Stability and Fragmentation of Complex Structures in Ferrofluids

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We use quaternion molecular dynamics to determine the equilibrium structure, the stability, and the dynamics of fragmentation of magnetic particle aggregates as a function of applied magnetic field and temperature. In a colloidal suspension the particles form complex one-dimensional structures. At low fields and beyond a critical size, rings are more stable than chains. Rings orient perpendicularly to an applied field and can be activated to fragment into chains. This activation barrier vanishes and rings fragment spontaneously at a higher critical field.

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Ferrofluids are complex systems consisting of a colloidal suspension of magnetite particles in a viscous liquid. The near-spherical particles with a typical diameter of 100 Å, carrying a large permanent magnetic moment of typically $10^4\mu_B$, are covered by an approximately 20 Å thick surfactant layer which prevents them from coalescing at room temperature [1]. Spontaneous formation of complex labyrinthine [2] and branched [1] macroscopic structures has been observed and theoretically addressed [3–8] in these systems at low temperatures and in applied magnetic fields.

Much less is known about the formation and disintegration of aggregates containing only a few magnetite particles as a function of temperature and applied magnetic field. The strong dipole-dipole interaction between the particles had been believed to lead to the formation of chain structures only [9]. Very recently, this finding has been challenged by postulated single and double ring structures in zero field [5,6]. A behavior similar to that of ferrofluids has been predicted for colloidal suspensions of ferroelectric particles [10]. Chain formation has been observed also in electrorheological fluids, where electric dipole moments are induced by an applied electric field [11–14], so that all interparticle interactions are isotropic in the absence of external fields.

In this Letter, we show that even in systems containing very few particles the presence of permanent dipole moments leads to the formation of complex one-dimensional structures, which are stable at moderate temperatures and applied fields. We find that at elevated temperatures and high applied fields these systems disintegrate in an intriguing fashion.

The potential energy U of a system of superparamagnetic particles with a magnetic moment $\vec{\mu}_i$ in an externally applied magnetic field $\vec{B}_{\rm ext}$ consists of the interaction between each particle and the applied field, and a pairwise interaction between the particles. This can be expressed as

$$U = \sum_i -\vec{\mu}_i \cdot \vec{B}_{\rm ext} + \sum_{j>i}(u_{ij}^{dd} + u_{ij}^{nm}). \quad (1)$$

The dipole-dipole interaction u_{ij}^{dd} between two identical particles, separated by $\vec{r}_{ij} = \vec{r}_j - \vec{r}_i$ and carrying the magnetic moment $\vec{\mu}_i = \mu_0\hat{\mu}_i$ [15], has the form [16]

$$u_{ij}^{dd} = (\mu_0^2/r_{ij}^3)[\hat{\mu}_i \cdot \hat{\mu}_j - 3(\hat{\mu}_i \cdot \hat{r}_{ij})(\hat{\mu}_j \cdot \hat{r}_{ij})]. \quad (2)$$

There have been significant efforts to determine the nonmagnetic part of the interaction u_{ij}^{nm} between colloidal particles [17,18], suggesting a soft-core repulsion at very short distances and a weak short-range surfactant-modified attraction [19]. In this study we selected the functional form

$$u_{ij}^{nm}(r_{ij}) = \epsilon\left[\exp\left(-\frac{r_{ij}-\sigma}{\rho_1}\right) - \exp\left(-\frac{r_{ij}-\sigma}{\rho_2}\right)\right], \quad (3)$$

which is isotropic and close to the form used by Tejero *et al.* [20]. To reproduce the properties of a typical ferrofluid, such as that used in Ref. [1], we consider magnetite particles with a diameter $\sigma = 100$ Å and a mass $m = 1.64 \times 10^6$ amu, which carry a magnetic moment $\mu_0 = 2.1 \times 10^4\mu_B$. The energy scale of the dipolar interaction between neighboring particles separated by $r_{ij} = \sigma$ is given by $\mu_0^2/\sigma^3 \simeq 2.37 \times 10^{-2}$ eV. Choosing $\rho_1 = 2.5$ Å, $\rho_2 = 5.0$ Å, and $\epsilon = 8 \times 10^{-3}$ eV in Eq. (3) yields a potential with a strongly repulsive core and a weakly attractive ($\lesssim$10% of the maximum dipole-dipole interaction) "sticky skin" around the particles with a short range of $\lesssim$20 Å. We note that the particle mass and the viscosity of the suspending liquid have no effect on the equilibrium structures, but affect the dynamics.

