Thermodynamics of interacting single-domain superparamagnetic particles frozen in the nodes of the regular cubic lattice

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(Dated: August 12, 2020)

In this work, we study the effect of dipole-dipole interparticle interactions on the static thermodynamic and magnetic properties of an ensemble of immobilized monodisperse superparamagnetic particles. We assume that magnetic particles are embedded on the nodes of the regular cubic lattice so, that particle translational degrees of freedom are turned out. The relaxation of the magnetic moments of the particles occurs by the Néel mechanism. The easy axes are distributed according to the particular textures: these are (i) aligned parallel or (ii) perpendicular to the direction of an external field. This model is investigated using theory and computer simulation taking microscopic discrete structure explicitly into account. The theory is based on the virial expansion of the Helmholtz free energy up to the second virial coefficient. The analytical approximations of the Helmholtz free energy, the static magnetization, and the initial magnetic susceptibility are derived for both texturing types (i) and (ii) as functions of the height of the magnetic crystallographic anisotropy energy barrier for internal superparamagnetic rotation of magnetic moments inside the particles. The obtained theoretical results describing the model system are compared against Monte-Carlo simulation data.

I. INTRODUCTION

Smart materials, called also responsive or intelligent materials, are special materials that have one or more properties that can be significantly changed in a controlled fashion by external stimuli, for example magnetic field. Such materials include magnetic composites which is produced by embedding magnetic nanoparticles in liquid or polymer matrix. The examples of these composites are ferrofluids, magnetic elastomers, ferrogels, magnetic emulsions, and various biocompatible magnetic filling [1–3]. Nowadays, such materials are widely used in various medical applications because of the ability to actively respond to applied magnetic field. For example, they are an indispensable tool in magnetic hyperthermia, in which micromotions of ferroparticles in an alternating magnetic field leads to heating and destruction of tumor cells [4–8].

The response of the magnetic composites to the applied magnetic field is determined by two main physical mechanisms of the magnetic moment orientational relaxation in nanosized particles. They are the Brownian rotation of particles with fixed magnetic moments and the superparamagnetic Néel rotation of the magnetic moments inside the particles due to thermal fluctuations [9–10]. For ensemble of nanoparticles, suspended in some liquid carriers, known as ferrofluids, both mechanisms take place. But in the case, when particles are embedded in some polymer matrix or biological tissues, the particles often lose their translational and orientational degrees of freedom. In this case, the superparamagnetic Néel relaxation becomes the major mechanism determining the magnetic properties of the ensembles of such immobilized particles.

Nowadays there exist many established synthesis techniques that make it possible to generate magnetic composite with different microscopic architecture [8] [11–15]. A different distribution of magnetic particles inside the sample leads to a significant change in its bulk properties [16–18]. In addition, interparticle dipole-dipole interactions have a strong effect on the macroproperties of the system, and this is manifested differently in liquid or polymer based composites. So, the strong interparticle dipole-dipole interactions lead to aggregation in the ferrofluid [19–22], whereas in the system of immobilized ferroparticles the interparticle interactions can only be a cause of the structuring of the magnetic moments of the particles, since the particles themselves remain stationary [23–25]. The effects of dipole-dipole interactions on the bulk properties of ferrofluids are well understood theoretically [26–30], experimentally [31–33], and by computer simulation methods [27–29, 34], while the theory of the effect of interactions on immobilized superparamagnetic particles still remains a challenge.

In our recent studies, using statistical-mechanical theory and computer simulations, we investigated magnetic response of the system of immobilized interacting single-domain particles distributed randomly [18] or placed at the nodes of a simple cubic lattice [25] within an implicit solid matrix. In the first work [18] superparamagnetic particles with uniaxial magnetic anisotropy were considered. The relaxation of the magnetic moments of particles occurs by the Néel mechanism. The easy axes were distributed according to the particular textures: these are aligned parallel or perpendicular to an external magnetic field, or randomly distributed. The initial magnetic susceptibility was found to depend on magnetic crystallographic anisotropy barrier (measured with respect to the thermal energy by a parameter σ) in very different ways for various texture. With a parallel texture, the initial

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susceptibility increases with increasing $\sigma$, while with a perpendicular texture, the initial susceptibility decreases. With a random distribution, the initial susceptibility is independent on $\sigma$. In all cases, including interactions between particles leads to an enhancement of the initial susceptibility, but the enhancement is much stronger for the parallel texture than for the perpendicular or random textures. In the second work [25] we assumed that ferroparticles are embedded on the nodes of the simple cubic lattice (SCLF) and can rotate at the lattice nodes under the influence of the external magnetic field and as a result of the interparticle dipolar interactions, but the particles cannot change their position. The magnetic properties of SCLF and ferrofluid, modeled by a system of dipole hard spheres (DHS), were compared. It has been found that at low intensities of the dipole-dipole interaction the magnetization of DHS and SCLF is the same. For strong and moderate dipolar coupling regime and at the weak magnetic field, the magnetization of the DHS system is higher than the magnetization of SCLF, while the opposite tendency is observed at stronger fields. The reasons of this behavior were discussed in the article [25].

These two works [18, 25] provided deep and important information about the relationship between microstructure and macroproperties of the magnetic composites. Nevertheless, the theory is still incomplete and the topic is not fully understood. The aim of this work is to combine previous research and study a new model – a monodisperse system of immobilized interacting single-domain spherical ferroparticles, with uniaxial magnetic anisotropy, placed at the nodes of a simple cubic lattice.

II. MODEL AND METHODS

A. Model

The sample under consideration consists of $N$ immobilized superparamagnetic spherical nanoparticles distributed by the regular way at the simple cubic lattice nodes with period $a$. All particles have the same magnetic-core diameter $d$ and magnetic moment $m = v_m M_s$, where $M_s$ is the bulk saturation magnetization, $v_m = \pi d^3 / 6$ is the magnetic core volume. The radius vector and magnetic moment of particle $i$ are $\hat{r}_i = r_i \hat{r}_i$ and $\mathbf{m}_i = m_i \Omega_i$, respectively, where $\hat{r}_i = (\sin \theta_i \cos \phi_i, \sin \theta_i \sin \phi_i, \cos \theta_i)$ and $\Omega_i = (\sin \omega_i \cos \xi_i, \sin \omega_i \sin \xi_i, \cos \omega_i)$ are unit vectors.

The magnetic moment of a particle has two degenerate ground-state directions, these being parallel and anti-parallel to the easy axis, denoted by the vector $\mathbf{n}_i$. The Nel energy $U_N$ as a function of the angle between $\mathbf{m}_i$ and $\mathbf{n}_i$ is given by

$$U_N(i) = -K(v_m \Omega_i \cdot \mathbf{n}_i)^2,$$

where $\mathbf{n}_i$ is a unit vector, $K$ is the magnetic crystallographic anisotropy constant (a material property).

