How to use Kelvin Forces to tune dynamically the interaction between colloids and dipolar polymers.

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INTRODUCTION & AIM

The Chains made by the sequential linking of colloidal particles are known as colloidal polymers. If the particles carry either electric o magnetic dipoles then such chains are known as dipolar colloidal polymers of dipolar filaments [1, 2]. Both, electric and magnetic cases, can be studied in very similar way as physical equations that model their behavior only differ by a prefactor, and they are also a proxy in a first approach to the molecular polymers carrying a dipole. In the case of electrical dipoles, an example at the molecular level are zwitterionic chains, and the glycocalyx as an example of dipolar brushes. On the other hand, for the magnetic case, chemical polymers usually only exhibit magnetic behavior bellow 100K, instead they colloidal counterparts have witnessed a broad development in the last decades: initially, micron-sized magnetic-filled para-magnetic latex beads where used as monomers to form the magnetic chains [3]. Further progresses was done using DNA to link micron-sized particles [4]. The first attempts to use sub-micrometric particles (0.3-0.8μm) where reported during 2003 -2008 [5]. Further improvements have been possible, and the use of nanoparticles with sizes below 50nm to form mesoscopic one dimensional structures has become a reality. Very recently, Benkoski et al [7] have reported the optical visualization of ferromagnetic particles (size 23.5nm) organizing into microscopic 1D chains which can be assembled into dense filament arrays. Those studies has set the onset to the creation of ensembles of chains anchored by one of their ends to a surface (magnetic brushes) [5,7-10].

AFM scan of a magnetic filament. After K Erglis *et al.*, *J. Phys.: Condens. Matter* **20**, 204107 (2008)
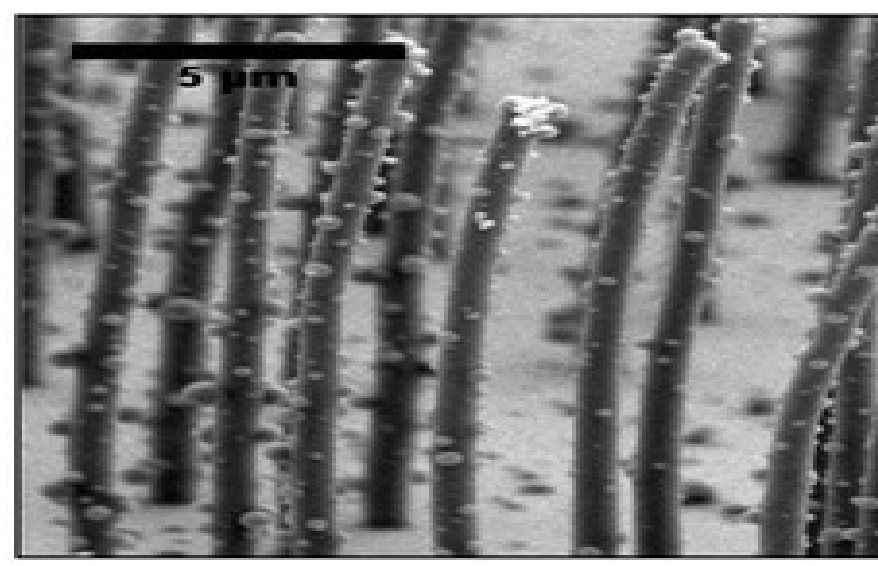
Example of magnetic brush. After B.A. Evans *et al.*, *Nanoletters*, **7**, 1428 (2007)

METHOD

We use Langevin Dynamics simulations where the dipolar filaments (or colloidal polymers) are modeled using a coarse-grained bead-spring model where each magnetic bead is represented as a soft sphere of radius σ and bears a point dipole located in its center. The magnetic effects are simulated via point dipoles located at the center the beads that interact according to the potential

$$U_{ij}^{dip} = \frac{\mu_0}{4\pi} \left(\frac{\vec{\mu}_i \cdot \vec{\mu}_j}{|\vec{r}_{ij}|^3} - \frac{3[\vec{\mu}_i \cdot \vec{r}_{ij}][\vec{\mu}_j \cdot \vec{r}_{ij}]}{|\vec{r}_{ij}|^5} \right)$$

$$\vec{r}_{ij} = \vec{r}_i - \vec{r}_j$$

The magnetic force and torque acting on a certain particle i are:

