_0\gamma\frac{H^3}{G_0}\varphi K,\\
K &= \int_2^\infty g_0(r^2\mu' q' G_B - 6\mu H_B q)d\rho.
\end{aligned} \tag{21}$$

V. RESULTS AND DISCUSSION

In order to calculate the integrals in (20) and (21), one needs to determine the initial distribution function g_0 as well as the functions $A_B(\rho)$, $B_B(\rho)$, $G_B(\rho)$, and $H_B(\rho)$. We choose the distribution function g_0 of the hard spheres in the isotropic nondeformed composite by using the simplest form, which takes into account the steric interaction between the particles and the short-range order, created by this interaction [34]:

$$g_0 = \begin{cases} 0, & r < d\\ 1 + 8\varphi\left(1 - \frac{3r}{4d} + \frac{r^3}{16d^3}\right), & d < r < 2d\\ 1, & r > 2d. \end{cases} \tag{22}$$

It has been noted that the explicit analytical forms of $A_B(\rho)$, $B_B(\rho)$, $G_B(\rho)$, and $H_B(\rho)$ in the whole range of ρ are unknown. Some numerical values of these functions are tabulated in [28,33]; however, they are given for different magnitudes of ρ, which is why these tables are inconvenient for numerical integration in (20) and (21).

In order to get acceptable estimates for J and K, we suggest the following extrapolation forms for the functions $A_B(\rho)$, $B_B(\rho)$, $G_B(\rho)$, and $H_B(\rho)$, which coincide with the asymptotic values of the functions (9) and (14) in the corresponding limiting cases with respect to ρ:

$$\begin{aligned}
A_B(\rho) &= \begin{cases} 1 - 4.077(\rho - 2) & \text{for} \quad 2 < \rho < 2.13\\ 5\rho^{-3} - \frac{40}{3}\rho^{-5} + 25\rho^{-6} & \text{for} \quad \rho > 2.13, \end{cases}\\
B_B(\rho) &= \frac{0.406\left(\frac{16}{3}\right)(2\rho)^{-5}}{\left(\frac{16}{3}\right)(2\rho)^{-5} + 0.406(2^{-5} - \rho^{-5})},\\
G_B(\rho) &= \frac{2(\rho-2)\left|1 - \frac{3}{2}\rho^{-1} + \rho^{-3} - \frac{15}{4}\rho^{-4}\right|}{2(\rho-2) + \left|1 - \frac{3}{2}\rho^{-1} + \rho^{-3} - \frac{15}{4}\rho^{-4}\right|},\\
H_B(\rho) &= \frac{0.401(\rho-1)}{0.401(\rho-2)+1}.
\end{aligned} \tag{23}$$

The results of calculations of these functions, by using the extrapolations (21) and the tabulated values of [28,33], are shown in Fig. 2. A comparison of these results allows us to consider the simple extrapolations (21) as quite acceptable

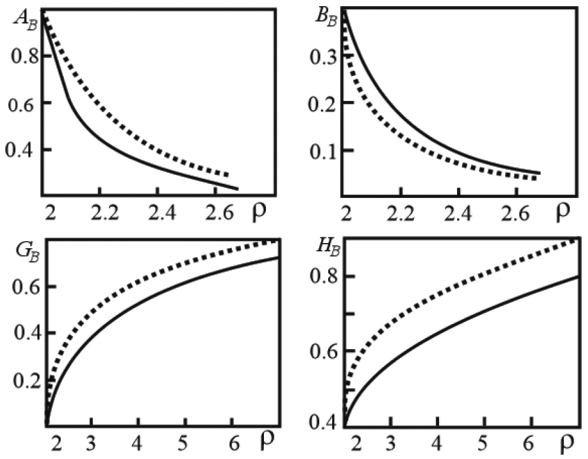

FIG. 2. Functions $A_B(\rho)$, $B_B(\rho)$, $G_B(\rho)$, and $H_B(\rho)$, calculated by using the forms (23) (solid lines) and the tables of [28,33] (dotted ones).

approximations for the first estimates of the integrals J and K. Substituting (22) and (23) into the integrals in (20) and (21), we get

$$J \approx 2.5 - 0.213\varphi, \quad K \approx 48 + 99\varphi. \tag{24}$$

One needs to note that the parameters J and K are determined by using the form (22) of the distribution function g_0. The first terms on the right-hand side of (22) correspond to the stepwise function

$$g_0 = \begin{cases} 0, & r < 2 \\ 1, & r > 2 \end{cases}$$

typical for the ideal gas of the hard spheres. In this approximation $J \approx 2.5$ and $K \approx 48$. The second, proportional to the concentration φ, terms appear in (24) due to the spatial correlations between the spherical particles, mirrored by the term with φ in Eq. (22).