The interaction between magnetic moment $\mathbf{m}_i$ and uniform external magnetic field $\mathbf{H}$ is described by Zeeman energy

$$U_m(i) = -\mu_0 (\mathbf{m}_i \cdot \mathbf{H}) = -\mu_0 m H (\Omega_i \cdot \hat{h}),$$

where assumed that the applied magnetic field $\mathbf{H}$ has the strength $H$ and the orientation $\hat{h}$. The pair dipole-dipole interaction of two particles $i$ and $j$ obeys to the anisotropic potential $U_d$

$$U_d(ij) = \frac{\mu_0 m^2}{4 \pi r_{ij}^3} \left[ (\Omega_i \cdot \Omega_j) - 3(\Omega_i \cdot \hat{r}_{ij})(\Omega_j \cdot \hat{r}_{ij}) \right],$$

where $r_{ij} = r_{ij}(\hat{r}_{ij} = \hat{r}_j - \hat{r}_i)$ has the meaning of the center-center separation vector with length $|r_{ij}| = r_{ij}$.

The total potential energy normalized by the thermal energy $k_B T = \beta^{-1}$ has the following form

$$\beta U = \beta \sum_{j>i=1}^{N} U_d(ij) - \sigma \sum_{i=1}^{N} (\Omega_i \cdot \mathbf{n}_i)^2 - \alpha \sum_{i=1}^{N} (\Omega_i \cdot \hat{h}),$$

where the dimensionless anisotropy parameter $\sigma = \beta v_m K$ and Langevin parameter $\alpha = \beta \mu_0 m H$ are introduced. The relations between the pair magnetic interaction and the thermal energy is measured by the effective dipolar coupling constant $\lambda_e$

$$\lambda_e = \frac{\mu_0 m^2 \beta}{4 \pi a^3},$$

the definition of which takes into account that two particles located in the nodes of the simple cubic lattice can not be closer than the lattice period $a \geq x$.

Two types of orientational distributions of the easy axes will be considered: aligned (i) parallel and (ii) perpendicular to the direction of an external field $\mathbf{H}$. To simplify analytical calculations, easy axes of both configuration are assumed to be aligned along the laboratory $Oz$ axis namely $\hat{n}_i = (0, 0, 1)$, so the Nel energy can be represented as

$$U_N(i) = -\sigma \cos^2 \omega_i.$$

The direction of external magnetic field $\mathbf{H}$ is set (i) $\mathbf{H} = H(0, 0, 1)$ in parallel configuration so that

$$U_m^l(i) = -\alpha \cos \omega_i$$

and (ii) $\mathbf{H} = H(1, 0, 0)$ in perpendicular configuration so

$$U_m^p(i) = -\alpha \sin \omega_i \cos \xi_i.$$

For vanishing of demagnetization fields, we will assume that the sample container has a long cylindrical shape elongated in the direction of an external magnetic field $\mathbf{H}$. The sample geometries studied in this work are given in Fig. [1]
FIG. 1. Monodisperse system of immobilized single-domain superparamagnetic ferroparticles placed at the nodes of a simple cubic lattice at external magnetic field for (a) parallel and (b) perpendicular configurations.

B. The Helmholtz Free Energy of ensemble of immobilized particles

1. Ideal system

The definition of the Helmholtz free energy $F$ contains configurational integral $Z$ so, that

$$
\beta F = - \ln (Z).
$$

To extract the contribution of the dipole-dipole interaction it is convenient to split the Helmholtz free energy $F$ into two parts

$$
F = F_{id} + \Delta F.
$$

The first term corresponds the ideal system of superparamagnetic non-interacting particles in applying magnetic field, the configurational integral $Z_{id}$ of which is

$$
\beta F_{id} = - \ln (Z_{id}), \quad Z_{id} = \prod_{k=1}^{N} \int p(r_k) d\mathbf{r}_k d\Omega_k \times \exp \left( \sum_{i=1}^{N} [\alpha (\mathbf{\Omega}_i \cdot \mathbf{\hat{h}}) + \sigma \cos^2 \omega_i] \right),
$$

$$
d\mathbf{r}_k = r_k^2 \sin \theta_k d\theta_k d\phi_k, \quad d\Omega_k = \frac{1}{4\pi} \sin \omega_k d\omega_k d\xi_k.
$$

In this definition $p(r_k)$ describes the probability of the location of the particle $k$ in the given point in the volume

$$
p(r_k) = \delta (r_k - r_k^{(0)}).
$$

The 'lattice position' of the particle $r_k^{(0)}$ may obey to a regular or a random law. For both cases the normalization rule is

$$
\int p(r_k) d\mathbf{r}_k = 1.
$$

Therefore in the integrand function of Eq. (12), there are no dependencies from the particles’ positions. With this integration, all particles are equivalent to each other. This allows us to rewrite $Z_{id}$ as follows

$$
Z_{id} = \left( \int d\Omega_1 \exp \left[ \alpha (\mathbf{\Omega}_1 \cdot \mathbf{\hat{h}}) + \sigma \cos^2 \omega_1 \right] \right)^N,
$$

the result of which can be calculated numerically for each set of parameters $\alpha$ and $\sigma$ and fixed direction of vector $\mathbf{\hat{n}}_1$. It worth be stressed, that the Helmholtz free energy of ideal system

$$
\frac{\beta F_{id}}{N} = - \ln \left( \int d\Omega_1 \exp \left[ \alpha (\mathbf{\Omega}_1 \cdot \mathbf{\hat{h}}) + \sigma \cos^2 \omega_1 \right] \right),
$$

does not depend on parameter $\lambda$, which characterizes the dipole-dipole interparticle interactions.

2. System with interparticle dipole-dipole interactions

The second term $\Delta F$ in (10) corresponds to the contribution of the dipole-dipole correlations in the Helmholtz free energy

$$
\beta \Delta F = - \ln \left( \frac{Z}{Z_{id}} \right).
$$
Reduced the method of [25], which was developed for linear term and it is limited by the second virial coefficient obtained due to the logarithm expansion of (19) up to the third order in terms of the dipolar energy $U_d$. It should be emphasized that approximation (24) is obtained due to the logarithm expansion of (19) up to the linear term and it is limited by the second virial coefficient level, that means the consideration of the interparticle interactions in all ferroparticle pairs only.