$$\vec{F}_i = -\nabla_{\vec{r}_i} U$$

$$\vec{\tau}_i = \vec{\mu}_i \times \left(-\nabla_{\vec{\mu}_i} U \right)$$

In difference to traditional bead models, the links between monomers are implemented as springs attached onto the surface of the particles at the points at which the surface intersects the line given by the direction of the magnetic dipole. It is easy to show that the effect of such springs can be modeled using the *"Spring onto Surface"* (SOS) potential:

$$U_{sos}(\vec{r}_1, \vec{r}_2, \hat{\eta}_1, \hat{\eta}_2) = \frac{1}{2} K_{sos} \left(\vec{r}_1 - \vec{r}_2 - (\hat{\eta}_1 + \hat{\eta}_2)\frac{\sigma}{2} \right)^2 \qquad \hat{\eta}_i = \vec{\mu}_i / |\vec{\mu}_i|$$

The beads or monomers that form the magnetic filament repel each other via a soft core potential which mimics the steric repulsion. In addition, for the so-called sticky particles (those in poor solvent condition), the monomers possess an attractive interaction. Both interactions are modeled via truncated-shifted Lennard-Jones potentials. The dipole moments rotate due to the thermal motion of particles as a whole block with them. Therefore dipole rotations and particle motions are effectively coupled, the *SOS* potential adds an extra degree of coupling between particles and dipoles.
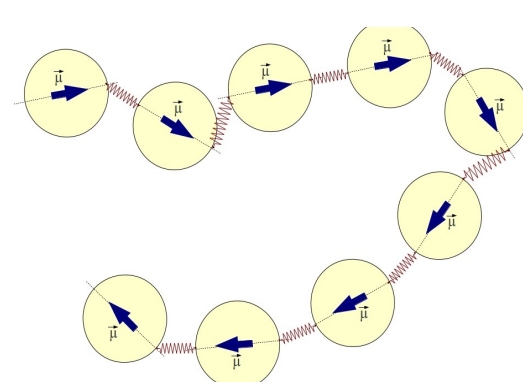
RESULTS & DISCUSSION