Molecular dynamics (MD) simulations of a system of magnetic spherical tops with nonvanishing mass and inertia are nontrivial due to the additional orientational degrees of freedom and the divergence of the corresponding equations of motion if Euler coordinates are used. We described the dynamics of the system using the quaternion formalism [21–23] and used a fourth-order Runge-Kutta algorithm to integrate the equations of motion.

The first question we address is the equilibrium structure of small aggregates. Our results are summarized in Fig. 1. The dipole-dipole interaction tends to align the

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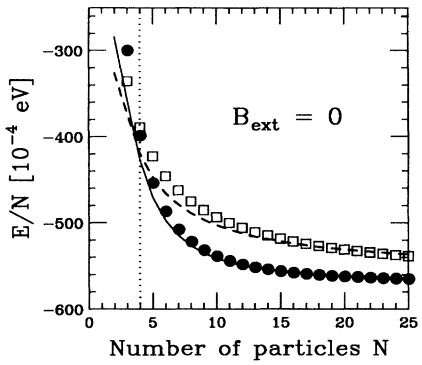

FIG. 1. Energy per particle E/N of chain (□) and ring (●) aggregates of N magnetic particles in zero applied field. The solid and dashed lines are analytical results for rings and chains, respectively.

dipoles ferromagnetically in a linear structure. As compared to a finite straight chain of aligned dipoles, a ring structure is more stable if the energy gain from connecting the chain ends outweighs the energy loss due to the misalignment of neighboring dipoles. Our results, given by the data points in Fig. 1, indicate that in zero field rings are favored over chains for all systems with more than three particles, in agreement with recently published data [5,6]. Our numerical results are well reproduced by a simplified model which is based on the following assumptions. (i) All interparticle interactions in Eq. (1) are restricted to nearest neighbors only. (ii) Nonmagnetic interactions are approximated by those of hard spheres with a fixed nearest-neighbor distance of $\sigma = 100$ Å. (iii) To compensate for the neglect of beyond-nearest neighbors in the second term of Eq. (1), the dipole-dipole interaction u_{ij}^{dd} is scaled by a constant factor α. For an N-membered chain and ring in zero field, this model gives the energy per particle as

$$E^0_{\text{chain}}(N)/N \simeq -\alpha(2\mu_0^2/\sigma^3)(1 - 1/N), \quad (4)$$

$$E^0_{\text{ring}}(N)/N \simeq -\alpha(2\mu_0^2/\sigma^3)[3 + \cos(2\pi/N)]/4. \quad (5)$$

We find that $\alpha = 1.2$ gives an excellent fit to our numerical data shown in Fig. 1. We note that Eq. (4) is similar to an expression derived in Ref. [6]. Since infinite rings and chains are locally indistinguishable, our analytic and numerical results converge to the same limiting value $E/N \approx -5.7 \times 10^{-2}$ eV.

Next, we study the *stability* of these structures in nonzero applied field. Chains are most stable when aligned with the field. Unconstrained rings, however, prefer to flip perpendicular to the field. We have studied the response of an $N = 10$ particle system to an external field at $T = 0$. Our results are summarized in Fig. 2. Below the lower critical field B_l, rings are most stable, as schematically indicated in the upper part of Fig. 2(a). In the field range $B_l < B_{\text{ext}} < B_u$, the ring structure becomes metastable, yet its transformation to the stable chain is an activated process. Beyond the upper critical field

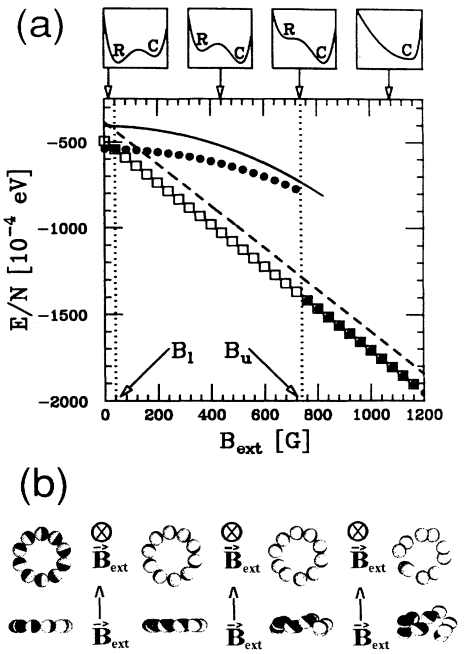

FIG. 2. (a) Energy per particle E/N of an aggregate of $N = 10$ magnetic particles in applied magnetic field B_{ext}. The data points represent optimized ring (●) and chain (□) geometries. The corresponding analytical results for rings and chains are given by the solid and dashed lines, respectively. Schematic diagrams depicting important phases in the energetics of the ring (R) to chain (C) transition are shown in the top part of the figure. (b) Snapshots of the (meta)stable structures occurring during the breakup of rings in an applied magnetic field, in bottom and side views. The particles are represented by spheres and the orientation of their magnetic dipole by the north (black) and south (white) hemispheres.