Combining the relations (1) with (17) and (18), one can get

$$\begin{aligned} \sigma_m &= \sigma_m^{(1)} + \sigma_m^{(2)}, \\ \sigma_m^{(1)} &= \tfrac{1}{2}\varphi\mu_0\langle M_x\rangle^{(1)}H = G_m^{(1)}\gamma, \\ \sigma_m^{(2)} &= \tfrac{1}{2}\varphi\mu_0\langle M_x\rangle^{(2)}H = G_m^{(2)}\gamma. \end{aligned} \tag{25}$$

Here $\sigma_m^{(1)}$ and $\sigma_m^{(2)}$ are the magnetically induced parts of the total stress σ, which appear due to the change of the particles' mutual disposition, as a consequence of, respectively, the macroscopic shear deformation of the isotropic composite and the combination of this deformation with the magnetically induced particles rearrangement. The parameters $G_m^{(1)}$ and $G_m^{(2)}$ are the corresponding parts of the magnetic contributions to the total shear modulus G, which can be written as

$$G = G_{el} + G_m^{(1)} + G_m^{(2)}.$$

Taking into account (18), (20), (21), (24), and (25), we arrive at the following results:

$$\begin{aligned} G_m^{(1)} &= -0.3\mu_0\varphi^2H^2(2.5 - 0.213\varphi), \\ G_m^{(2)} &= \frac{2}{35}\varphi^2\frac{\mu_0^2H^4}{G_0}(48 + 99\varphi). \end{aligned} \tag{26}$$

If the rearrangement of the particles, induced by their magnetic interaction, is insignificant ($|G_m^{(1)}| > G_m^{(2)}$, i.e., $G_0 \gg \mu_0H^2$) the field reduces the total shear modulus G of the composite ($G_m^{(1)}$ is negative). In the opposite case ($\mu_0H^2 > G_0$), the magnetically induced anisotropy of the particles' dispositions is strong enough ($G_m^{(2)} > |G_m^{(1)}|$) and the magnetic field enhances the modulus. It should be noted that in very soft gels this rearrangement can lead to the appearance of chainlike and other heterogeneous anisotropic structures (see, for example, [15,17]). However, analysis of these strong structural transformations is beyond the present consideration.

The second term (-0.213φ) in parentheses in the formula (26) for $G_m^{(1)}$ takes place due to correlations in the positions of the particles in the composite. This term reduces the absolute value of $G_m^{(1)}$ and enhances the total modulus G.

Let us estimate now the moduli $G_m^{(1)}$ and $G_m^{(2)}$. By using the typical magnitudes $\varphi \sim 0.1$ and $H \sim 100$ kA/m in the first relation in (26), we get $|G_m^{(1)}| \sim 10^2$ Pa. The second relation in (26) leads to the estimate $G_m^{(2)}/G_0 \sim (\varphi\mu_0H^2/G_0)^2$; the same magnitudes of the field and the concentration give $G_m^{(2)}/G_0 \sim (10^3\ \text{Pa}/G_0)^2$. Therefore, for the soft gels with $G_0 \sim 10^3$ Pa, the modulus $G_m^{(2)}$, which appears due to the magnetically induced rearrangement of the particles, is quite comparable with the host polymer modulus G_0. The term $G_m^{(1)}$, for these parameters of the system, is an order of magnitude less than G_0 and $G_m^{(2)}$.

It is interesting to discuss the effect of the *multipolar* interaction (3) between the particles as compared with the effect of the often-used simplest dipole-dipole approximation. In the last approximation, the energy U of the interparticle interaction and the component M_x of the particle magnetization can be obtained from Eqs. (3) and (4), setting $a_i = 0$ and $c_i = 0$ for $i = 4, \ldots, 7$. After that, instead of (24), we get

$$J \approx 1.62 - 1.68\varphi, \quad K \approx 9.1 + 6\varphi. \tag{27}$$

A comparison of (24) and (27) shows that the multipolar effects are significant and must be taken into account for the determination of macroscopic properties of magnetic gels. Nevertheless, in both approximations the parameter J is positive. This means that $G_m^{(1)}$ is negative.

