Z. Phys. D 40, 539–541 (1997)

ZEITSCHRIFT
FÜR PHYSIK D

Self-assembly of magnetic nanostructures

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Received: 5 July 1996 / Final version: 23 October 1996

Abstract. We use Monte Carlo and quaternion molecular dynamics simulations to study the self-assembly of intriguing structures which form in colloidal suspensions of small magnetite particles. We show that the only stable isomers with few particles, a ring and a chain, can be efficiently interconverted using a magnetizable tip. We propose to use the oscillating dipole field of the tip to locally anneal the aggregates to either a ring in zero field or a chain in nonzero applied field.

PACS: 75.50.Mm

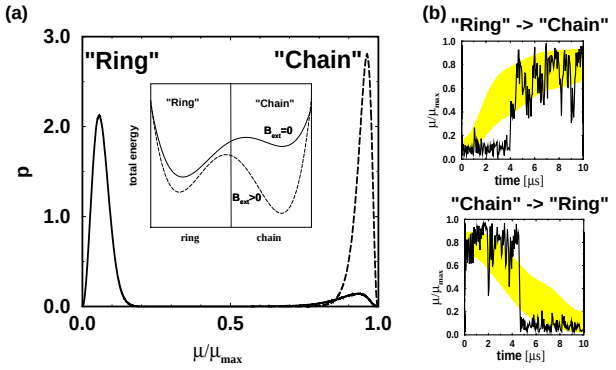

Fig. 1. a Magnetic moment distribution p at $B_{\rm ext}$ = 0 (*solid line*) and $B_{\rm ext}$ = 100 Gauss (*dashed line*), both at T = 300 K. **b** Temporal evolution of the total magnetic moment of the aggregate during the assembly causing the transformation from a ring to a chain, and transformation from a chain to a ring. The *solid lines* illustrate successful trajectories and the gray shaded areas statistical ensemble averages

Given the present advanced stage of miniaturization, the most promising way to significantly reduce the dimension of devices involves a transition from micro-manufacturing to self-assembly of nanostructures [1]. Inspired by the richness of structures observed in aggregates of magnetic nanoparticles [2, 3] and the possibility of their structural transformation [4, 5], we propose a hybrid thermodynamic self-assembly technique capable of producing magnetic patterns of unprecedented packing density [6]. The key ingredients are a system of magnetic nanoparticles in a colloidal suspension, resonant magnetic heating on the nanometer scale that we postulate, and the possibility to manipulate individual nanostructures using a local magnetic field. In the following, we prove our technique to work using realistic Monte Carlo and Molecular Dynamics simulations addressing the self-assembly, the field-assisted interconversion, and the long-term stability of the magnetic nanostructures.

In the following, we will describe microscopically the structural and magnetic transitions in microcanonical and canonical ensembles of few magnetic particles. Commercially available spherical nanoparticles of magnetite are covered by a thin surfactant layer to inhibit irreversible coalescence in a viscous liquid at room temperature [2]. Such colloidal suspensions, called ferrofluids, have recently become a focus of experimental and theoretical attention due to their interesting behavior in applied magnetic fields [2, 3, 7–12]. We will discuss the effect of field and temperature on the stability of the individual isomers, which – for few particles – are known to be either a chain or a ring [4]. More important, we will show how to locally modify their equilibrium structure by changing the field and temperature (assembly of nanostructures) and how to distinguish magnetically between the different isomers (detection of nanostructures).

The Hamiltonian describing our model system of six [13] magnetic particles has been described in [4] and can be easily parametrized [14]. Depending on the magnetic field, the equilibrium geometry of this system at low temperatures is either a ring with zero total magnetic moment or a chain with the magnetic moment $\mu = \mu_{\rm max} = N\mu_0$. As illustrated in the inset of Fig. 1a, rings are more stable in zero field, whereas chains are more stable in high magnetic fields $B_{\rm ext}$ [4]. The large minimum potential energy barrier per particle $\Delta E \approx 0.16$ eV, corresponding to a "melting" temperature $T_M \approx 630$ K, prevents metastable chains in zero field from closing to rings at room temperature. On the other hand, rings do not fragment into chains, unless exposed to high magnetic fields $B_{\rm ext} \gtrsim 600$ Gauss [4, 5], and hence are not disturbed by the low fields generated by aggregates in neighboring cells. This establishes the required stability of the magnetic structure [15].

