FLEXIBLE MAGNETIC FILAMENTS AS MICROMECHANICAL SENSORS

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Abstract

Flexible magnetic filaments made from the self-assembly of monodisperse superparamagnetic colloids exhibit a buckling instability allowing to measure the bending rigidity of single molecules or biomolecular assemblies.

Keywords: Magnetic filaments, Elasticity measurement, Micromechanics

1. Introduction

Superparamagnetic colloids have been used for several years for widely different applications: applying very small forces [5] or torques [6] to DNA molecules, directly measuring colloidal force-distance profiles [1], targeting and isolating biomolecules or cells[7], and more recently, separating in size large DNA fragments [2]. Here, we describe a novel type of magnetic material: long flexible filaments made of assembled submicronic superparamagnetic colloids, which combine the elastic properties of worm-like chains and the expected response to an external field. Indeed, under magnetic field, these filaments adopt a multiple hairpin metastable configuration which depends on their length and on the bending rigidity of linkers.

The linkers structure may vary from a single adsorbed macromolecule to a more complex biological sandwiched architecture. As a first application of these assembled structures, we describe a novel technique to probe the bending rigidity of these various types of molecular linkers. This technique widens the range of micromechanical measurements focused on bending modes, beyond direct fluctuation analysis [4], optical tweezer techniques [3] and elastohydrodynamic coupling [8].

2. Making flexible magnetic filaments

The magnetic filaments are obtained by combining the self-assembling ability of dipolar colloids and the possibility to control the formation of permanent links with field intensity. Using this method, filaments longer than 200 μm with various kinds of linkers can be made.

One example of such flexible magnetic filaments is shown on fig.1. They are made from monodisperse superparamagnetic colloidal particles (radius $a = 375$ nm) supplied by

Ademtech linked by spontaneously adsorbed polyacrylic acid (PAA, Mw 250000, Sigma). Upon application of the field, the induced dipole moment in each particle leads to their aggregation into filaments, one particle thick, with a length equal to the cell thickness. Applying a sufficiently strong field (25 mT), allows PAA molecules to irreversibly link particles [9]. After removing the field, the chains bend under their own weight as seen in fig. 1. Similar, but shorter filaments have also been made with bisbiotin-polyethyleneglycol linkers using the specific interaction between biotin and streptavidin [10].
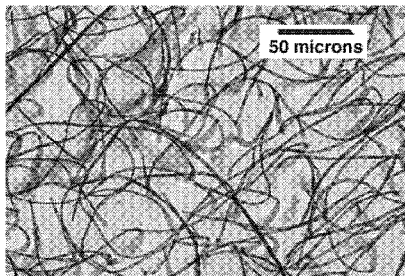

Figure 1. Flexible magnetic filaments made with PAA linkers. Optical microscopy.
Particle diameter : 0.75 μm.

3. Bending instability

The elastic properties of the filaments lead to a new type of instability observed when the filaments are first oriented with a magnetic field, then submitted to a sudden 90° rotation of the field. Depending on the chain length, we observe three distinct behaviors (fig. 2). Short chains bend slightly and then rotate to align with the new field direction. Longer chains bend into hairpin shapes, with two straight ends aligned with the field, separated by a curved section. Still longer chains can form multiple bends. Hairpins and multiple bent chains are metastable, the lowest energy corresponding to a chain completely aligned with the field. These bent configurations occur because the viscous dissipation associated to the rotation of a rigid rod of length L increases as L^3. Thus, rotating the chain in two separate parts reduces the dissipation by a factor of two. A linear stability analysis shows that, for given elastic properties, there is a critical chain length Lc below which rigid rod rotation is the fastest mode. This critical length is proportional to $(a\lambda_p/b_H)^{1/2}$ where λ_p is the persistence length of the filaments and b_H is the ratio of the magnetic interaction energy to the thermal energy k_BT. For lengths L larger than Lc, the bending modes are the fastest modes of deformation and the filaments deform into hairpin shapes or more complex shapes with multiple bends.

