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Supplementary Information
Effect of magnetic field gradients on the aggregation dynamics of colloidal magnetic nanoparticles

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In this Supplementary Information we provide further details regarding the employed ferrofluid samples and Derjaguin–Landau–Verwey–Overbeek (DLVO) calculations supporting their colloidal stability.

1. DESCRIPTION OF THE SAMPLES

The samples were provided by Dr. N. Buske, MagneticFluids, Köpenicker Landstr. 203, D-12437 Berlin, Germany, webpage www.magneticfluids.de (e-mail: n.buske@magneticfluids.de).
According to the data from the manufacturer, the sample consists of stable particles with a size (measured by Dynamic Light Scattering (DLS)) of 145 nm (with a polydispersity index of 0.2) and zeta potential $\zeta \simeq 40$ mV. Both the size of the colloids and their ζ potential are typical of superparamagnetic colloids obtained in many applications. According to the fabricant, these colloids are made from magnetite nanocrystalls of 6-7 nm in size with a zeta potential of about 25 mV. The nanocrystalls are obtained from coprecipitation and they further aggregate into stable hydrosols of about 145 nm in size and zeta potential of 40 mV, as shown in Figure 1. These hydrosols can be further treated with organic acids, like citric acid (C) or carboxymethylated dextran (D) in order to obtain negativelly charged colloids (not employed in this study).

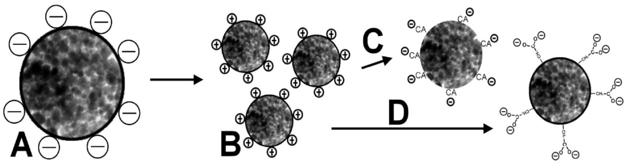

FIG. 1: Scheme of preparation of magetite hydrosols: Coprecipitated magnetite particles (A) with a core size of 6-7nm were dispersed in HCl-solution, and magnetically classified into agglomerates of different size (B), The positively charged particles were modified with organic acids, like citric acid (C) or carboxymethylated dextran (D). (Figure credits: S. Wulff and N. Buske (N. Buske, MagneticFluids, Köpenicker Landstr. 203, D-12437 Berlin, Germany.))

2. COLLOIDAL STABILITY

In the absence of a magnetic field, the colloidal dispersion is stabilized by electrostatic surface charge against coagulation by Van der Waals forces. A quantitative analysis of the stability of magnetic colloids can be done using the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [1, 2]. We calculate first the attractive Van der Waals force. In a recent work [3], van der Waals forces for different iron oxides (magnetite, maghemite and hematite) were computed using Lifshitz theory employing accurate data for the response functions. In the case of magnetite particles, the obtained Hamaker coefficient was $A \simeq 10.45$ k$_B$T. The potential as a function of the separation r between particles of radius R can be described by:

$$V_{\mathrm{vdw}} = -\frac{A}{6}\left[\frac{2}{s^2+4s} + \frac{2}{(s+2)^2} + ln\frac{s^2+4s}{(s+2)^2}\right]. \quad (1)$$

Where $s = r/R$ in Eq.(1). In Figure 2, we show the predictions of Eq.(1) for the nanoparticles considered in our study. We indicate the stable/unstable regions as in ref.[3], in which Van der Waals interactions were considered to induce instability for separations at which these interactions were stronger than twice the thermal energy ($V_{\mathrm{vdw}} < -2k_BT$). In our case, it corresponds to separations underneath 13.5 nm, which are much smaller than the size of the particles. This implies that these colloids can be stabilized either adding a thin coating layer or by electrostatic stabilization, which induces an energy barrier at distances close to the surface.

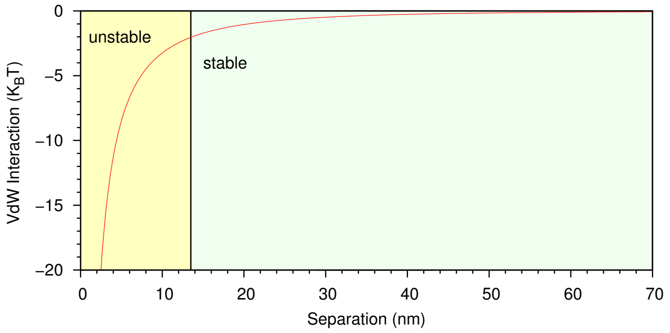

FIG. 2: Van der Waals interaction potential between two magnetite spheres (diameter 145 nm). The region of unstability at which the interaction is stronger than -2k$_B$T is indicated.

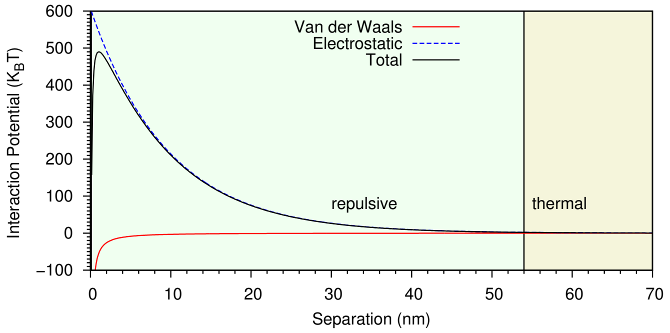

FIG. 3: DLVO interaction potentials (Van der Waals, electrostatic and total) calculated with Eqs. (1) and (2). We indicate the region at which electrostatic repulsion dominates over Van der Waals and thermal motion (repulsive) and the region at which thermal motion dominates.

The samples considered here were stabilized electrostatically at pH=3. The surface charge σ of the colloids can be estimated from the zeta potential ζ using the Grahame equation [2]:

$$\sigma = \frac{e}{2\pi\lambda_B\lambda_D}\sinh\frac{e\zeta}{2k_BT}, \qquad (2)$$

where e is the electronic charge, $\lambda_B = 0.71$ nm is the Bjerrum length and $\lambda_D = 9.61$ nm is the Debye length for our samples (corresponding to pH=3 obtained with added HCl acid). Using our value of $\zeta = 40$ mV we obtain $\sigma \simeq 0.02$ e/nm^2 which is a typical surface charge for colloids. The electrostatic repulsive interaction between two colloids at a separation r is given by (Derjaguin approximation):

$$V_{\rm DL} = 16k_BT\frac{R}{\lambda_D}\tanh\frac{e\zeta}{4k_BT}e^{-r/\lambda_D}. \qquad (3)$$

In Figure 3 we plot $V_{\rm DL}$ using Eq.(3) together with the Van der Waals interaction $V_{\rm vdw}$ (Eq. (1)) and the total DLVO interaction ($V_{\rm DL} + V_{\rm vdw}$). We obtain that electrostatic repulsion clearly dominates over Van der Waals interaction (except at close contact) and a huge energy barrier against flocculation (about $600k_BT$) is obtained at separations of the order of 1 nm. These calculations support our observations that the employed samples remain stable over long periods of time.

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