Dipolar forces in dipolar Brushes [1]: If we consider a brush made of dipolar chains, and we consider the force profiles acting on a non-magnetic large colloid: we found they change drastically when an external field is applied to the dipolar brushes. Force profiles are no longer monotonously increasing as the distance decreases, instead a force barrier appears. If the grafting density of the brush is large enough, there exist a region in which the brush exerts an attractive force on the colloidal particles (negative values for the force on the force profile), and a stationary point exist. The existence of a stationary point and observed force profiles can be explained through a combination of steric repulsive forces and attractive Kelvin forces between the non-dipolar parts of the system. Kelvin forces arise from the mismatch in polaritzation/magnetization in different parts of the system.
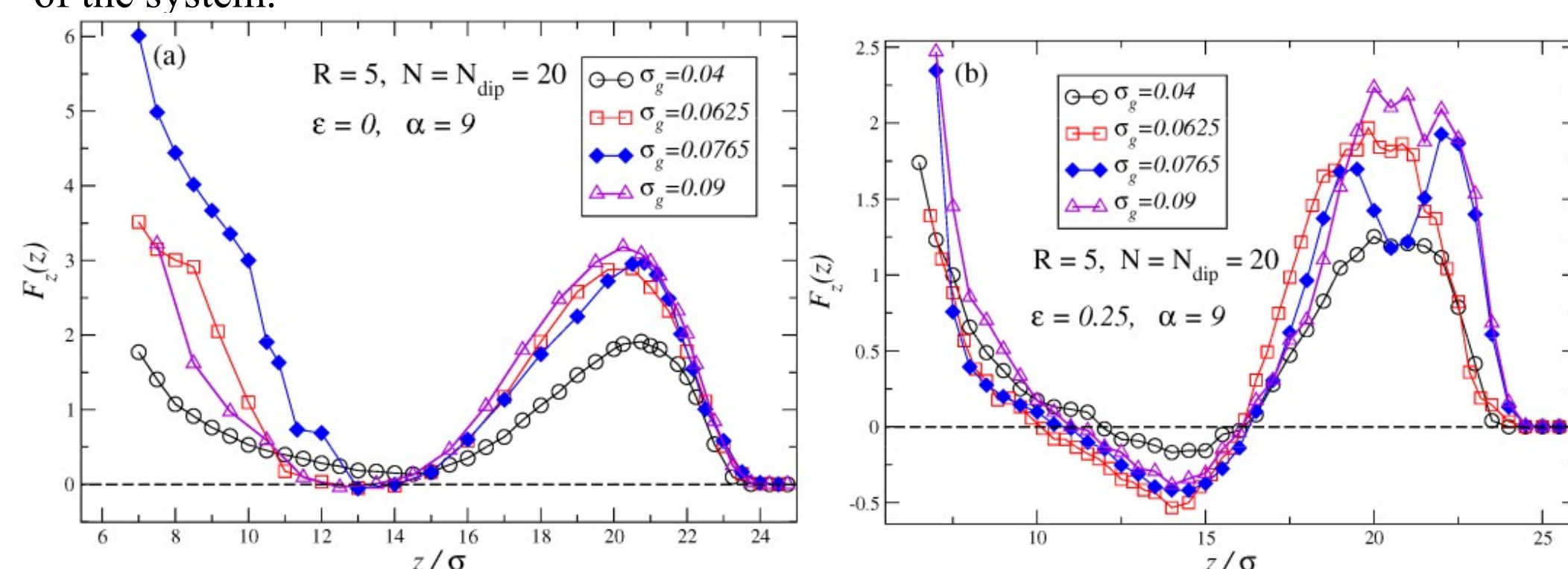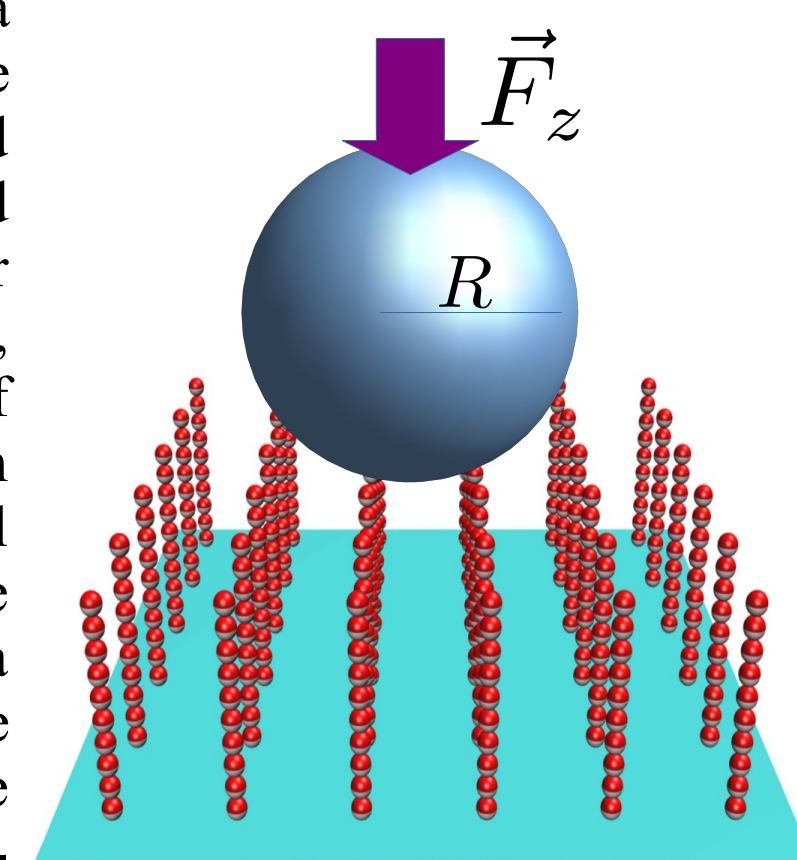
Depletion forces induced by dipolar colloidal polymers [2]: Two large colloidal particles of radius R, located at an interface where a bath of dipolar colloidal polymers exist suffer depletion forces which can be modulated via external magnetic fields: by tuning the strength of the field is possible to observe stable points in the force profiles. Results show that this type of dipolar baths have the potential for controlling externally the distance between large colloidal particles, which is a step forward to the creation of magnetic colloidal tweezers. Force profiles can be explained again via existence of Kelvin forces in combination with traditional depletion forces of steric nature.
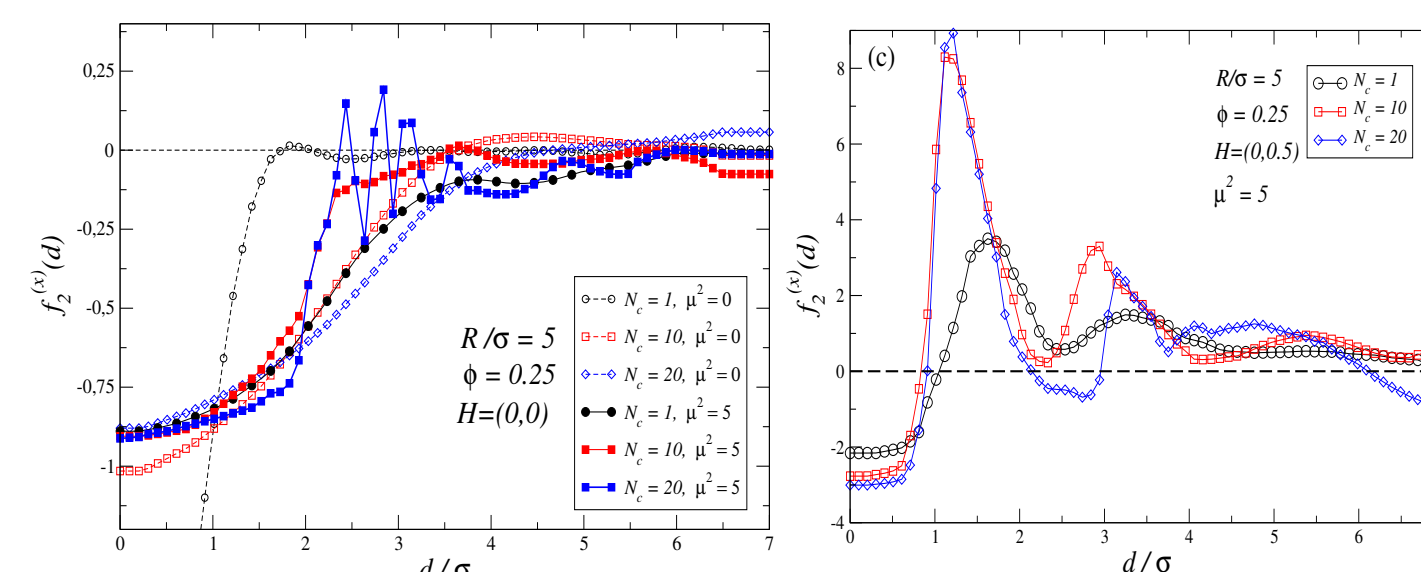
As H increases, a gradual transition from attractive to repulsive force profiles is observed.

