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Scanning probe microscopy on magnetic colloidal particles

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Abstract

We report some first results on magnetite and iron nanoparticles studied with atomic force microscopy (AFM). AFM images the particles on a smooth substrate, and their lateral diameter, height and polydispersity are determined and discussed. The use of magnetic force microscopy (MFM) on such small particles is explored both experimentally and theoretically. We present models which allow to estimate with MFM the magnetic moment of a single superparamagnetic nanosphere, which cannot be done with other techniques.

Keywords: Colloidal nanoparticles; Atomic force microscopy; Magnetic force microscopy; Granulometry

1. Introduction

Electron microscopy (TEM, SEM) is still the most commonly used microscopy technique for visualizing colloidal particles, though scanning probe microscopy (atomic force microscopy (AFM), magnetic force microscopy (MFM)) is a serious alternative which provides more information about particles. Scanning probe microscopy relies on the interaction between the specimen and a nanometric tip attached to a cantilever, which scans the sample surface in different operating modes. They are briefly described in the following sections. More details and discussions will be presented in a future paper [1].

2. AFM characterization

Iron particles (Fig. 1) and magnetite particles (Fig. 2), previously dispersed in cyclohexane and grafted with pure oleic acid, were imaged in air with the Nanoscope IIIa (Multimode AFM, Digital Instruments). Mica was used as a substrate. AFM measurements were carried out in tapping mode on dried samples. In this regime, the cantilever oscillates close to the resonance and the tip only slightly touches the surface. Standard silicon tips were used.

Both height and phase images (Fig. 1) are useful for visualizing the particles, but the cluster composition is better seen in the phase image (Fig. 1, right image). Clusters of few particles are mainly formed during drying, due to the capillary forces, even when highly diluted samples were used. Substrate derivatization with mercaptosilanes and Formvar, respectively, was not effective in reducing clustering significantly.

Height and (lateral) diameter distributions of particles were analyzed using height images. Aggregates, as seen in the phase images, were manually removed. The results for both types of particles are presented in Table 1. In comparison with the TEM mean diameter, the particle mean height obtained with AFM is smaller, mainly due to the deviation from the spherical shape of particles. The AFM mean diameter is larger than the TEM mean diameter due to the tip convolution. The AFM mean diameter determination can be affected by the arbitrary height of the chosen analysis plane (also called threshold plane), which is a plane above and parallel to the substrate, raised in order to eliminate noise and to define the particle boundaries. Therefore the substrate was flattened (after the particles were masked for this operation) and a median filter was then applied once

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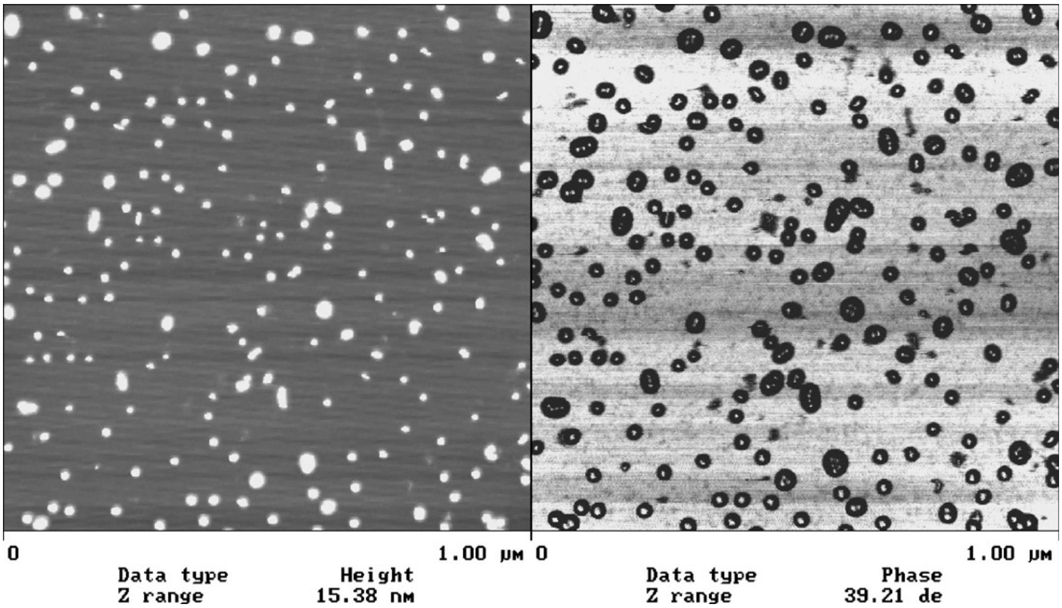

Fig. 1. Height and phase image of iron particles (the colloid was prepared and kindly provided by K. Butter).

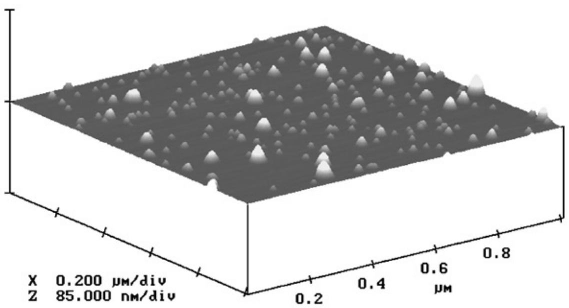

Fig. 2. Surface view of magnetite particles (the colloid was prepared and kindly provided by D. Bica).