This definition of $\Delta F$ is valid for the regular types of particle distribution in the system volume, such as SCLF or other types of lattices. For the random distribution of ferroparticles in sample volume it is necessary to average (24) over all possible random configurations. It means that in the limit every particle $j$ in sum of (24) can occupy any position in the sample volume except the position of particle $1$:

\[
\frac{Z}{Z_{id}} = \frac{1}{Z_{id}} \prod_{k=1}^{N} \int p(\mathbf{r}_k) d\mathbf{r}_kd\mathbf{Ω}_k \exp \left(- \sum_{j>i=1}^{N} \beta U_d(ij) \right) + \sum_{i=1}^{N} \left[ \alpha(\mathbf{Ω}_i \cdot \hat{\mathbf{h}}) + \sigma \cos^2 \omega_i \right],
\]

(20)

where $Z$ is the configurational integral of the SCLF, including dipole-dipole interaction. Introducing the Boltzmann-weighted averaging over the magnetic moment orientation of the particle $k$

\[
d\Psi_k = \frac{d\mathbf{Ω}_k \exp \left[ \alpha(\mathbf{Ω}_k \cdot \hat{\mathbf{h}}) + \sigma \cos^2 \omega_k \right]}{\int d\mathbf{Ω}_1 \exp \left[ \alpha(\mathbf{Ω}_1 \cdot \hat{\mathbf{h}}) + \sigma \cos^2 \omega_1 \right]},
\]

(21)

one can rewrite definition (20) in more compact form

\[
\frac{Z}{Z_{id}} = \prod_{k=1}^{N} \int p(\mathbf{r}_k) d\mathbf{r}_kd\Psi_k \prod_{j>i=1}^{N} \left( 1 + f_{ij} \right),
\]

(22)

\[
f_{ij} = \exp (-\beta U_d(ij)) - 1,
\]

(23)

where $f_{ij}$ is the Mayer function. This approach is reproduced the method of [25], which was developed for $\sigma = 0$. The main difference is the definition of the Boltzmann-weighted integration $d\Psi_k$ [21], which in our case also depends on the anisotropy parameter $\sigma \geq 0$ and coincides with the same from [25] for $\sigma = 0$. Therefore, it is possible to apply the final results for configurational part of the Helmholtz free energy from [25] to our system with the new definition of operator $d\Psi_k$:

\[
\frac{\beta \Delta F}{N} = - \frac{1}{2} \sum_{j=2}^{N} \left\langle f^{(0)}_{1j} \right\rangle.
\]

(24)

where $f^{(0)}_{1j} = \int p(\mathbf{r}_1) d\mathbf{r}_1 f_{1j}$, the Mayer function of the particles $1$ and $j$ in their 'lattice positions'. The angle brackets in (24) denote a Boltzmann-weighted integration [21] over the orientation of both particles $1$ and $j$

\[
\left\langle f^{(0)}_{1j} \right\rangle = \int f^{(0)}_{1j} d\Psi_1 d\Psi_j.
\]

(25)

It should be emphasized that approximation (24) is obtained due to the logarithm expansion of (19) up to the linear term and it is limited by the second virial coefficient level, that means the consideration of the interparticle interactions in all ferroparticle pairs only.

Dipole-dipole potential $U_d$ includes the dependencies over both translational and orientational degrees of freedom of the particles $1$ and $j$. Applying the Boltzmann-weighted integration over the magnetic moment’s orientations $\mathbf{m}_1$ and $\mathbf{m}_j$, it is possible to represent the value of $\beta \Delta F$ in the common form

\[
\frac{\beta \Delta F}{N} = - \frac{1}{2} \sum_{j=2}^{N} \left\langle \frac{1}{\lambda_e} \left( -\beta U_d(1j) \right)^{3} \right\rangle.
\]

(26)

\[
b_1 = \sum_{j=2}^{N} \left\langle \frac{1}{\lambda_e} \left( -\beta U_d(1j) \right)^{2} \right\rangle,
\]

(27)

\[
b_2 = \sum_{j=2}^{N} \left\langle \frac{1}{\lambda_e} \left( -\beta U_d(1j) \right)^{3} \right\rangle.
\]

(28)

The coefficients $b_1$, $b_2$ and $b_3$ are different for parallel and perpendicular configurations and will be discussed for each case separately.

C. Parallel configuration of SCLF with superparamagnetic nanoparticles

Parallel configuration corresponds to the illustration in Fig. 1(a), that means $\langle \mathbf{Ω}_1 \cdot \hat{\mathbf{h}} \rangle = \langle \mathbf{Ω}_i \cdot \hat{\mathbf{n}}_i \rangle = \cos \omega_1$. In this case the ideal part of the Helmholtz free energy (18) is equal to

\[
\frac{\beta F_{id}}{N} = - \ln \left[ Q_0(\alpha, \sigma) \right],
\]

(31)

where

\[
Q_0(\alpha, \sigma) = \frac{1}{2} \int_{-1}^{1} \exp \left( \alpha t + \sigma t^2 \right) dt,
\]

(32)

\[
Q_0(\alpha, 0) = \frac{\sinh \alpha}{\alpha}.
\]

(33)
The Boltzmann-weighted integration over the orientation of particle magnetic moment for parallel configuration looks like

\[ d\Psi_k = \frac{d\Omega_k \exp(\alpha \cos \omega_k + \sigma \cos^2 \omega_k)}{Q_0(\alpha, \sigma)}. \]  

(34)

Details of the averaging of the coefficients \( b_1, b_2, b_3 \) over magnetic moment orientations and particle positions are derived in Appendix A. The final analytical expression for \( \Delta F \) expansion can be presented as

\[ \frac{\beta \Delta F}{N} = -2.0944Q_1^2(\alpha, \sigma)\lambda_c \]

\[ - [1.939Q_2^2(\alpha, \sigma) + 1.4003] \lambda_c^2 \]

\[ - [0.1611Q_3^2(\alpha, \sigma) + 1.5595Q_1(\alpha, \sigma)Q_3(\alpha, \sigma)] \]

\[ - 0.7285Q_4^2(\alpha, \sigma)\lambda_c^3, \]  

(35)

where additional functions \( Q_k(\alpha, \sigma) \) are defined in Appendix A. It is well known that the virial expansion for a system with dipole-dipole interactions is an alternating series \([36, 37]\), and therefore it is very sensitive to truncation of the series. Hence, it could be more efficient to transform the virial expansion of the Helmholtz free energy \((35)\) into the logarithmic form \((19)\):

\[ \frac{\beta \Delta F}{N} = -\ln \left\{ 1 + 2.0944Q_1^2(\alpha, \sigma)\lambda_c \right\} \]

\[ + [1.9390Q_2^2(\alpha, \sigma) + 1.4003] \lambda_c^2 \]

\[ + [0.1611Q_3^2(\alpha, \sigma) + 1.5595Q_1(\alpha, \sigma)Q_3(\alpha, \sigma)] \]

\[ - 0.7285Q_4^2(\alpha, \sigma)\lambda_c^3 \}, \]  

