Dynamic Roughening and Fluctuations of Dipolar Chains

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Nonmagnetic particles in a carrier ferrofluid acquire an effective dipolar moment when placed in an external magnetic field. This fact leads them to form chains that will roughen due to Brownian motion when the magnetic field is decreased. We study this process through experiments, theory and simulations, three methods that agree on the scaling behavior over 5 orders of magnitude. The rms width goes initially as $t^{1/2}$, then as $t^{1/4}$ before it saturates. We show how these results complement existing results on polymer chains, and how the chain dynamics may be described by a recent non-Markovian formulation of anomalous diffusion.

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Existing observations of collective Brownian motion in polymer chains are restricted to averaged behavior in polymer melts or, in the case of single chain observations, subject to ambiguous interpretations. The latter fact is due to the existence of several active mechanisms in these systems, i.e., long-range hydrodynamic as well as dipolar interactions [1]. In this Letter we introduce direct experimental observations of Rouse behavior [2] of single particle chains along with a theoretical analysis to explain why. Recent understanding of the experimental interactions explains why both the hydrodynamic and dipolar interactions are suppressed in our case, as opposed to existing studies. While existing measurements are interpreted in terms of theories based on such interactions our experiment lends itself directly to the simpler Rouse model.

Magnetic holes [3–5] are nonmagnetic micrometer sized spheres suspended in a ferrofluid, much larger than the magnetite nanoparticles in suspension. In an external magnetic field $\mathbf{H}$, these holes acquire an effective dipolar moment equal to the opposite of the dipolar moment of the displaced ferrofluid. When placed between two nonmagnetic glass plates the spheres acquire interactions that may be fine-tuned to produce well defined separation distances and interparticle forces [4]. In a constant field, particles aggregate to form chains.

We study the kinematic roughening of an initially straight chain which is parallel to the glass plates, and much longer than the space between them. This changes the hydrodynamic interaction forces from $1/r$ to $1/r^2$, effectively making them short range, as is the $1/r^4$ behavior of the dipolar forces.

The tunability of the experimental interactions allows us to observe the scaling behavior over a significantly larger range (5 orders of magnitude in the dynamic domain) than has been possible in earlier studies.

In the end we show how the Markovian N-particle description of the entire chain may be contracted to a non-Markovian description of a single particle in the chain. This is done by integrating out all interaction degrees of freedom. What is left is a generalized Langevin equation with long term memory. It has recently been shown how such an equation may be used to predict anomalous diffusion exponents [6], and indeed these exponents coincide with our independent predictions and measurements. This system is the first experimental realization confirming this theory.

The ability of particle chains to change the rheological properties of their carrier fluids has given rise to practical applications and designs such as dampers, hydraulic valves, clutches, and brakes [7]. In constant fields (electric or magnetic, depending on the nature of the dipoles), these chains aggregate laterally [8] due to their thermal fluctuations. Therefore, the precise quantification and understanding of these fluctuations along an *isolated* dipolar chain is an important component to understand the aggregation phenomena in constant fields of magnetorheological [9] or electrorheological [10] fluids, as well as in systems of magnetic holes [11].

We note that also by coating the microspheres with bioactive materials, such as streptavidin [12], they may be used for the direct manipulation of single strands of DNA. For such an application the quantitative control of Brownian fluctuations is essential.

In the experiments monodisperse polystyrene spheres [13] of diameters $a = 3.0$ or 4.0 μm were dispersed in a kerosene based ferrofluid [14] of susceptibility $\chi = 0.8$ and viscosity $\eta = 6 \times 10^{-3}$ Pa s, inside a glass cell of thickness $d = 10$ μm and lateral extent 38×8 mm. A pair of outside coils produced magnetic field strengths up to $H = 20$ Oe. The setup was mounted under an optical microscope with an attached video camera recording four frames per second. Low volume fractions ($<1\%$) of microspheres were used and chains were grown [11] by applying a constant field of about $H = 18$ Oe parallel to the thin ferrofluid layer for about 20 min. Because of the nonmagnetic character of the glass plates, particles are centered midway between them [4].

The cell was searched for long isolated chains of 30–120 spheres. The field was then reduced to a constant

value H in the range $2 \leq H \leq 10$ Oe while the motion of one long chain was recorded and analyzed. One pixel of the video image corresponded to 0.5 μm, and the uncertainty in particle position could be reduced to 0.2 μm by utilizing the intensity profile of the pixels showing the particle. The experiments illustrated in Fig. 1 are challenging in part because this accuracy is needed to reveal the scaling behavior of the chains.