Table 1
Statistics on AFM imaged particles

Particles	h (nm)	d (nm)	p (%)	d_{TEM} (nm)
Magnetite	6.4	16.6	15.1	8.6
Iron	7.7	15.5	12.2	9.5

Mean height (h), mean diameter (d), and diameter polydispersity (p) were determined. d_{TEM} is the mean diameter measured with TEM.

in order to reduce noise, so that we reduced the threshold height as much as possible. From Table 1, one can also infer that the iron particle shape is closer to the spherical one than that of magnetite particles. The AFM mean diameter can be improved by deconvolution. This procedure is affected by the fact that the tip radius can vary considerably from one probe to another. Therefore, for a certain tip, the apex radius was estimated by means of three methods: numerical "blind tip characterization" technique [2] applied on an image of magnetite particles (the colloids prepared by G. van Ewijk, mean diameter of 19 nm in the image–not presented), the same method applied on an image of a "Nioprobe" tip characterizer with very sharp peaks, and finally, a manual estimation technique using the same "Nioprobe" image. The determined tip radiuses differ whether numerical (7 nm) or manual (18 nm) methods are applied. Our study shows that the first method gives the best results. The corrected lateral diameters were close to each other (14–15.3 nm). After removing the aggregates, we obtained a mean diameter of approximately 12 nm, closer to the TEM mean diameter (9.1 nm).

3. MFM study

MFM experiments on magnetite particles were performed in dynamic lift mode, after measuring the topography in tapping mode. In lift mode the cantilever oscillates at a certain distance (called lift height) from the sample and the tip follows the topographic profile. The derivative of the magnetic force ($F' = \partial F/\partial z$) acting on the tip changes the resonant frequency (v_0) of the probe, according to the relation: $\Delta v \approx -v_0 F'/(2k)$, where k is the spring constant of the cantilever [3].

Electrical forces and particle attachment to the tip were suppressed by depositing a gold layer of at least 5 nm on the sample surface. We used standard magnetic tips with a 50 nm CoCr coating. The physical characteristics of a tip were determined from an SEM image: the height was $L = 14.5\,\mu m$ and the apex radius $R = 51.4\,nm$.

Experimentally, a topographic interference ($\Delta\nu$ up to 4–5 Hz) was noticed many times in the lift mode image (lift heights between 15 and 45 nm), which makes it very difficult to measure the magnetic signal. Sometimes no signal was measured. In order to see if such small particles are measurable with MFM, we calculated the force derivative after integrating the stray (dipolar) field from a spherical magnetite particle over the magnetic layer volume of a modeled tip. The tip is considered a cone with a mean half angle of $\theta_0 = 17°$. For superparamagnetic particles with low anisotropy energy, $\boldsymbol{m}_p \| \boldsymbol{M}_t$. m_p is the mean magnetic moment of the magnetite particle and M_t the CoCr alloy vertical magnetization, assumed to be uniform (more cases and discussions in Ref. [1]). This model gives the maximum MFM signal. The tip is positioned above the particle center, which was chosen as the origin of the axes. First, the integral is calculated over the entire cone, so that F' is given by

$$F' = \frac{\mu_0 m_p M_t}{4\pi} \frac{\partial^2}{\partial z^2} \int_0^{\arctan(L \tan\theta_0/(z+L))} \sin\theta \, d\theta \times \int_{z \tan\theta_0/(\cos\theta(\tan\theta_0 - \tan\theta))}^{(z+L)/(\cos\theta)} r^2 \, dr \times \int_0^{2\pi} d\phi \left(\frac{3\cos^2\theta - 1}{r^3} \right).$$

r, θ and ϕ are the spherical coordinates and z is the vertical coordinate of the tip apex. The integral over the non-magnetic cone core is then subtracted. The final result is presented in Fig. 3, together with that obtained by assuming a dipole–dipole interaction between tip apex and particle (and together with the case $m_p \perp M_t$—elliptical "rigid dipole" particle). Taking into account the presence of the necessary gold layer which covers the sample, one can see that at lift heights attained in the experiment (corresponding to $z > 10\,nm$) the signal is close to the lower limit of detection (approximately 1 Hz).

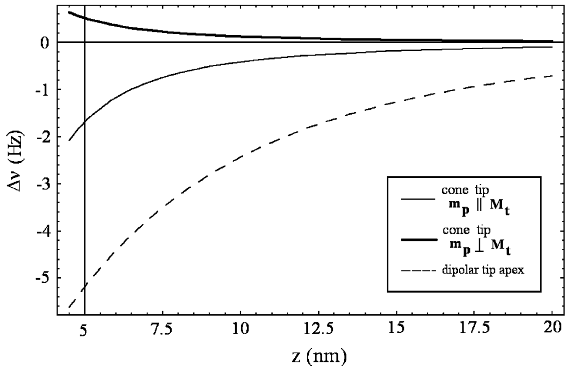

Fig. 3. Shift in the resonant frequency versus the distance between the modeled tip apex and the center of the particles.

4. Conclusions

AFM can provide reliable height and approximate diameter of colloidal nanoparticles. Deconvolution improves the determined particle diameter with almost 50%. The tip characterization depends on the used techniques; the best method was found to be the blind characterization method applied on the image to be deconvoluted. The shift in the resonant frequency of an MFM probe due to a superparamagnetic magnetite nanosphere was calculated in the frame of two models. The magnetite particles dispersed in conventional ferrofluids produce a signal too small to be detected by MFM in its present state. However, we expect a measurable signal if measurements are done in vacuum or for larger particles ($d > 15\,nm$). Then, the magnetic moment of a single particle can be determined using the proposed models.

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