(36)

so that the terms from the right-hand side of the Eq. \((35)\) are the first terms of the Maclaurin expansion of the logarithm in \((36)\). The advantage of the logarithmic form is that the logarithm of a polynomial is less sensitive to polynomial truncation at the low order in \(\lambda_c\)-expansion. Firstly suggested in \([38]\), this method allowed to expand the theory’s applicability range over both volume particles’ concentration and dipolar coupling constant for the prediction of the dipolar hard sphere fluid properties \([25, 59, 40]\). The typical behavior of the dipole-dipole contribution in the Helmholtz free energy \(\Delta F\) as a function of the anisotropy parameter \(\sigma\) is shown in Fig. 2 with \(\alpha = 0, 1, 2, \) and 5, and a rather large value of intensity of dipole-dipole interactions \(\lambda_c = 0.5\). For \(0 \leq \sigma \leq 5\) one can note more fast increasing of contribution \(\Delta F\) than the same for \(\sigma > 5\). In parallel configuration, anisotropy axes play a role addition stimulus to alignment of magnetic moments along the external magnetic field, that leads to increasing of the Helmholtz free energy with increasing anisotropy parameter \(\sigma\). The dependence of \(\Delta F\) from the intensity of the external magnetic field is shown in Fig. 3 with \(\sigma = 0, 2, 5, \) and 10, and \(\lambda_c = 0.5\). The contribution \(\Delta F\) is more sensitive to change of anisotropy parameter in intermediate magnetic fields \(1 \leq \alpha \leq 5\), whereas at \(\alpha \approx 10\) different between values of \(\Delta F\) with grows of \(\sigma\) is not sensitive.

**D. Perpendicular configuration of SCLF with superparamagnetic nanoparticles**

Perpendicular configuration is illustrated in Fig. 1(b), that corresponds \((\Omega_i \cdot \hat{h}) = \sin \omega_i \cos \xi_i\). In this case the ideal part of the Helmholtz free energy \((18)\) is equal to

\[ \frac{\beta F_{id}}{N} = -\ln \left[ R_0(\alpha, \sigma) \right], \]  

(37)
\[ R_0(\alpha, \sigma) = \int_0^1 \exp(\sigma t^2) I_0(\alpha \sqrt{1-t^2}) dt, \]  
\[ R_0(\alpha, 0) = \frac{\sin \alpha}{\alpha}. \]  
(38)  
(39)

Here \( I_0(x) \) is the modified Bessel function of zero order.

The Boltzmann-weighted integration over the orientation of particle magnetic moment for perpendicular configuration looks like

\[ d\Psi_k = \frac{d\Omega_k \exp(\alpha \sin \omega_k \cos \xi_k + \sigma \cos^2 \omega_k)}{R_0(\alpha, \sigma)}. \]  
(40)

Details of the averaging of the coefficients \( b_1, b_2, b_3 \) over magnetic moment orientations and particle positions are derived in Appendix B. The final analytical expression for \( \Delta F \) in the logarithmic form is

\[ \frac{\beta \Delta F}{N} = -\ln \left\{ 1 + 2.0944 R_1^2(\alpha, \sigma) \lambda_c + 1.4542 R_2^2(\alpha, \sigma) + 4.3627 R_3^2(\alpha, \sigma) - 2.9085 R_3(\alpha, \sigma) + 1.8851 \lambda_c^2 + 2.8736 R_4(\alpha, \sigma) R_5(\alpha, \sigma) - 0.1429 R_4(\alpha, \sigma) R_6(\alpha, \sigma) + 0.2454 R_5(\alpha, \sigma) R_6(\alpha, \sigma) - 1.3856 R_4^2(\alpha, \sigma) - 0.4960 R_5^2(\alpha, \sigma) - 1.3856 R_6^2(\alpha, \sigma) \lambda_c^3 \right\}. \]  
(41)

Functions \( R_k(\alpha, \sigma) \) are defined in Appendix B.

The dependence of the dipole-dipole contribution in the Helmholtz free energy \( \Delta F \) as a function of the anisotropy parameter \( \sigma \) is shown in Fig. 4 with \( \alpha = 0, 1, 2, \) and \( 5 \) and different value of \( \lambda_c = 0.5 \) (black curve). In the area of low values of anisotropy parameter the increase of magnetic field intensity leads to increasing of the dipole-dipole contribution in the Helmholtz free energy, but than all curves coincide with each other and show constant value for \( \sigma \geq 8 \). It means that for perpendicular configuration the dipolar part of the Helmholtz free energy \( \Delta F \) for model system with \( \sigma \gg 0 \) depends mainly on the intensity of dipolar interaction \( \lambda \) and almost independent of \( \alpha \) and \( \sigma \). This fact can be found also from Fig. 5, where the \( \Delta F \) is shown as a function of \( \alpha \). At \( \sigma = 10 \) (green curve) the behavior of \( \Delta F \) is not very sensitive to increasing of the Langevin parameter.

![FIG. 4. The contribution of the dipole-dipole interactions \( \Delta F \) for perpendicular configuration as a function of the anisotropy parameter \( \sigma \) for the system with \( \lambda_c = 0.5 \) and different value of \( \alpha = 0, 1, 2, 5 \). The value of \( \alpha \) grows from bottom to top.](image)

![FIG. 5. The contribution of the dipole-dipole interactions \( \Delta F \) for perpendicular configuration as a function of the Langevin parameter \( \alpha \) for the system with \( \lambda_c = 0.5 \) and different value of \( \sigma = 0, 5 \), and 10.](image)

### E. Simulation

In order to check the accuracy of the new theory and find the range of its applicability, its predictions were thoroughly tested against computer simulation data. Monte Carlo (MC) simulations were carried out in the canonical \((NVT)\) ensemble for \( N = 512 \) dipolar hard spheres embedded at the lattice nodes. The model configuration was generated inside a cubic box, for which 3D periodic boundary conditions were applied. To vanish all demagnetization effects the Ewald summation with conducting boundary conditions was used for computing the long-range dipole-dipole interactions between ferroparti-
cles. It was assumed that the external magnetic field was directed along the \(Oz\) axis. The easy axes were unit vectors parallel to (i) the laboratory \(Oz\) axis in parallel configuration and (ii) the laboratory \(Ox\) axis in perpendicular configuration. To overcome the anisotropy barrier for large values of \(\sigma\), there were two equiprobable types of rotational move: the ordinary random displacement and a flip move \(m \rightarrow -m\) [18]. Typical run lengths consisted of \(10^6\) attempted rotations per particle after equilibration. Estimates of statistical errors were calculated using the blocking procedure described in [41]. In all cases, the obtained values of statistical errors does not exceed the size of symbols using for simulation data on the plots.

