

MODELLING OF THE INTERACTIONS BETWEEN MAGNETIC NANOPARTICLES IN AQUEOUS SOLUTIONS

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Abstract. The ability of magnetic nanoparticles and their aggregates to form larger structures or new materials is primarily based on the interactions between individual particles. The article analyzes the behavior of spherical nanoparticles Fe_3O_4 placed in an aqueous base solution as a result of their mutual interactions, i.e. repulsive (electrostatic forces) and attractive (van der Waals forces and dipolar magnetic forces) for the full range of parameter values. Considering the application of magnetic aqueous suspensions in industry or environmental research, the presented method allows for a preliminary selection of the parameters of the dispersed material and the solution so as to obtain a suspension with the desired properties.

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1. Introduction

We deal with colloidal suspensions in a wide variety of materials, such as colloidal dispersions, biological fluids, and food products. The intermolecular interactions acting between particles in all these cases play an important role in determining material properties, such as durability or stability [1]. In addition, the recent emergence of measurement techniques allowing for direct and precise measurement of the forces acting between particles in suspensions enables an in-depth analysis of these phenomena.

In this paper, assuming pairwise additivity of interatomic dispersion energies, we will focus on magnetic colloidal particles. Since the model presented here applies to iron oxide nanoparticles with a diameter smaller than 30 nm, it can be assumed that they are uniformly magnetized and single-domain [2, 3]. However, due to the magnetic dipole-dipole attractions, aqueous suspensions of magnetic nanoparticles are often not stable and agglomerate quickly [4]. Moreover, there is always a short-range attraction force between particles, known as the van der Waals force, which significantly increases the tendency of nanoparticles to agglomerate.

Fortunately, the magnetic particles are usually coated with acidic and basic surface groups. When a colloidal particle is suspended in the solution, the surface groups on the particle dissociate in the proton transfer reaction and take on a charge. The greater the electrostatic charge, the stronger the repulsion of the nanoparticles, and thus the greater the stability of the colloidal suspension [5]. The intensity of this process is directly related to the pH value of the solution, which determines the degree of relative acidity or alkalinity of the aqueous solution at a given temperature.

The paper aims to develop and evaluate a microscopic model of interactions between two immersed colloidal particles in an aqueous solution so that the conclusions of the research provide useful guidance in the study of much more complex systems.

2. Interactions

The most widely used model describing the conditions of suspension stability is the DLVO theory, which takes into account only two types of forces acting between particles in a liquid medium [6, 7], i.e. electrical forces and van der Waals forces. When dealing with a suspension of magnetic nanoparticles, we have to additionally take into account the magnetic dipole-dipole interactions to get a complete description [8, 9].

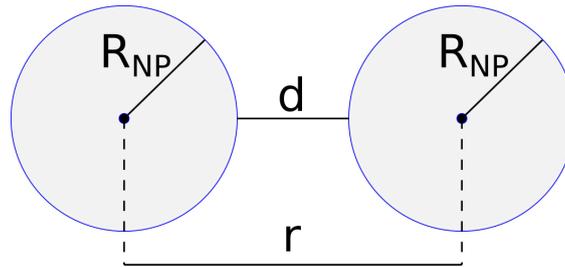


Fig. 1. Schematic diagram of two nanoparticles

2.1. Electrostatic interaction

On contact with an aqueous solution, iron oxide nanoparticles acquire a pH-dependent surface charge: positive for $\text{pH} < \text{PZC}$, where PZC is the point of zero charge, and negative otherwise. The PZC values of magnetic nanoparticles differ depending on their preparation (in our case $\text{PZC} = 6.7$). Electrostatic interactions occur when nanoparticles carry surface charges, causing the accumulation of counterions in the solution. Therefore, a characteristic feature of colloidal solutions is the presence of a double layer of electric charges near the surface of each particle, which leads to their mutual repulsion and thus ensures the stability of the suspension. The double-layer electrostatic forces decay exponentially with the separation distance according to the formula

$$E_{el} \sim \exp(-d/\lambda_D)/r, \quad (1)$$

where $r = d + 2 R_{NP}$, d denotes the distance between the sphere surfaces, R_{NP} is the sphere's radius (Fig. 1), and the Debye screening length λ_D describes the characteristic length-scale.