In order to obtain an equation of motion for chains we define the lateral displacement of particle i, h_i, from the initial straight line. A particle pair at a separation r and angle θ to the external magnetic field experiences a coupling energy $U = \mu_f \sigma^2 (1 - 3\cos^2\theta)/(4\pi r^3)$, where $\sigma = -\pi a^3 [\chi/(6 + 4\chi)]\mathbf{H}$ [3,15]. The ratio of the maximum interaction energy over the thermal energy $k_B T$ characteristic of the random forces due to the molecular motion in the solvent is defined as [16] $\lambda = (\mu_f \sigma^2)/(2\pi a^3 kT)$. In Fig. 1 the initial value $\lambda = 866$ is reduced to $\lambda = 24$. Neglecting all magnetic interactions but the nearest neighbor ones and performing a Taylor expansion of the magnetic interaction potential around the minimal energy configuration, a straight line with spacing a, the lateral component of the magnetic force on sphere i is $F_i^M = \alpha(h_{i+1} - 2h_i + h_{i-1})$, with $\alpha = \pi \mu_f \bar{\chi}^2 H^2 a/12 = 6\lambda kT/a^2$. Since the Reynolds number in this system is very small (typically $\mathrm{Re} = 10^{-5}$), the hydrodynamic forces are linear in the particle velocity, and $F_i^H = -\kappa \dot{h}_i$, where $\kappa = 3\pi\eta a$.

Newton's second law for the ith sphere is then

$$m\ddot{h}_i = F_i^M + F_i^H + \zeta_i(t), \tag{1}$$

where the fluctuating force $\zeta_i(t)$ is due to the molecular nature of the fluid and gives rise to the Brownian motion of the particle. At time scales exceeding the viscous damping time $t_m = m/\kappa = a^2\rho/18\eta \approx 10^{-7}$ s, the inertial term $m\ddot{h}_i$ is negligible. Because of the presence of confining plates, inertial motion in the fluid also decays on this time scale, so that we can neglect any non-Markovian corrections to Eq. (1) as well as such corrections in the fluctuating force [17]. We may therefore write $\langle \zeta_i(t)\zeta_j(0)\rangle = 2\kappa k_B T \delta(t)\delta_{ij}$, where the prefactor reflects the equipartition of particle kinetic energy, i.e., $k_B T = \langle m\dot{h}_i^2 \rangle$ [18]. Combining the above equations Eq. (1) can be written

$$\dot{h}_i = \frac{\alpha}{\kappa}(h_{i+1} + h_{i-1} - 2h_i) + \frac{1}{\kappa}\zeta_i(t). \tag{2}$$

For spatial scales above a, this reduces to the Rouse model, $\kappa \partial h/\partial t = \alpha a^2 \partial^2 h/\partial^2 x^2 + \zeta_i(t)$, famous in polymer dynamics but usually not confirmed by experiments because of hydrodynamic interactions [2]. This also corresponds to the Edwards-Wilkinson equation, model for kinetic interface growth [19].

We consider an isolated chain of N particles and are interested in the dynamic roughening of the chain. To observe this experimentally λ is decreased from a value

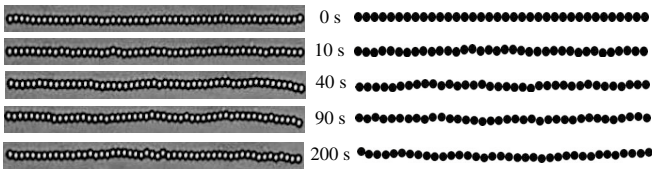

FIG. 1. Typical dynamic roughening of dipolar chains of 52 magnetic holes of diameter 4 μm after a sudden decrease of the external magnetic field: experiments (left) and simulations (right).

$\lambda_0 \gg 1$ to a finite value still greater than 1 (so that the chain does not melt).

It is convenient to describe this by using the discrete space-Fourier transform along the chain $\tilde{h}_n = \frac{1}{N} \times \sum_{j=0}^{N} h_j e^{-2i\pi nj/N}$, for $n = 0 \cdots N-1$. Equation (2) then takes the form

$$\dot{\tilde{h}}_n = -\omega_n \tilde{h}_n + \tilde{\zeta}_n/\kappa, \tag{3}$$

with the dispersion relation $\omega_n = 2\alpha[1 - \cos(2\pi n/N)]/\kappa$, and random terms obeying $\langle \tilde{\zeta}_m(t)\tilde{\zeta}_n^*(0)\rangle = 2\kappa k_B T \delta(t)\delta_{mn}/N$. Equation (3) is easily solved to give

$$\tilde{h}_n(t) = \tilde{h}_n(0)e^{-\omega_n t} + \int_0^t dt' e^{-\omega_n(t-t')}\tilde{\zeta}_n(t')/\kappa. \tag{4}$$