The Helmholtz free energy can not be measured by numerical method directly, therefore its derivatives (the scalar magnetization and the initial magnetic susceptibility) were used to investigation the validity of the new theory. For both parallel and perpendicular configurations, the fractional magnetization was computed in the simulation as

\[
M = \frac{1}{N} \left( \sum_{i=1}^{N} \cos \omega_i \right)_t, \quad (42)
\]

where \(\langle \ldots \rangle_t\) means the average over simulation time. The initial magnetic susceptibility was calculated at \(\alpha = 0\) in the \(z\) direction only:

\[
\chi = \chi_L \left( \sum_{i=1}^{N} \cos \omega_i \right)^2_2 \left( \frac{3}{N} \right), \quad (43)
\]

where the Langevin susceptibility \(\chi_L\) can be express via parameter \(\lambda_e\) using the relation \(\rho = 1/a^3\) for the simple cubic lattice

\[
\chi_L = \frac{4\pi \mu_0 \rho m^2}{3k_B T} = \frac{4\pi}{3} \lambda_e. \quad (44)
\]

To check the simulation algorithm with large values of anisotropy parameter, the ideal system of superparamagnetic ferroparticles was modeled where interparticle interaction turned off. In this case the exact theoretical results are known:

\[
M_{id} = -\frac{\partial}{\partial \alpha} \left( \frac{\beta F_{id}}{N} \right), \quad (45)
\]

\[
\chi_{id} = -\frac{1}{V} \frac{\partial^2 F_{id}}{\partial H^2} \bigg|_{H=0}, \quad (46)
\]

where \(F_{id}\) is defined by [31] for parallel configuration and [37] for perpendicular configuration. In Fig. 6 and 7 one can find the excellent agreement between obtained simulation data and ideal approximations (45) and (46) for both magnetization and the initial magnetic susceptibility.

**III. RESULTS**

The analytical expression of the Helmholtz free energy allows us to obtain predictions for various magnetic and thermodynamic properties of the system. So, the scalar magnetization is defined by
FIG. 8. The static magnetization as a function of the Langevin parameter $\alpha$ for systems with (a) $\lambda_e = 0.1$, (b) 0.3 and (c) 0.5. Solid lines correspond new theories for $M_{||}$ and $M_{\perp}$, dashed lines are ideal approximation [45]. Symbols are from Monte-Carlo simulations. Results are shown for parallel (red squares and lines) and perpendicular (blue circles and lines) configurations with $\sigma = 5$ and for system with $\sigma = 0$ (black triangles and lines).

\[ M = M_{id} - \frac{\partial}{\partial \alpha} \left( \frac{\beta \Delta F}{N} \right), \]  

(47)

where $\Delta F$ can be found from (36) for parallel configuration and (41) for perpendicular configuration. The second term takes into account the interparticle dipole-dipole interactions in model system. Three systems were considered: with $\lambda_e = 0.1$, 0.3, and 0.5. The Langevin susceptibilities for these systems are equal to $\chi_L = 0.42$, 1.26, and 2.1 respectively. In Fig. 8 theoretical static magnetization curves are compared with MC simulation data. For $\sigma = 0$ (black curves), the theoretical predictions for both parallel and perpendicular configurations are coincident with each other, that was expected. In this case it should be noted the excellent agreement of the new theory (solid lines) with the simulation data for all considered systems, whereas the ideal approximation (dashed lines) works quite good only for system with a weak interactions ($\lambda_e = 0.1$). The same can be said about the perpendicular configuration with $\sigma = 5$ (blue curves). The magnetization of the parallel configuration
with $\sigma = 5$ increases rapidly with increasing of the magnetic field intensity, and the dipole-dipole interaction effect is more pronounced in this case. However for $\sigma = 5$ and $\lambda_e = 0.5$ small deviation between new theoretical formula (47) and simulation data is observed in the range of magnetic field $1 \leqslant \alpha \leqslant 2$.

The typical behavior of the magnetization can be described as follows: the increasing of $\sigma$ leads to the increasing of the magnetization in parallel case and decreasing the same in perpendicular configuration. This fact is clear illustrated in Fig. 9 where the simulation snapshots are given for model system with $\lambda_e = 0.5$ and $\alpha = 1$. Fig. 9 (a) corresponds the case when $\sigma = 0$ and scalar magnetization is equal to $M = 0.45$. The presence of the easy axis with $\sigma = 5$ along the external magnetic field leads to an increase in scalar magnetization almost twice, that is shown in Fig. 9 (b). Perpendicular configuration with $\sigma = 5$ is given in Fig. 9 (c), where the magnetic response of the system on the external magnetic field is very weak.

In this case the magnetic moments formed chains in the direction of the easy axis so that the scalar magnetization in direction of $\hat{n}_i$ is equal to zero, although a pronounced regular structure of the magnetic moments of all particles in the system is not yet observed for these parameters of the system.

The initial slope of magnetization curve is characterized by the initial magnetic susceptibility, which can be determined via the Helmholtz free energy as

$$\chi = \chi_{\text{id}} - \frac{1}{V} \left. \frac{\partial^2 \Delta F}{\partial H^2} \right|_{H=0}. \quad (48)$$

The comparison between theoretical predictions of $\chi$ and MC results is given in Fig. 10. Results are shown for both parallel and perpendicular configurations. As for ideal approximations (46), there is a significant discrepancy between dashed curves and simulation data in all considered systems, for parallel configuration especially.
FIG. 10. The initial magnetic susceptibility $\chi$ as a function of the anisotropy parameter $\sigma$ for systems with (a) $\lambda_e = 0.1$, (b) 0.3 and (c) 0.5. Solid lines correspond new theories for $\chi_\parallel$ and $\chi_\perp$, dashed lines are ideal approximation (46). Symbols are from Monte-Carlo simulations. Results are shown for parallel (red squares and lines) and perpendicular (blue circles and lines) configurations.

Even for weakly interacting system with $\lambda_e = 0.1$, that corresponds Fig. 10 (a), the difference between susceptibilities of the non-interacting (red dashed line) and interacting particles (red solid line) for parallel configuration is surprisingly large. Interactions lead a quick growth of susceptibility, and new theory (48) allows to accurate describe this behavior of $\chi_\parallel$. One can note the good agreement between new theory (solid lines) and MC data (symbols) for both parallel and perpendicular configurations at $\lambda_e = 0.1$. With increasing of $\lambda_e$ up to 0.3 in Fig. 10 (b), small deviation between new theory (48) and simulation data appears in the parallel configuration (red color), while for the perpendicular configuration (blue color), the agreement of theoretical and numerical results is still good. The MC results for the parallel configuration at $\lambda_e = 0.5$ (Fig. 10 (c)) demonstrate unexpectedly effect: non-monotonic behavior of susceptibility with increasing of $\sigma$. Note that the maximum achievable susceptibility value in this case is $\chi_\parallel \simeq 9$ at $\sigma \simeq 5$.