B_u, the activation barrier disappears and rings transform spontaneously into chains. Our results, presented as data points in Fig. 2(a), have been obtained by optimizing initial chain and ring configurations using Eq. (1) and the conjugate gradient method.

The intriguing dynamics of the *activated* breakup of rings in an applied magnetic field is illustrated in Fig. 2(b) by snapshots of the (meta)stable structures, which are presented in bottom and side views. The positions of the magnetic particles and the direction of their magnetic dipoles, represented by the orientation of their north (black) and south (white) hemispheres, illustrate the distinct stages of the ring breakup process which correspond to the four schematic energy diagrams at the top of Fig. 2(a).

At very small fields, near-perfect rings, oriented perpendicular to the field, are the most stable. In this case, all magnetic dipoles lie normal to the field and show a near-ferromagnetic alignment. At somewhat higher fields, the magnetic dipoles show a tendency to align with the field, without changing the aggregate geometry. This gains the system the magnetic orientation energy of individual particles, at the cost of a diminished dipole-dipole attraction

between the particles. The ring subsequently buckles, as if attempting to fragment into short chains which would align with the field. At fields $B_{\rm ext} > B_u$, the rings break up spontaneously into these chains. This behavior is essentially correctly described by the following analytical expression for an N-membered chain and ring in an external field $B_{\rm ext} < B_u$:

$$E_{\rm chain}(N, B_{\rm ext})/N \simeq E^0_{\rm chain}(N)/N - \mu_0 B_{\rm ext}, \quad (6)$$

$$E_{\rm ring}(N, B_{\rm ext})/N \simeq E^0_{\rm ring}(N)/N - B^2_{\rm ext}\sigma^3/2\alpha[5 + \cos(2\pi/N)], \quad (7)$$

as seen from a favorable comparison with our numerical results in Fig. 2(a).

It is interesting to note that field-induced breakup of the ring occurs via changes in orientation of the dipoles with essentially no change in the shape of the ring. A transition from attractive to repulsive dipole-dipole interactions u^{dd}_{ij} occurs due to the competition between the two magnetic energy terms in Eq. (2). Both terms tend to align the dipoles: the first antiferromagnetically, the dominating second term ferromagnetically. Suppose that all interacting particles are fixed in position, whereas all their dipole moments are aligned parallel to each other and at an angle θ with respect to their connecting vector. Inspection of Eq. (2) shows that for θ exceeding $\theta_c \approx 54.7°$ the dipolar interaction changes from attractive to repulsive. This value lies close to the critical angle displayed in Fig. 2(b).

We discuss now the thermal stability of magnetic aggregates in the field region $B_l < B_{\rm ext} < B_u$ where the ring geometry, which is stable in zero applied field, becomes metastable. Even though the transition from a metastable ring to the stable chain is an activated process in this field region, it will occur at sufficiently high temperatures. In order to estimate the thermal stability of rings at these fields, we performed a corresponding MD study for a microcanonical ensemble representing an $N = 10$ particle system [24]. We started by randomly perturbing the optimized ring geometry. At each value of the applied field $B_{\rm ext}$, we heated up the system stepwise with kinetic energy doses $\Delta E = 3 \times 10^{-3}$ eV, each followed by an equilibration time $\tau = 1$ μs [25]. We found time steps $\Delta t = 5 \times 10^{-11}$ s to be sufficiently small for a precise integration of the equations of motion of the heavy magnetic particles.

Our results for the thermal stability of rings in an applied magnetic field are summarized in Fig. 3. Each data point represents 2×10^6 time steps computed in simulations with 10 different starting configurations. We found it necessary to inspect a larger ensemble of trajectories in order to compensate for the nonergodicity of isolated few-particle systems. We estimated the activation barrier for breakup in three independent ways. At each field, we first investigated the minimum *total energy increase* which made a ring fragment within our simulation time. Next, we