Setting $\tilde{h}_n(0) = 0$ and taking the thermodynamic average of the square of the above equation leads to

$$\langle \tilde{h}_n(t)\tilde{h}_m^*(t)\rangle = \frac{k_B T}{\kappa N}\frac{1 - e^{-2\omega_n t}}{\omega_n}\delta_{mn} \tag{5}$$

for $n \neq 0$, and $\langle |\tilde{h}_0(t)|^2\rangle = (2k_B T/\kappa N)t$. It is seen from Eq. (5) that each Fourier mode is initially in a free diffusion regime, $\langle |\tilde{h}_n(t)|^2\rangle \sim t$, for $t \ll \tau_n = 1/2\omega_n$ and saturates when $t \gg \tau_n = 1/2\omega_n$. The minimum and maximum saturation times are, respectively, $\tau_{N/2} = \tau = \kappa/8\alpha$ and $\tau_1 = N^2\tau/\pi^2$ for the shortest and longest wavelength.

We are interested in the mean square width of the chain $W^2 = \sum_i (h_i - \sum_j h_j/N)^2/N = \sum_{n=1}^{N-1}\langle |\tilde{h}_n|^2\rangle$. When $t \ll \tau$ all Fourier modes are in free diffusion and $W^2 \approx 2k_B T t/\kappa$. This result arises only because of the existence of a shortest wavelength a in the system. In the continuum limit $a \to 0$, $\tau \to 0$ and this regime does not exist. Later on the modes associated with progressively longer wavelengths reach their saturated states, which is reflected in a new scaling behavior of W. By inserting Eq. (5) in the above expression for W^2 it is straightforward to show that it satisfies the Family-Vicsek scaling form $W^2 = NF(t/N^2)$. Moreover, the exact form of F may be obtained. Along with the expressions for τ, κ, and α this gives the result

$$\frac{W^2 H^2 a}{N k_B T} = \begin{cases} \frac{2N}{3\pi\eta}\frac{H^2}{N^2}t & \text{when } t \ll \tau \\ \sqrt{\frac{8}{\pi^3 \eta \mu_f \bar{\chi}^2}}\sqrt{\frac{H^2}{N^2}t} & \text{when } \tau \ll t \ll \tau N^2/\pi^2 . \\ \frac{2}{\pi\mu_f\bar{\chi}^2} & \text{when } t \gg \tau N^2/\pi^2 \end{cases}$$

The hydrodynamic coupling between the particles and the confining plates was taken into account by renormalizing the drag coefficient as $\eta/\eta_o = 2/[1 - 9a/16d] - 1 = 1.40$ (1.7) for $a = 3$ μm (4 μm) [20]. This scaling law was checked in 15 experiments where chains of $N = 36$ to 59 spheres of diameters 3 or 4 μm were allowed to evolve from states where λ was reduced to values between 2.7 and 267. In Fig. 2 the average of the scaled width $WH\sqrt{a/N}$ is displayed as a function of the scaled time H^2t/N^2. The average is taken both over time intervals of $0.01t$ and over different experiments.

The relevance of the long-range nature of the dipolar interactions and of the linearization of the magnetic interactions was studied via Brownian dynamics simulations, where Eq. (1) without the $m\ddot{h}_0$ term was solved, this time with the full dipolar form of the magnetic interactions computed for every particle pair. A repulsive potential $\sim \exp(-100r/a)$ when $r < a$ was used to prevent any significant overlaps. The average width over 100 simulations was evaluated for $N = 36$, $a = 3$ μm, and $H = 4$ Oe. Figure 2 demonstrates that both the simulations and theoretical results agree with experimental measurements in all three scaling regimes, although the crossover between the $t^{1/2}$ and $t^{1/4}$ regimes extends over a full decade. The $W \sim t^{1/4}$ regime is visible over roughly 2.5 decades. The high variance around the average of W in the saturated regime comes from the small number (three) of experiments that were carried out at this reduced time. Lubrication or cohesion forces between the particles are irrelevant for the collective behavior of these lateral fluctuations, as shown by the agreement between experiments and simulations, where these were absent. This can be attributed to the presence of surfactants in the ferrofluid, preventing flocculation of the particles, and to the fact that lubrication forces act mainly along the direction

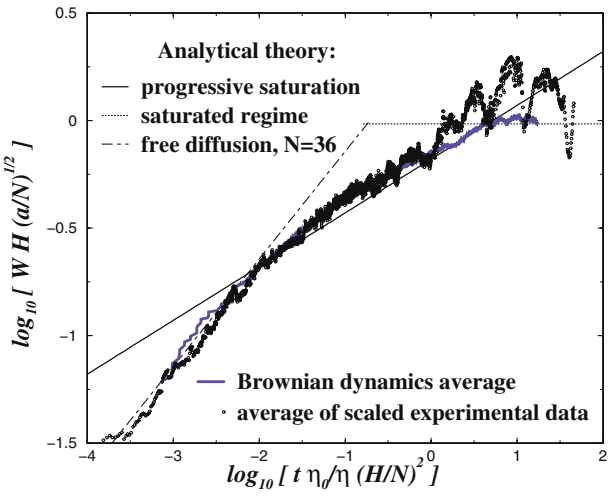

FIG. 2 (color online). Scaling of the random mean square width of the transverse displacements: theory, experiments, and Brownian dynamics result. The units are Oe, μm, μm, and seconds for H, a, W, and t, respectively.

of separation vectors between neighboring particles, which are close to the field direction, and have thus a negligible contribution to the transverse components studied here [21].