The potential reason of this behavior is that the total magnetic moment of system decreases due to appearance of magnetically compensated structures. This suggestion
can be confirmed from a visual examination of the simulation snapshots given in Fig. 11. The viewing angle on the system is changed to more clarity, so, that the blue vectors correspond to the direction of the $Oz$ axis. All systems have a high value of the anisotropy parameter $\sigma = 20$, that leads to a rigid alignment of the magnetic moments along the easy axes. For system with $\lambda_e = 0.3$ (Fig. 11 (a)), there are no regular structures in magnetic moments' direction: snapshot contains many possible variants of alignment of magnetic moments in inner chains along the easy axis. Fig. 11 (b) shows that for system with $\lambda_e = 0.5$ it is possible to note the pronounced way of arrangement of magnetic moments in chains along the easy axes: these are directed mainly in one direction within a single chain. Increasing the intensity of dipole interactions up to $\lambda_e = 1$ (Fig. 11 (c)), we have additional tendency in antiparallel alignment of chains along the easy axes, which as a result leads to a further decrease in the system’s susceptibility. This case requires some discussion. The plane perpendicular to $\hat{n}_i$ in Fig. 11 (c) has a clear checkerboard pattern, since there are four antiparallel nearest neighbors for each chain parallel to $\hat{n}_i$. For a single particle it is possible to conclude the following observations about its six nearest neighbors: two of them are form the most conducive orientation “head-to-tail”; the next four are included in the second advantageous orientation “side-by-side”. Magnetic response of such system turns out very weak and needs the strong applied magnetic field to get the magneto-active material.

From Fig. 11 one can conclude that the dependency of $\chi_\parallel$ as a function of $\lambda_e$ at the fixed value of $\sigma$ also has non-monotonic type. This fact was observed in Ref. 24 at $\sigma = 0$ and the Molecular Dynamic simulation results are denoted in Fig. 12 by black symbols with dashed black curve. It should be noted the excellent agreement between new theory (48) and simulation data up to $\lambda_e \sim 1.25$, when there are no structural transformations in magnetic systems. The further increasing of the interaction intensity leads to the decreasing of susceptibility, the reason of which is a particular behavior of the dipole ordering: almost all magnetic moments have been aligned in the long antiparallel chains along the direction of the easy axis. During the current investigation, the dependency of $\chi_\parallel$ as a function of $\lambda_e$ was calculated for systems with the easy axis, anisotropy parameters of which had the values $\sigma = 2$ and 10. The obtained MC results are denoted in Fig. 12 as red symbols with dashed red curve and blue symbols with dashed blue curve respectively. The increasing of $\sigma$ causes a shift of the susceptibility maximum to left. One can see that the value of this shift from $\sigma = 0$ to 2 turns out bigger than the same from $\sigma = 2$ to 10. Also it worse be stressed that the susceptibility fall begins when the value $\chi_\parallel \simeq 9$ is reached regardless of the value of the anisotropy parameter $\sigma$. This is consistent with the results from the Fig. 10 (c): susceptibility increases with increasing of $\sigma$ up to the value of $\chi_\parallel \simeq 9$ and decreases further. This fact al-

FIG. 11. Simulation snapshots of the model system with $\alpha = 0$ and $\sigma = 20$. Results are shown for parallel configurations with (a) $\lambda_e = 0.3$, (b) $\lambda_e = 0.5$ and (c) $\lambda_e = 1.0$. Different arrow colors correspond to different orientations of magnetic moments. The viewing angle on the system is changed to more clarity.
allows to conclude that the model system of ferroparticles can demonstrate the maximum value of susceptibility in parallel configuration $\chi_\parallel \simeq 9$, and it is the inner property of considered way of ferroparticles placement at the nodes of the simple cubic lattice. It should be emphasized that in a system of interacting immobilized superparamagnetic particles located randomly, the pronounced regular structuring of the magnetic moments of particles is not observed for the parameters under consideration [18].

New theory is able to predict the magnetic properties of the model system in the range of parameters $\lambda_e$ and $\sigma$, for which the susceptibility value turns out $\chi_\parallel \leq 9$ and there are no regular structuring of the particle’s magnetic moment in the systems. To clarify this range, it is possible to plot the phase diagram using the MC data from Fig. 12:

- at $\lambda_e = 0.3$ new theory works well up to $\sigma = 20$,
- at $\lambda_e = 0.5$ new theory works well up to $\sigma = 5$,

and from Fig. 12:

- at $\sigma = 0$ new theory works well up to $\lambda_e = 1.25$,
- at $\sigma = 2$ new theory works well up to $\lambda_e = 0.7$,
- at $\sigma = 10$ new theory works well up to $\lambda_e = 0.4$.

The range of the applicability of the new theory is denoted as grey area in Fig. 13. The area above dashed line indicates on the ordered state with the presence of ferromagnetic chains arranged antiferromagnetically in zero fields, that leads to the susceptibility decreasing. Antiferromagnetic ordering of the magnetic moments was also discovered in the study of the ground state of dipoles embedded in the simple cubic lattice nodes in the absence of the external magnetic field [12].

The deviation of new theory from the results of computer modeling in Figs. 10 (c), 12 is connected with consideration only pair correlations in the system and truncation of the Helmholtz free energy expansions (36), (41) up to the third power of the effective dipolar coupling constant. To expand the given scope of the new theory, one can try to increase the number of terms in the virial series. However, applying the virial expansion method it is difficult to construct the theoretic approach valid for the systems with strong dipolar regime. In this case, an alternative method can be used, for instance [43, 44].

IV. CONCLUSION

The static magnetic response of the simple cubic lattice of the interacting superparamagnetic dipoles has been studied by theory and simulation. The potential energy of the system has included one-particle dipole-easy axis interaction, one-particle dipole-field interaction, and long-range interparticle dipole-dipole interactions. Two orientational distributions of particle’s easy axis in the system have been considered: aligned parallel and perpendicular to the direction of an external magnetic field. For both cases, the theoretical expansion for the Helmholtz free energy in logarithmic form has been derived considering pairwise dipole-dipole interactions from the rigorous methods of statistical physics. Using the obtained formula for the Helmholtz free energy, the magnetic properties have been investigated in...
the broad range of parameters. The theoretical predictions have been critically compared with MC simulation data.

For parallel configuration, the magnetic moments are preferably aligned along the direction of the field, that provides the strong magnetic enhancement. For perpendicular configuration, the magnetic moments are held by the easy axes in the direction of perpendicular to the field and magnetization decreases with grows of anisotropy parameter $\sigma$. In both cases, the interparticle dipole-dipole interactions lead to an increase of magnetization, but this enhancement is much stronger for the parallel configuration. The ideal approach is not capable to describe the simulation data adequately, whereas the theory derived in this paper turned out much more efficient.

The susceptibility curves from MC simulations have been observed with increasing of anisotropy parameter or the dipole-dipole interaction intensity. Notice, that for a system of interacting immobilized superparamagnetic particles located randomly, the initial magnetic susceptibility increases monotonically with growth of anisotropy parameter or the dipole-dipole interaction intensity [15]. Secondly, for any set of intrinsic parameters, the maximum achievable value of $\chi_{\parallel}$ has been equal to $\approx 9$. This allows us to conclude that the model system based on the simple cubic lattice undergoes a phase transition in the ordering of magnetic moments. There has been determined the area of parameters $\lambda$, and $\sigma$, where structural transformations are absent. In this area, the theoretic susceptibility curves turned out in the good agreement with MC data. The obtained results about magnetic properties of the simple cubic lattice with the immobilized superparamagnetic nanoparticles in nodes are important in the development of functional magnetic materials with controlled properties.