In general, when the pH of the solution is greater than the PZC and continues to increase, the surface charge density also increases, whereas the decay length of electrostatic interactions decreases sharply with increasing ion concentration. In the latter case, the Debye length λ_D , which occurs in Eq. (1), is inversely proportional to the square root of the bulk ionic concentration and usually ranges between 0.1 and 100 nm [10].

2.2. Van der Waals interaction

In the case of an isolated pair of non-magnetic molecules in an electrolyte solution, there is an attractive dipole-dipole interaction derived from induced dipoles [11]:

$$E_{vdW} = -C/r^6, \quad (2)$$

where C is the London constant and r denotes the center-to-center distance between particles. Such interactions between induced or permanent dipoles are ubiquitous in nature and, despite their relative weakness, of great importance. The common name of van der Waals interactions has been adopted for them.

Taking as a starting point van der Waals forces acting between atoms, one can determine the forces acting already between macroscopic objects [12]. To simplify calculations, we will only consider identical spherical particles. Then, assuming the additivity of the interatomic dispersion energies, the total interaction between two macroscopic spheres containing q atoms per volume unit is given by the following expression [13]:

$$E_{vdW} = - \iint_{V_1 V_2} q^2 \lambda / r^6 dv_1 dv_2, \quad (3)$$

where V_1 and V_2 designate total volumes of the two particles, and λ is the London – van der Waals constant. It can be proved that for two identical particles, the van der Waals interaction is always attractive, and therefore, at sufficiently high suspension concentrations, this leads to the formation of stable aggregates as a result of particle collisions caused by Brownian motion.

However, it is known that the attractive van der Waals potential requires the presence of stabilizing repulsive forces between atoms. As two atoms get close to each other, they begin to interpenetrate, and thus their electron clouds begin to overlap. Hence, according to the Pauli exclusion principle, a very strong repulsion occurs. The attractive van der Waals interaction supplemented by the steep repulsion term gives the Lennard-Jones (LJ) potential. This is a very useful empirical function that describes the interaction energy between two atoms

$$E_{LJ} = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6], \quad (4)$$

where ε is the potential well depth, σ is the distance at which the LJ potential between the two atoms is zero, and r is the center-to-center distance. Sample plots of the LJ potential for pairs of identical atoms are presented in panel a) in Figure 2. As it is usually done, the LJ potential parameters (σ, ε) for the interaction of different atoms can be obtained from the homonuclear parameters by applying combination rules [14]. The combination rule for heteronuclear distances σ is an arithmetic mean of the homonuclear distances, and for the well depth ε , the geometric mean value is applied.

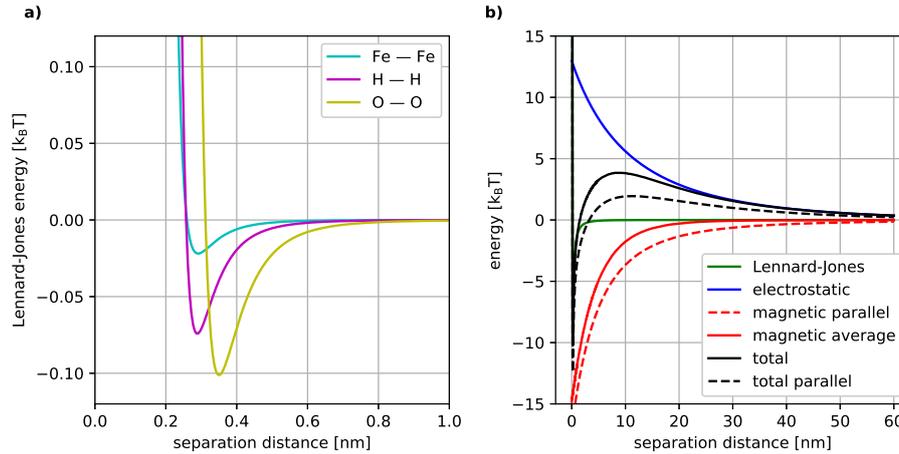


Fig. 2. a) Examples of LJ potentials between identical atoms, b) Electrostatic energy, van der Waals energy, and dipole-dipole magnetic energy