Next, we studied the efficiency of the field-assisted assembly process. Results of a room temperature Monte Carlo simulation in applied fields $B_{\rm ext}$ = 0 and $B_{\rm ext}$ = 100 Gauss

are presented in Fig. 1a. These data indicate that upon the application of a high magnetic field for sufficiently long time, the majority of the systems will form a chain. In absence of a field, after careful annealing, the majority of the systems will form a ring. Both isomers can be easily distinguished by separate peaks in the distribution of magnetic moments. Consequently, we will use the magnetic moment as the single characteristic of the nanostructure.

In order to estimate the time needed to assemble a nanostructure, we performed Molecular Dynamics simulations of the transition between a ring and a chain in a microcanonical ensemble of six magnetite particles. We made use of the quaternion formalism [16–18] to avoid divergencies in the orientational equations of motion which would otherwise occur in this system of magnetic spherical tops (with a nonvanishing mass and inertia) due to discontinuities in Euler angle coordinates. We used time steps $\Delta t = 5\times10^{-11}$ s and integrated the equations of motion numerically using a fourth-order Runge-Kutta algorithm, since this method proved to be more stable and to better conserve the energy than alternate integration schemes.

These and our above Monte Carlo studies suggest that heating up the system 100 K above room temperature reduces the average time for a structural transformation by one order of magnitude and hence significantly accelerates the assembly. On the other hand, the higher vibrational entropy of the chain in zero field (as compared to the ring) plays an increasingly important role at these higher temperatures. This has no adverse effect on the ring-to-chain conversion in nonzero fields, but reduces the fraction of rings in zero field and hence the efficiency of the chain-to-ring conversion.

The feasibility of a high packing density of nanostructures depends on the availability of an extremely localized source of magnetic field and heat. As a promising technical realization, we suggest to use a soft magnetic nanotip, surrounded by a coil, as the source of localized static and oscillating magnetic field. This nanoscopic electromagnet assembly can be suspended on a cantilever using the technology developed for the Atomic Force Microscope (AFM) [19]. The capability to assist in the assembly and detection of magnetic nanostructures with a precision of $100 - 1000$ Å might be relatively simple to achieve in view of the AFM's success to obtain atomic resolution [19].

For field assisted assembly, a sharp magnetic tip has several advantages. (i) The field inhomogeneity guarantees that neighboring structures are not disturbed and that magnetite particles aggregate faster in the tip region. (ii) The tip can be used to generate a locally large static field to assemble a chain. (iii) Fast field reversal can be used to detach any aggregate from the tip. (iv) An oscillating high-frequency field, generated by the tip, can be used to excite preferentially the transverse bending modes of the chain, hence accelerating ring closure in a cooling environment [20].

The sharp tip, suspended on the cantilever of a Magnetic Force Microscope, can also be used to investigate the magnetic structures. The detection process is initiated by applying a weak inhomogeneous magnetic field which will attract only magnetic aggregates (chains, but *not* nonmagnetic rings) to the tip. The presence of a chain attached to the tip will lead to a lowering of the mechanical resonance frequency of the cantilever-tip system that can be detected. This allows for a discrimination between a chain and a ring in a nondestructive way.

We model the magnetic tip by a nonmagnetic cone with an opening angle of 60°, which is rounded off at the end and terminated by a magnetizable sphere (see Fig. 2). The diameter of this sphere, σ_{tip} = 400 Å, is twice that of the magnetite particles in the colloidal suspension, and its magnetic moment is aligned with the cone axis. The nonmagnetic part of the interaction between the tip and the magnetite particles is assumed to be purely repulsive. In analogy to the nonmagnetic interaction between the particles [14], it is given by $u_r = \epsilon \exp(-d/\rho_1)$, where d is the minimum distance between the surfaces of the tip and the magnetite particle in the colloid. The inhomogeneous magnetic field produced by this tip attracts magnetic aggregates and aligns their magnetic moment with the cone axis.