ACKNOWLEDGEMENTS

The reported study was funded by RFBR, project number 20-02-00358.

APPENDIX A: PARALLEL CONFIGURATION

For parallel configuration the results of the averaging over magnetic moment orientations of the coefficients $b_1$, $b_2$, $b_3$ can be written in the following form

$$b_1 = 2Q_1^2(\alpha, \sigma)\gamma_{12},$$

$$b_2 = \frac{36}{35}Q_2^2(\alpha, \sigma)\gamma_{24} + \frac{2}{3}Q_2(\alpha, \sigma)\left(1 - \frac{Q_2(\alpha, \sigma)}{7}\right)\gamma_{22} + \frac{1}{3}\left(1 + \frac{Q_2^2(\alpha, \sigma)}{5}\right)\gamma_{20},$$

$$b_3 = \frac{6}{77}\left(3Q_1(\alpha, \sigma) - 5Q_2(\alpha, \sigma)\right)^2\gamma_{36} + \frac{18}{11}\left(4Q_1(\alpha, \sigma)Q_3(\alpha, \sigma) - 3Q_2^2(\alpha, \sigma)/7\right)\gamma_{34} + \frac{1}{7}\left(3Q_2^2(\alpha, \sigma) + Q_3^2(\alpha, \sigma)\right)\gamma_{32} + \frac{1}{42}\left(-\frac{6Q_1(\alpha, \sigma)Q_3(\alpha, \sigma)}{5} + 3Q_1^2(\alpha, \sigma)\right)\gamma_{30},$$

where several functions have been introduced as

$$Q_1(\alpha, \sigma) = \frac{1}{2Q_0(\alpha, \sigma)}\int_{-1}^{1}\exp(\alpha t + \sigma t^2)\, dt, \quad (A.4)$$

$$Q_1(\alpha, 0) = L(\alpha),$$

$$L(\alpha) = \coth\alpha - \frac{1}{\alpha},$$

$$Q_2(\alpha, \sigma) = \frac{3}{4Q_0(\alpha, \sigma)}\int_{-1}^{1}\exp(\alpha t + \sigma t^2)\, dt^2 - \frac{1}{2}, \quad (A.5)$$

$$Q_2(\alpha, 0) = L_3(\alpha),$$

$$L_3(\alpha) = 1 - 3\frac{L(\alpha)}{\alpha},$$

$$Q_3(\alpha, \sigma) = \frac{1}{2Q_0(\alpha, \sigma)}\int_{-1}^{1}\exp(\alpha t + \sigma t^2)\, dt^3, \quad (A.6)$$

$$Q_3(\alpha, 0) = L(\alpha) - \frac{2}{3}L_3(\alpha).$$

The numbers $\gamma_{pq}$ involve the summation of position dependent expressions over nodes of the cubic lattice, limited by cylinder size:

$$\gamma_{pq} = \sum_{j=2}^{N} \frac{1}{r_{1j}^3} P_q \left(\frac{\bar{z}_{1j}}{r_{1j}}\right), \quad (A.7)$$

In this definition is introduced the dimensionless interparticle separation vector $\bar{r}_{1j} = r_{1j}/a$, where $\bar{z}_{1j}$ is $z$-component of vector $\bar{r}_{1j}$ in a laboratory coordinate system, showed in Fig. 1 (a). $P_q$ ($q = 0, 2, 4, 6$) in (A.7) denote the polynomials of Legendre. It is assumed that the particle 1 is fixed at the origin of the laboratory frame. All the other nodes of the simple cubic lattice except $(\bar{x}_1, \bar{y}_1, \bar{z}_1) = (0, 0, 0)$ can be occupied by the particle 1

$$-R \leq \bar{x}_j \leq R,$$

$$-R \leq \bar{y}_j \leq R,$$

$$-hR \leq \bar{z}_j \leq hR,$$

$$(\bar{x}_j)^2 + (\bar{y}_j)^2 \leq R^2,$$

$$(\bar{x}_j)^2 + (\bar{y}_j)^2 + (\bar{z}_j)^2 > 0.$$

$$\gamma_{pq} = \sum_{j=2}^{N} \frac{1}{r_{1j}^3} P_q \left(\frac{\bar{z}_{1j}}{r_{1j}}\right).$$

In this definition is introduced the dimensionless interparticle separation vector $\bar{r}_{1j} = r_{1j}/a$, where $\bar{z}_{1j}$ is $z$-component of vector $\bar{r}_{1j}$ in a laboratory coordinate system, showed in Fig. 1 (a). $P_q$ ($q = 0, 2, 4, 6$) in (A.7) denote the polynomials of Legendre. It is assumed that the particle 1 is fixed at the origin of the laboratory frame. All the other nodes of the simple cubic lattice except $(\bar{x}_1, \bar{y}_1, \bar{z}_1) = (0, 0, 0)$ can be occupied by the particle 1

$$-R \leq \bar{x}_j \leq R,$$

$$-R \leq \bar{y}_j \leq R,$$

$$-hR \leq \bar{z}_j \leq hR,$$

$$(\bar{x}_j)^2 + (\bar{y}_j)^2 \leq R^2,$$

$$(\bar{x}_j)^2 + (\bar{y}_j)^2 + (\bar{z}_j)^2 > 0.$$

$$\gamma_{pq} = \sum_{j=2}^{N} \frac{1}{r_{1j}^3} P_q \left(\frac{\bar{z}_{1j}}{r_{1j}}\right).$$

In this definition is introduced the dimensionless interparticle separation vector $\bar{r}_{1j} = r_{1j}/a$, where $\bar{z}_{1j}$ is $z$-component of vector $\bar{r}_{1j}$ in a laboratory coordinate system, showed in Fig. 1 (a). $P_q$ ($q = 0, 2, 4, 6$) in (A.7) denote the polynomials of Legendre. It is assumed that the particle 1 is fixed at the origin of the laboratory frame. All the other nodes of the simple cubic lattice except $(\bar{x}_1, \bar{y}_1, \bar{z}_1) = (0, 0, 0)$ can be occupied by the particle 1

$$-R \leq \bar{x}_j \leq R,$$

$$-R \leq \bar{y}_j \leq R,$$

$$-hR \leq \bar{z}_j \leq hR,$$

$$(\bar{x}_j)^2 + (\bar{y}_j)^2 \leq R^2,$$

$$(\bar{x}_j)^2 + (\bar{y}_j)^2 + (\bar{z}_j)^2 > 0.$$

$$\gamma_{pq} = \sum_{j=2}^{N} \frac{1}{r_{1j}^3} P_q \left(\frac{\bar{z}_{1j}}{r_{1j}}\right).$$