Since it has been proved [15] that the integration shown by Eq. (3) can also be performed for the LJ potential, therefore the LJ forces between two macroscopic spheres can be calculated, provided the concentration of the different atoms is known. For iron oxide nanoparticles in an aqueous solution, we can determine the concentration of magnetite and water based on material data available in the literature. Then, knowing that the magnetite molecule consists of three iron atoms and four oxygen atoms, and the water molecule consists of two hydrogen atoms and one oxygen atom, we can determine the total LJ energy between the spherical particles from the LJ energies between the various pairs of atoms.

2.3. Dipole-dipole magnetic interaction

The magnetic forces between particles are much weaker than electrostatic forces, but their role increases significantly in the case of single-domain magnetic nanoparticles. This happens because a single-domain nanoparticle is always magnetized to saturation magnetization, and the magnetic moments are directed uniformly over the nanoparticle volume. Typically, magnetic nanoparticles have a distinguished magnetic anisotropy; the so-called easy axis. The deviation of the nanoparticle magnetization from this direction requires additional energy, but for simplicity,

we consider the case where the nanoparticle magnetization always lies along the easy axis.

The magnetic dipole-dipole interaction relates directly to the mutual arrangement of two vectors, i.e. magnetic dipoles, and the interaction energy can be expressed as:

$$E_{d-d} = \frac{\mu}{4\pi} \frac{\vec{m}_1 \cdot \vec{m}_2 - 3(\vec{m}_1 \cdot \vec{e}_r)(\vec{m}_2 \cdot \vec{e}_r)}{|r|^3}, \quad (5)$$

where μ is the medium permeability, r is the distance between magnetic dipoles, and \vec{e}_r is the unit vector of the line between the centers of the magnetic dipoles. It should be noted that the formula can be applied both to atomic magnetic moments and to spherical nanoparticles [18]. If we describe both magnetic moments in the spherical coordinate systems, then their arrangement can be represented by their polar angles $\theta_{1,2}$ and azimuthal angles $\phi_{1,2}$.

$$\begin{aligned} \vec{m}_1 &= |m_1| (\cos(\theta_1) \cos(\phi_1) \vec{e}_x + \cos(\theta_1) \sin(\phi_1) \vec{e}_y + \sin(\theta_1) \vec{e}_z) \\ \vec{m}_2 &= |m_2| (\cos(\theta_2) \cos(\phi_2) \vec{e}_x + \cos(\theta_2) \sin(\phi_2) \vec{e}_y + \sin(\theta_2) \vec{e}_z) \end{aligned}$$

where $\vec{e}_x, \vec{e}_y, \vec{e}_z$ denote the unit vectors in the Cartesian coordinate system. Without losing generality we can assume that $|m_1| = |m_2|$ and $\vec{e}_r = \vec{e}_z$. Then Eq. (5) takes the following form:

$$E_{d-d} = \frac{\mu |m|^2}{4\pi |r|^3} (\cos(\theta_1) \cos(\theta_2) \cos(\phi_1 - \phi_2) - 2 \sin(\theta_1) \sin(\theta_2)) \quad (6)$$

Since the directions of the dipole moments change under the influence of thermal motions of the medium molecules, we can determine the average value of magnetic energy E_{d-d}^{av} taking into account all possible mutual positions of both magnetic dipoles.

$$E_{d-d}^{av} = \frac{\mu |m|^2}{4\pi |r|^3} A \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_0^{2\pi} \int_0^{2\pi} \cos(\theta_1) \cos(\theta_2) \exp\left(-\frac{E_{d-d}}{k_B T}\right) E_{d-d} d\phi_2 d\phi_1 d\theta_2 d\theta_1 \quad (7)$$

where

$$A^{-1} = \int_{-\pi}^{\pi} \int_{-\pi}^{\pi} \int_0^{2\pi} \int_0^{2\pi} \cos(\theta_1) \cos(\theta_2) \exp\left(-\frac{E_{d-d}}{k_B T}\right) d\phi_2 d\phi_1 d\theta_2 d\theta_1 \quad (8)$$