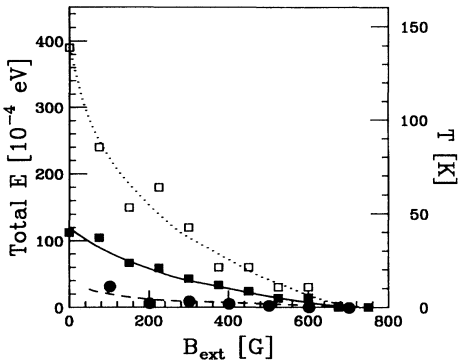

FIG. 3. Simulation results for the activated transition from an $N = 10$ particle ring to a chain, as a function of the applied field $B_{\rm ext}$. The minimum *total energy* increase found to break up a ring in our molecular dynamics runs is denoted by □. The lowest calculated *potential energy barrier* along a trajectory connecting a ring and a chain is denoted by ■. The computed *activation barrier for the spiral opening mechanism* of the ring is denoted by ●. The smooth curves serve as guides to the eye.

investigated the lowest *potential energy barrier* within all our trajectories. This barrier occurs as a saddle point in the complex potential energy surface between the optimized ring and the optimized chain, and its value corresponds to the minimum required initial kinetic energy of a ring which would surely make it fragment into a chain after an infinite amount of time. Third, we realized that our extensive, yet still limited, MD simulations were not able to provide us with information about other lower-lying, yet kinetically barely accessible transition states which occupy only a small volume in phase space. Using a guided search, we found the energetically least costly ring to chain transition to proceed via a "spiral opening mechanism," where two neighboring particles are separated in the direction of the ring axis and allowed to transform to a chain. In order to provide a rough estimate of the "melting temperature" of the rings, we used the equipartition theorem to translate the energy scale on the left vertical axis into the temperature scale on the right vertical axis of Fig. 3.

Finally, we calculated the lower and upper critical fields associated with the stability of N-particle rings in an applied magnetic field as a function of the aggregate size N. Our numerical results, presented in Fig. 4, are in good agreement with the analytic expressions based on our simplified model,

$$B_l(N) \simeq \alpha(2\mu_0/\sigma^3)\{1/N - [1 - \cos(2\pi/N)]/4\}, \quad (8)$$

$$B_u(N) \simeq \alpha(\mu_0/\sigma^3)[5 + \cos(2\pi/N)]\left[\frac{1 + \cos(2\pi/N)}{3 + \cos(2\pi/N)}\right]^{1/2}. \quad (9)$$

We find the value of $B_u(N)$ to increase monotonically with increasing aggregate size N, and finally to saturate at a value $B_u(\infty) = 826.5$ G [26] for an infinitely large ring

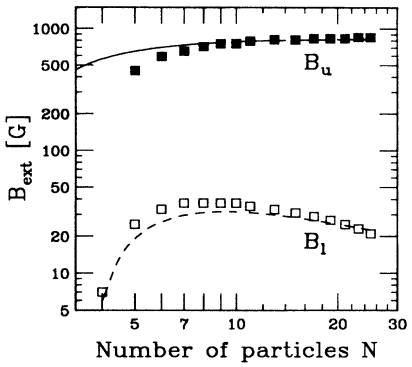

FIG. 4. Simulation results for the lower critical field B_l (□) and the upper critical field (■) as a function of aggregate size N. Analytic results for B_l and B_u are given by the dashed and solid lines, respectively.

which is locally indistinguishable from a chain lying perpendicular to the applied field. A nonzero value of the lower critical field B_l, which we observe for $N \geq 4$, is indicative of the ring configuration becoming metastable or unstable with respect to the chain. We find B_l to reach its maximum value for $N \approx 7-10$, and then to decrease monotonically to $B_l(\infty) = 0$. This last result follows simply from the fact that while in absence of an applied field an infinite chain and ring are energetically degenerate, even an infinitesimally small field is sufficient to stabilize a field-aligned chain with respect to the ring.

In summary, we used quaternion molecular dynamics and structure optimization techniques to determine the equilibrium geometry, the stability, and the fragmentation dynamics of small aggregates of superparamagnetic particles in a colloidal suspension as a function of applied magnetic field and temperature. We found these magnetic particles to aggregate into ferromagnetically ordered one-dimensional structures as observed in very dilute ferrofluids with strong magnetic coupling [27]. More complex equilibrium structures, such as multiple rings [5,6], complex knots [4], prolate spheroids [7], and body-centered tetragonal structures [8], occur in larger or bulk systems. Small aggregates with $N > 3$ particles are rings which orient perpendicular to the field. At sufficiently high temperatures of typically few tens of degrees kelvin, an activated transition to the more favorable chain structure can occur above a lower critical field, typically $B_l < 50$ G. This activation barrier vanishes and rings break spontaneously into chains beyond the upper critical field of typically $B_u \lesssim 10^3$ G.

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