The result $G_m^{(1)} < 0$, from the first point of view, is rather unexpected. Its microscopic explanation can be given from the following considerations.

Let us suppose that we determine the component M_x of particle 1 in Fig. 3. This component appears due to magnetic interaction between particle 1 and some particle 2. Because the

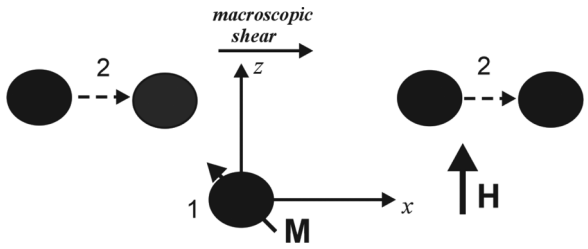

FIG. 3. Sketch of the positions of particle 2 before and after the macroscopic shear. The dashed arrows illustrate the particle 2 displacement. The vector **M** is magnetization of particle 1.

initial spatial distribution of the particles is isotropic, particle 2, with equal probability, can be situated either to the left or symmetrically to the right of the axis Oz. Obviously, if particle 2 is to the left of this axis, the magnetization vector **M** of the first particle deviates to the left (i.e., M_x is negative); if particle 2 is situated to the right of Oz, the component M_x is positive. Because of the symmetrical positions of the second particles in the nondeformed sample, the resulting value of M_x, before deformation, is zero. However, after the shear, the left particle 2 becomes closer to particle 1 than the right particle. That is why its influence on the magnetization **M** is stronger than the effect of the right particle. As a consequence, the resulting vector **M** is deviated to the left of the axis Oz, i.e., the resulting component M_x is negative. This leads to the negative sign of the term $G_m^{(1)}$.

VI. CONCLUSION

We have suggested a model of the effective shear modulus of magnetic gels with a random and isotropic spatial distribution of spherical magnetizable particles in an elastic matrix. The model is based on the mathematically regular approximation of the pair interaction between the particles and takes into account the effects of the elastic (through the host matrix deformations) as well as magnetic interaction between the particles. The appearance of internal anisotropy of the composite, because of the particles' rearrangement under the magnetic interaction, is taken into account.

Our analysis shows that, if the magnetically induced anisotropy of the composite is insignificant, magnetic interaction between the particles leads to decreasing dependence of the effective shear modulus on the applied magnetic field. If the anisotropy is strong enough, the modulus increases with the field.

It should be noted that the presented results were obtained under the assumption that the particles are spherical and magnetically soft (do not have remnant magnetization). That is why the particles do not rotate (turn round) under the action of the local magnetic field. In real composites these conditions can be broken. Moreover, on the stage of composite synthesis and matrix polymerization, some of the particles can form various heterogeneous aggregates. In the cured matrix these aggregates can turn round, under the field and the shear action, as whole clusters. This effect can mask the effects of the interparticle interaction considered in the present work and induce an increasing dependence of the composite modulus on the applied field. Analysis of these situations requires detailed study and is left for future work.

Keeping in mind the development of a mathematically regular approach, we have considered only relatively small displacement of the particles in the elastic matrix. In soft ferrogels the particles, under the action of a strong field, can undergo large displacements and form various anisotropic heterogeneous structures. These structural transformations induce hysteretic magnetic and mechanic behavior of the composites [15,17]. An approach for the description of these phenomena has been suggested in [35].