The summation (integration) was performed using the Monte Carlo method, where the Boltzmann factor $\exp(-E_{d-d}/k_B T)$ weighs the probability of each magnetic moment configuration. In panel b) of Figure 2, a solid red line represents E_{d-d}^{av} values. To illustrate the effect of averaging the magnetic interaction for all magnetic dipoles settings, we additionally present the magnetic energy for the case if both dipoles were directed identically (called "magnetic parallel").

3. Energy landscapes

We can now determine the total energy of two identical spherical Fe_3O_4 nanoparticles as a result of their interaction, i.e., attractive (van der Waals forces and dipolar magnetic forces) and repulsive (electrostatic forces) (see panel b) of Fig. 2). Studying the energy landscape of interacting nanoparticles is a prerequisite for the design and control of colloidal processes [16, 17].

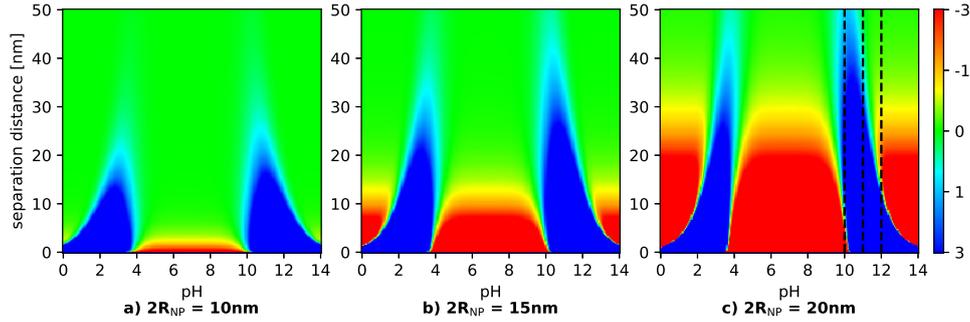


Fig. 3. Total energy landscape (in $k_B T$ units) for two nanoparticles with different radii in an aqueous solution (without salt). The energy values are mapped to colors as in the color bar on the right side of panel c)

In Figure 3, we show how changing the size of nanoparticles changes the sign and magnitude of interactions. As can be seen for the pH around the PZC, when there are no electric charges accumulated on the nanoparticle surfaces, the attractive van der Waals and magnetic forces dominate. Moreover, when the size of the nanoparticles increases (but they remain single-domain) their dipole moments also increase, and thus the magnetic forces become increasingly attractive.

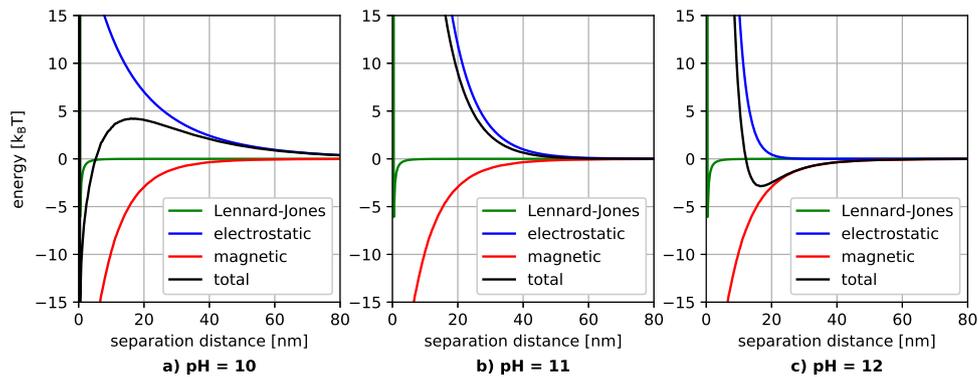


Fig. 4. The energies of two interacting nanoparticles with the radius $R_{NP} = 10$ nm as a function of the separation distance along the three paths marked in panel c) in Figure 3 with dashed lines