Varying H, one can tune the location and number of stable points.

CONCLUSION

In this contribution we show via Langevin Dynamics numerical simulations how the properties of both dipolar polymer brushes and dipolar colloidal solutions can be strongly modulated through external applied fields. In the case of dipolar polymer brushes external fields can be used to modify force profiles and favour the entrapping and retention of colloidal particles inside them for a later release [1]. Alternatively, by choosing right external field strengths it is also possible to develop force barriers that prevent colloidal particles from reaching the surface where polymers forming the brush are attached. In the case of solutions of dipolar colloids, external applied fields can be used to modify the depletion force profiles among two large non-dipolar particles immersed in the dipolar solution. The modulation of the orientation and strength of the external field allows the possibility to use these suspensions as funneling tools to create aligned clusters of non-magnetic colloidal particles, colloidal tweezers able to control the distance between two large colloidal particles, and ratchets [2].

[1] A. Fuster-Aparisi and Joan J. Cerdà, Polymers 2025, 17, 366.. **[2]** Joan J. Cerdà et al, Polymers 2024, 16, 820. **[3]** Furst et al., Langmuir 14,7334 (1998);PRL 82, 4130, (1999). **[4]** Dreyfus et al , Nature 437, 862, (2005). **[5]** Tabata et al, Proc.IEEEE 6th Int.Conf .Micro.Electro. Mech. Systems 2003. Sigh et al. Nanoletters, 5, 2149, (2005);Langmuir 21, 11500, (2005). Toonder et al, Lap.Chip, 8, 533, (2008). Evans et al, Nanoletters 7, 1428,(2007). **[6]** Zhou et al, 3, 165, (2009). Keng et al, ACS Nano 1, 279,(2007). Bowles et al, Am. Chem.Soc. 129, 8694,(2007). Benkoski et al Poly. Phys. 46, 2267,(2008);J.Am.Chem. Soc 129, 6291,(2007); Langmuir 23, 3530, (2007). **[7]** Benkoski et al, Soft Matter,6,602, (2010). **[8]** Evans et al, Nanoletters 7, 1428,(2007). **[9]** Singh et al, Nanoletters 5, 2149, (2005).

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