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[1] G. Filipcsei, I. Csetneki, A. Szilagyi, and M. Zrınyi, Adv. Polym. Sci. **206**, 137 (2007).
[2] A. Boczkowska and S. F. Awietjan, Mater. Sci. Forum **636–637**, 766 (2010).
[3] M. van Bruggen and J. van Zon, Sensor. Actuat. A: Phys. **158**, 240 (2010).
[4] S. van Berkum, J. T. Dee, Albert P. Philipse, and B. H. Erné, Int. J. Mol. Sci. **14**, 10162 (2013).
[5] M. Bañobre-López, Y. Piñeiro-Redondo, R. De Santis, A. Gloria, L. Ambrosio, A. Tampieri, V. Dediu, and J. Rivas, J. Appl Phys. **109**, 07B313 (2011).
[6] B. Das, M. Mandal, A. Upadhyay, P. Chattopadhyay, and N. Karak, Biomed. Mater. **8**, 035003 (2013).
[7] A. Gloria *et al.*, J. R. Soc. Interface **10**, 20120833 (2013).
[8] Y. Li, G. Huang, X. Zhang, B. Li, Y. Chen, T. Lu, T. J. Lu, and F. Xu. Adv. Funct. Mater. **23**, 660 (2013).
[9] S. Panseri, C. Cunha, T. D'Alessandro, M. Sandri, G. Giavaresi, M. Marcacci, C. T. Hung, and A. Tampieri, J. Nanobiotechnol. **10**, 32 (2012).
[10] X. B. Zeng, H. Hu, L. Q. Xie, F. Lan, W. Jiang, Y. Wu, and Z. W. Gu, Int. J. Nanomed. **7**, 3365 (2012).
[11] R. K. Singh, K. D. Patel, J. H. Lee, E.-J. Lee, J.-H. Kim, T.-H. Kim, and H.-W. Kim, PLoS One **9**, e91584 (2014).
[12] M. T. Lopez-Lopez, G. Scionti, A. C. Oliveira, J. D. G. Duran, A. Campos, M. Alaminos, and I. A. Rodriguez, PLoS One **10**, e0133878 (2015).
[13] M. T. Lopez-Lopez, J. D. G. Durán, L. Y. Iskakova, and A. Y. Zubarev, J. Nanofluids **5**, 1 (2016).
[14] N. Kchit, P. Lancon, and G. Bossis, J. Phys. D **42**, 105506 (2009).
[15] G. V. Stepanov, S. S. Abramchuk, D. A. Grishin, L. V. Nikitin, E. Y. Kramarenko, and A. R. Khokhlov, Polymer **48**, 488 (2007).
[16] Y. Shen, M. F. Golnaraghi, and G. R. Heppler, J. Intell. Mater. Struct **15**, 27 (2004).
[17] G. Stepanov, D. Borin, Y. Raikher, P. Melenev, and N. S. Perov, J. Phys.: Condens. Matter **20**, 204121 (2008).
[18] G. Diguet, E. Beaugnon, and J. Y. Cavaille, J. Magn. Magn. Mater. **322**, 3337 (2010).
[19] D. Romeis, V. Toshchevikov, and M. Saphiannikova, Soft Matter **12**, 9364 (2016).
[20] D. S. Wood and P. J. Camp, Phys. Rev. E **83**, 011402 (2011); P. J. Camp, Magnetohydrodynamics **47**, 123 (2011).

[21] M. R. Jolly, J. D. Carlson, B. C. Muñoz, and T. A. Bullions, J. Intell. Mater. Syst. Struct. **7**, 613 (1996).
[22] K. Danas, S. V. Kankanala, and N. Triantafyllidis, J. Mech. Phys. Solids **60**, 120 (2012).
[23] Y. Han, W. Hong, and L. E. Faidley, Int. J. Solids Struct. **50**, 2281 (2013).
[24] S. R. Khimi and K. L. Pickering, Compos. Part B: Eng. **83**, 175 (2015).
[25] R. Cristensen, *Mechanics of Composite Materials* (Wiley, New York,1979).
[26] R. Rosensweig, *Ferrohydrodynamics* (Cambridge University Press, Cambridge, 1985).
[27] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuum Media* (Pergamon, London, 1960).
[28] G. K. Batchelor and J. T. Green, J. Fluid Mech. **56**, 4101 (1972).
[29] D. Borin, D. Günther, C. Hintze, G. Heinrich, and S. Odenbach, J. Magn. Magn. Mater. **324**, 3452 (2012).
[30] A. M. Biller, O. V. Stolbov, and Y. L. Raikher, J. Appl. Phys. **116**, 114904 (2014).
[31] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon, London, 1970).
[32] Y. Shkel and D. Klingenberg, J. Appl. Phys. **83**, 7834 (1998).
[33] G. K. Batchelor, J. Fluid Mech. **83**, 97 (1977).
[34] R. Balesku, *Equilibrium and Nonequilibrium Statistical Mechanics* (Wiley, New York, 1975), Vol. 1.
[35] A. Y. Zubarev, D. N. Chirikov, D. Y. Borin, and G. V. Stepanov, Soft Matter **12**, 6473 (2016).