In this definition is introduced the dimensionless interparticle separation vector $\bar{r}_{1j} = r_{1j}/a$, where $\bar{z}_{1j}$ is $z$-component of vector $\bar{r}_{1j}$ in a laboratory coordinate system, showed in Fig. 1 (a). $P_q$ ($q = 0, 2, 4, 6$) in (A.7) denote the polynomials of Legendre. It is assumed that the particle 1 is fixed at the origin of the laboratory frame. All the other nodes of the simple cubic lattice except $(\bar{x}_1, \bar{y}_1, \bar{z}_1) = (0, 0, 0)$ can be occupied by the particle 1

$$-R \leq \bar{x}_j \leq R,$$

$$-R \leq \bar{y}_j \leq R,$$

$$-hR \leq \bar{z}_j \leq hR,$$

$$(\bar{x}_j)^2 + (\bar{y}_j)^2 \leq R^2,$$

$$(\bar{x}_j)^2 + (\bar{y}_j)^2 + (\bar{z}_j)^2 > 0.$$
The cylinder is limited by the dimensionless radius $R$ and the height $2h$. The results for $\gamma_{pq}$ obtained for model system with $N \approx 25 \times 10^6$ ferroparticles are $\gamma_{12} = 2.0944$, $\gamma_{24} = 3.2257$, $\gamma_{22} = \gamma_{32} = 0$, $\gamma_{20} = 8.4016$, $\gamma_{36} = 0.6553$, $\gamma_{34} = 3.4081$, $\gamma_{30} = 6.6289$.

**APPENDIX B: PERPENDICULAR CONFIGURATION**

For perpendicular configuration the results of the averaging over magnetic moment orientations of the coefficients $b_1$, $b_2$, $b_3$ can be written in the following form

\begin{align}
b_1 &= 2R_1^3(\alpha, \sigma)\epsilon_1, \\
\frac{b_2}{\epsilon_2} &= 
\left(\frac{R_2^2(\alpha, \sigma) + 3R_3^2(\alpha, \sigma) - 2R_4(\alpha, \sigma) + 1}{4}\right) + 
\frac{9}{4}(2R_4(\alpha, \sigma) - 3R_3^2(\alpha, \sigma) - R_2^2(\alpha, \sigma) + 1) \epsilon_3 \\
\frac{b_3}{\epsilon_3} &= 
\frac{4}{3}R_3^3(\alpha, \sigma)\epsilon_4 + 
\frac{4}{3}\left[(R_4(\alpha, \sigma) - R_5(\alpha, \sigma))^2 + R_6^2(\alpha, \sigma)\right] \epsilon_5 + 
\frac{18}{3}\left[(R_4^2(\alpha, \sigma) + R_6^2(\alpha, \sigma) + R_5(\alpha, \sigma)R_6(\alpha, \sigma) - R_4(\alpha, \sigma)R_5(\alpha, \sigma)] \epsilon_6 + 
\frac{9}{3}(R_4(\alpha, \sigma) - R_5(\alpha, \sigma))R_6(\alpha, \sigma)\epsilon_7, \\
\end{align}

where additional functions have been introduced as

\begin{align}
R_1(\alpha, \sigma) &= \int_0^1 \exp(\sigma t^2) I_0(\alpha \sqrt{1-t^2}) \sqrt{1-t^2} dt \\
&\times [R_0(\alpha, \sigma)]^{-1}, \\
R_1(\alpha, 0) &= L(\alpha), \\
R_2(\alpha, \sigma) &= \int_0^1 \exp(\sigma t^2) I_2(\alpha \sqrt{1-t^2}) (1-t^2) dt \\
&\times [R_0(\alpha, \sigma)]^{-1}, \\
R_2(\alpha, 0) &= L_3(\alpha), \\
R_3(\alpha, \sigma) &= \int_0^1 \exp(\sigma t^2) I_0(\alpha \sqrt{1-t^2}) t^2 dt \\
&\times [R_0(\alpha, \sigma)]^{-1}, \\
R_3(\alpha, 0) &= \frac{L_3(\alpha)}{\alpha}, \\
R_4(\alpha, \sigma) &= \int_0^1 \exp(\sigma t^2) I_1(\alpha \sqrt{1-t^2}) \sqrt{1-t^2} dt \\
&\times [R_0(\alpha, \sigma)]^{-1}, \\
R_4(\alpha, 0) &= L(\alpha) - \frac{L_3(\alpha)}{\alpha}, \\
R_5(\alpha, \sigma) &= \int_0^1 \exp(\sigma t^2) I_3(\alpha \sqrt{1-t^2}) \sqrt{1-t^2} dt \\
&\times [R_0(\alpha, \sigma)]^{-1}, \\
R_5(\alpha, 0) &= L(\alpha) - 2\frac{L_3(\alpha)}{\alpha}, \\
R_6(\alpha, \sigma) &= \int_0^1 \exp(\sigma t^2) I_1(\alpha \sqrt{1-t^2}) \sqrt{1-t^2} dt \\
&\times [R_0(\alpha, \sigma)]^{-1}, \\
R_6(\alpha, 0) &= \frac{L_3(\alpha)}{\alpha}.
\end{align}

Here $I_k(x)$ is the modified Bessel function of $k$ order, the numbers $\epsilon_k$ involve the summation of position depended expressions over nodes of the cubic lattice, limited by cylinder size:

\begin{align}
\epsilon_1 &= \sum_{j=2}^{N} \frac{1}{r_{ij}} P_2 \left(\frac{\bar{x}_{ij}}{r_{ij}}\right) \simeq 2.0944, \\
\epsilon_2 &= \sum_{j=2}^{N} \frac{1}{r_{ij}^3} P_2 \left(\frac{\bar{x}_{ij}}{r_{ij}}\right) \simeq 3.3393, \\
\epsilon_3 &= \sum_{j=2}^{N} \frac{\bar{x}_{ij}^2 \bar{z}_{ij}^2}{r_{ij}^5} \simeq 0.1915, \\
\epsilon_4 &= \sum_{j=2}^{N} \frac{1}{r_{ij}} P_2 \left(\frac{\bar{x}_{ij}}{r_{ij}}\right) \simeq 1.4880, \\
\epsilon_5 &= \sum_{j=2}^{N} \frac{1}{r_{ij}^3} P_2 \left(\frac{\bar{x}_{ij}}{r_{ij}}\right) P_2 \left(\frac{\bar{z}_{ij}}{r_{ij}}\right) \\
&\simeq -0.7440, \\
\epsilon_6 &= \sum_{j=2}^{N} \frac{\bar{x}_{ij}^2 \bar{z}_{ij}^2}{r_{ij}^3} P_2 \left(\frac{\bar{z}_{ij}}{r_{ij}}\right) \simeq 0.0114, \\
\epsilon_7 &= \sum_{j=2}^{N} \frac{\bar{y}_{ij}^2 \bar{z}_{ij}^2}{r_{ij}^5} = \frac{(8\bar{y}_{ij}^2 - \bar{y}_{ij}^2 - \bar{z}_{ij}^2)}{r_{ij}^5} \simeq -0.0318.
\end{align}

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