It is known that iron oxide nanoparticles with a dimension of about 10 nm dispersed in an alkaline solution (roughly for a pH in the range of 10-12) form a stable

suspension. To show some details, energy plots were made for the two interacting nanoparticles for three pH values (see the dashed lines in Figure 3). As the plots for pH = 12 show, we can expect that two nanoparticles in the suspension will prefer an average distance of about 16.9 nm between each other (which corresponds to the position of the minimum total energy). For pH = 11, such an equilibrium distance no longer exists, and molecules begin to repel each other at distances below 50 nm. When the pH value drops to 10, an unstable equilibrium appears at a separation distance of nanoparticles of about 16.7 nm. As a result, by reducing the distance, both particles will repel each other, but when their energy allows them to come closer than 16.7 nm, they immediately begin to attract each other. Only at a distance of about 1 nm, the nanoparticles start to repel very strongly due to the presence of the inverse twelfth-power term in the LJ potential.

Based on the above results for two nanoparticles, it is possible to predict how magnetic nanoparticle suspensions will behave. As one can see, because each time there is a strong electrostatic repulsion, each time – albeit to a different degree – we are dealing with a relatively stable suspension. The case with pH = 12 will be the most stable, while for pH = 10 there will be a certain tendency to agglomerate nanoparticles. This is true for those nanoparticles that, due to thermal fluctuations, will be able to overcome the energy barrier and come within 16.7 nm of each other.

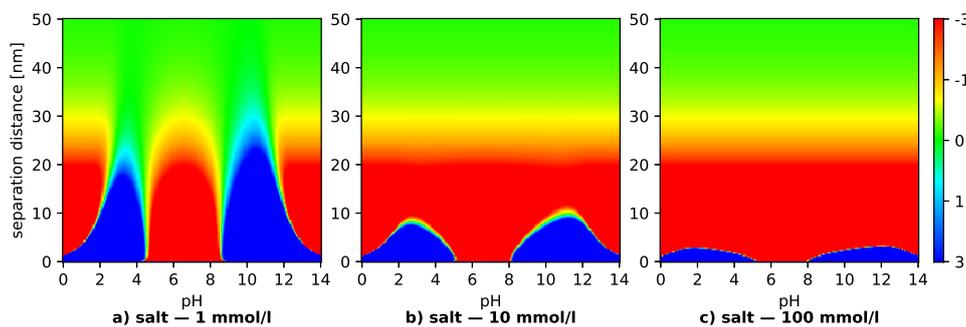


Fig. 5. Total energy landscape (in $k_B T$ units) for two nanoparticles with radius $R_{NP} = 10$ nm in an aqueous solution for various NaCl concentration. The energy values are mapped to colors as in the color bar on the right side of panel c).

The results so far have been obtained for aqueous solutions where salt was absent. Overall, water is very efficient at shielding charges and reducing electrostatic forces between ions [19]. An increase in the concentration of sodium chloride (NaCl) directly translates into an increase in the number of ions in solution, thus increasing the shielding effect of electrostatic interactions. This effect is shown in Figure 5 for three different concentrations.

4. Conclusions

Interaction forces acting between colloidal particles in aqueous suspensions largely determine the properties of various materials, e.g. in many industrial and environmental processes. An example of a magnetic colloidal liquid is an aqueous suspension of magnetic nanoparticles, and obtaining its colloidal stability is the first step in the preparation of new magnetic materials, incl. thin layers and composites.

The conclusions of our model are in qualitative agreement with the experimental results. Moreover, they enable a better understanding of the importance of individual types of interactions and a more detailed understanding of the process of stabilizing iron oxide suspensions in aqueous solutions. It is the first step toward a quantitative description of the formation of stable magnetic nanoparticle structures [20, 21] and at the same time controlling this process by tuning the values of the physicochemical parameters of the analyzed suspensions.

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