The dynamics of the structural transformation, assisted by the local field of a sharp magnetic tip, is illustrated in Fig. 1b. To accelerate a ring-to-chain conversion, we first heated the system locally. We found that an oscillating dipole field of frequency ν = 1 MHz, generated by changing periodically the direction of the dipole moment at the tip $\mu_{tip} = 7\times10^5\ \mu_B$, was most efficient in heating up the system by exciting resonantly its low-frequency eigenmodes, such as the bending mode. The system, which had reached an average temperature of 500 K after 5 μs, was subsequently cooled down during the next 5 μs in the *static* field of the tip dipole $\mu_{tip} = 7\times10^5\ \mu_B$ by extracting stepwise the energy doses of 15 meV, each followed by 1 μs equilibration time. The same annealing schedule has been used for a chain-to-ring conversion, with the exception of using a smaller value for the oscillating tip dipole moment $\mu_{tip} = 4\times10^5\ \mu_B$ during the annealing process and $\mu_{tip} = 0$ during the cooling process. As seen in Fig. 1b, the average time needed to convert a ring to a chain or vice versa lies close to 5μs [21].

The field-assisted assembly process with a sharp magnetic tip is illustrated in Fig. 2 by snapshots from a Molecular Dynamics simulation. At the starting point of our simulation, shown in Fig. 2a, the magnetite particles are randomly distributed and oriented in zero field. The assembly of a chain is initiated by a static magnetization of the tip. This causes the particles to aggregate in the region of strongest B_{ext}-field and to form a chain aligned with the field lines that is attached to the tip, as shown in Fig. 2b. Subsequent reversal of the magnetization of the tip causes the chain to detach from the tip, as shown in Fig. 2c. At this point, a stable chain is formed. As illustrated in Fig. 2d, applying a high-frequency dipole field excites the bending mode of the chain efficiently, facilitating closure to a ring. Figure 2e shows the spontaneous self-assembly of the ring structure after the field had been switched off. The stability of this structure increases as it cools down in the suspending liquid.

In conclusion, we proposed and modeled a hybrid self-assembly technique for aggregates consisting of magnetite nanoparticles, that is capable of producing magnetic patterns with unprecedented density. When viewed as information, this data density would by far exceed that of conventional magnetic and protein-based memories [22]. The key to tailored magnetic nanopatterns are the substantially different magnetic moments of the only stable isomers with few magnetite particles which are a ring and a chain. We proposed an

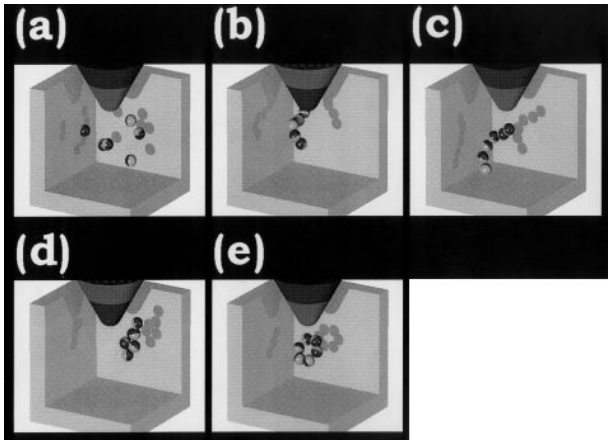

Fig. 2a–e. Snapshots of the nanostructure assembly process. The spheres represent the magnetite dipoles and the shading of the hemispheres the dipole orientiation. The cone in the *upper part* of the cell represents the magnetic tip as source of the localized magnetic field. Grey shading shows the polarity of the tip when a field is applied. **a** Initial random configuration in zero field. **b** In a static dipole field, particles form a chain attached to the tip. **c** Field reversal causes the intact chain to detach from the tip. **d** Local magnetic "heating" of the system by a high-frequency field of the tip excites predominantly the bending mode of the chain. **e** Spontaneous aggregation in zero field in the suspending liquid concludes the assembly to a ring

efficient process to assemble and to detect individual nanostructures using the localized static and oscillating dipole field of a sharp magnetic tip. We believe that the technique proposed here may bring us closer to nanopatterning on the atomic scale.

DT, PJ and SGK acknowledge financial support by the National Science Foundation under Grant Number PHY-92-24745 and the Office of Naval Research under Grant Number N00014-90-J-1396. Our extensive computer simulations have been performed on the CRAY-T3D/192 of the *Konrad-Zuse-Institute* in Berlin and the S400 supercomputer of the *Regionales Rechenzentrum für Niedersachsen*(RRZN) in Hannover.