4. Bending stiffness measurement

The equilibrium shape of the hairpins results from a balance between, on one hand, the magnetic force which tends to align the two ends of the chain with the field direction and, on the other hand, the elastic force resisting bending. This coupling is evidenced on

fig. 3: the hairpin curvature increases linearly with the applied field. The elastic nature of the filaments, evidenced by the reversibility of the deformation when the field is reduced, is due to the deformation of the linker molecules. The radius of curvature of the filament R is related to the curvature of the linker through: $R/R_l = 2a/l$ where l is the length of the linker. From the balance of magnetic and elastic energies in a curved filament, we derive the bending stiffness of the linker as: $\kappa = (\pi\, \mu_0 a^3 l/3)\, (\chi\, H/C)^2$ where χ is the magnetic susceptibility of the particles and C is the dimensionless $(2a/R)$ filament curvature.

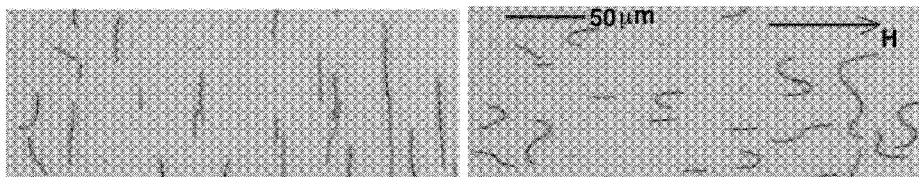Figure 2: Evolution of filaments of different lengths after a sudden 90° rotation of the field. Left: t = 0. Right t = 10s.
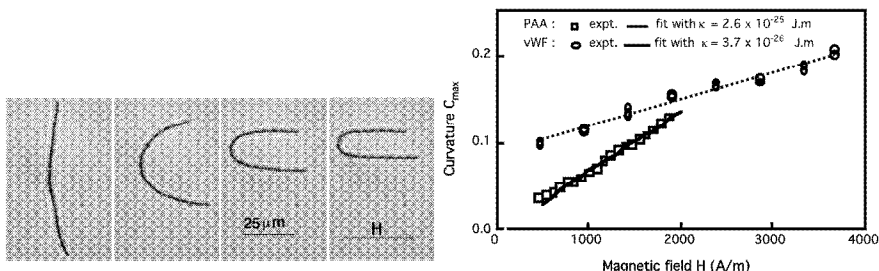

Figure 3: hairpin submitted to an increasing magnetic field (from left to right). Curves at right: hairpin curvature normalized by particle radius, as a function of field strength for two systems, PAA and vWF.

For PAA linkers with molecular weight 250 000, we find $\kappa = 1.3 \times 10^{-25}$ J.m. If we consider the linker molecule as an homogeneous elastic material bridging particles, from the size of the polymer, we derive an effective Young's modulus on the order of 10^3 Pa. If we the elasticity of the material is due to entanglements or reticulation points, E scales as $k_B T/\xi^3$ where ξ is the average distance between reticulation points. From the measured value of E, we get $\xi = 10$ nm which corresponds to the interparticular distance. We can then view the colloidal surfaces, where the polymer loops are adsorbed, as reticulation points constraining the motion of the polymer and giving rise to a finite elasticity.

We have also used the magnetic filaments to measure the rigidity of a molecular complex

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igG-vWF-igG. The von Willebrand factor (vWF) is a multimeric protein, with a molecular weight ranging from 520 000 up to 10^7 .It plays a key role in hemostasis, and its deformation under shear by the blood flow is thought to regulate platelet adhesion [11]. The immunoglobulin igG is directly grafted onto the particles bearing carboxylic surface groups. Given the low density of igG grafted on the particles, we estimate that there is a single molecular complex in each interparticle link.

The linker length is in this case, $l = 20$ nm, and the measured rigidity is 3×10^{-26} J.m, an order of magnitude smaller than the PAA. We do not have yet a physical model for the elasticity of the vWF, but the relativity high measured rigidity rules out a random coil behavior, which would lead a negligible bending stiffness.

5. Conclusions

Self-assembled magnetic filaments exhibit a new type of buckling instability leading to metastable hairpin shapes. From the knowledge of the linker length, the filament curvature leads to the mechanical properties of the linker molecule. Even very small deformations of submicronic entities can be measured because of the geometrical amplification mechanism due to the one-dimensional nature of the filament. We have demonstrated the application of this new technique for two different types of linkers: a polymer adsorbed onto the surface of the colloids and a biomolecular complex grafted on the particle surfaces. The flexible magnetic filaments should be very useful to probe the rigidity of biomolecular assemblies such as actin filaments linked by myosin or the pericentriolar matrix of centrosomes.

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