References

1. George M. Whitesides: Scientific American (September 1995), p. 146; Kaigham J. Gabriel: Scientific American (September 1995), p. 150
2. Hao Wang, Yun Zhu, C. Boyd, Weili Luo, A. Cebers, R.E. Rosensweig: Phys. Rev. Lett. **72**, 1929 (1994)
3. Akiva J. Dickstein, Shyamsunder Erramilli, Raymond E. Goldstein, David P. Jackson, Stephen A. Langer: Science **261**, 1012 (1993)
4. P. Jund, S.G. Kim, D. Tománek, J. Hetherington: Phys. Rev. Lett. **74**, 3049 (1995)
5. Peter Borrmann, Heinrich Stamerjohanns, Eberhard R. Hilf, Seong Gon Kim, Philippe Jund, David Tománek: (submitted for publication)
6. In contrast to the current definition of self-assembly, we discuss a technique to externally direct the self-assembly of ordered, thermodynamically stable structures
7. H. Zhang, M. Widom: Phys. Rev. E **49**, R3591 (1994); J. Mag. Mag. Mat. **122**, 119 (1993)
8. J.J. Weis, D. Levesque: Phys. Rev. E **48**, 3728 (1993); D. Levesque, J.J. Weis: Phys. Rev. E **49**, 5131 (1994)
9. A.S. Clarke, G.N. Patey: J. Chem. Phys. **100**, 2213 (1994)
10. Holly B. Lavender, Karthik A. Iyer, Sherwin J. Singer: J. Chem. Phys. **101**, 7856 (1994)
11. Thomas C. Halsey, Will Toor: Phys. Rev. Lett. **65**, 2820 (1990); Thomas C. Halsey, James E. Martin, Douglas Adolf: Phys. Rev. Lett. **68**, 1519 (1992); Thomas C. Halsey: Phys. Rev. E **48**, R673 (1993)
12. R. Tao, J.M. Sun: Phys. Rev. Lett. **67**, 398 (1991)
13. The exact number of particles in the system is not critical, since all systems with $4 \lesssim N \lesssim 14$ are known to have only the "ring" or the "chain" as their equilibrium structure [4, 8], and hence show the same physical phenomena
14. Our system contains spherical magnetite particles with a diameter σ = 200 Å, mass $m = 1.31\times10^7$ amu, inertia $I = 5.25\times10^7$ amuÅ^2, and a permanent magnetic moment $\mu_0 = 1.68\times10^5\ \mu_B$. Besides considering the interaction of the magnetic dipoles with the external magnetic field and their mutual dipole-dipole interaction, we introduce a pairwise nonmagnetic interaction between the particles, given by $u(r) = \epsilon\left[\exp\left(-\frac{r_{ij}-\sigma}{\rho_1}\right) - \exp\left(-\frac{r_{ij}-\sigma}{\rho_2}\right)\right]$, with ρ_1 = 5.0 Å, $\rho_2 = 2\rho_1$ = 10.0 Å, and $\epsilon = 64\times10^{-3}$ eV
15. The stability of the nanostructure can be independently increased by increasing the viscosity of the suspending liquid. This would make a creation of permanent devices possible
16. Herbert Goldstein: Classical Mechanics, 2nd edn., Reading Mass: Addison-Wesley 1980
17. D.J. Evans: Mol. Phys. **34**, 317 (1977); D.J. Evans, S. Murad: Mol. Phys. **34**, 327 (1977)
18. Michael P. Allen: Mol. Phys. **52**, 717 (1984)
19. G. Binnig, C.F. Quate, Ch. Gerber: Phys. Rev. Lett. **56**, 930 (1986); Appl. Phys. Lett. **40**, 178 (1982)
20. The oscillating external magnetic field may be used not only to excite the internal modes of chains and rings, but also to accelerate these aggregates back and forth, eventually causing an impact-induced fragmentation of the aggregate at the tip
21. We found that after 10 μs, $\approx$ 95% rings have converted successfully to chains, and $\approx$ 90% chains have converted to rings. A higher success rate can be achieved by a corresponding extension of the interconversion time
22. Robert R. Birge: Scientific American (March 1995), p. 90