It is also possible to obtain the dynamic scaling from the equilibrium behavior. For this purpose consider the departure Δh_i from an arbitrary initial configuration, i.e., $\Delta h_i(t, t_0) = h_i(t + t_0) - h_i(t_0)$. Using Eq. (4) again we find that the averaged space-Fourier transform of $\Delta h_i(t, t_0)$ obeys

$$\frac{\langle|\Delta\tilde{h}_n(t, t_0)|^2\rangle}{At} = \frac{1 - e^{-\omega_n t}}{\omega_n t}, \tag{6}$$

where $A = 2k_BT/3\pi\eta aN$. Above we have used the saturation level $\langle|\tilde{h}_n(t_0)|^2\rangle = k_BT/\kappa N\omega_n$ from Eq. (5). Comparing this expression with Eq. (5) shows that the lateral fluctuations at equilibrium behave similarly to the lateral displacements starting from a straight chain during the nonequilibrium roughening stage, but display an amplitude $\sqrt{2}$ times larger and develop 2 times more slowly.

In Fig. 3 we have compared the theory of Eq. (6) to $N = 57$, $a = 3$ μm experiments with $\lambda = 113$ and 18.1, for which $\tau = 0.022$ and 0.14 s. For each t the power spectrum $|\Delta\tilde{h}_n(t, t_0)|^2$, calculated using a Hamming window, was averaged over all possible t_0's in the 30 min the experiment lasted. The agreement between these experiments and this theory, where there are no free parameters, is satisfactory.

Finally, we sketch the structure of the connection between the present problem and the general framework of anomalous diffusion of particles in systems with memory [6]. We consider particle $i = 0$ and use Eq. (1) to integrate out the $i \neq 0$ variables. This does not modify the underlying physics of the system but allows us to map it on a non-Markovian description for this single particle, in a background consisting of both the fluid and the rest of

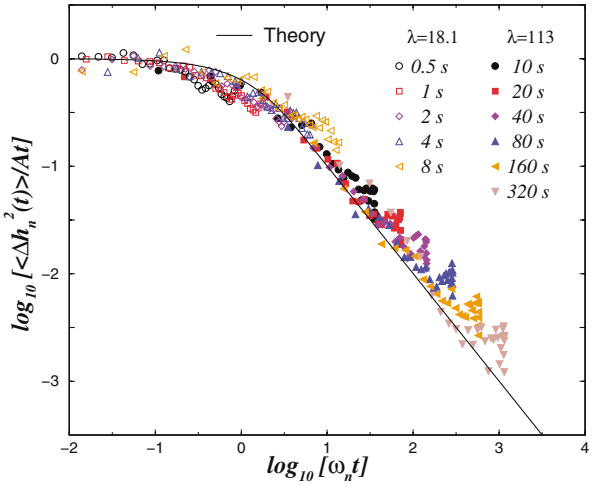

FIG. 3 (color online). Power spectrum of the space-Fourier transform of the fluctuations normalized by time.

the particles, which displays memory effects mathematically incorporated in a response function $\Gamma(t)$. By applying time Fourier transforms and neglecting all but the $i = 0$ mass it is possible to arrive at [21]

$$m\hat{\dot{h}}_0(\omega) = -m\hat{\Gamma}(\omega)\hat{h}_0(\omega) + \hat{F}(\omega), \quad (7)$$

where the time Fourier transform is denoted by hat symbols, $F(t)$ is the fluctuating part of the force, and $\tilde{\Gamma}(\omega) = (4/m)\sqrt{\alpha\kappa/i\omega}$ for $1/\tau_1 \ll \omega \ll 1/\tau$ and $\hat{\Gamma}(\omega) \sim (4/m)\sqrt{\alpha\kappa\tau_1/i}$ for $\omega \ll 1/\tau_1$. The inverse Fourier transform of Eq. (7) is a generalized Langevin equation of the Mori-Lee form [6],

$$m\ddot{h}_0(t) = -m\int_{-\infty}^{t} dt_1\Gamma(t - t_1)\dot{h}_0(t_1) + F(t). \quad (8)$$

From the exact form of $F(t)$ [21] the fluctuation dissipation theorem for such a generalized Langevin equation, $\langle F(t)F(0)\rangle = 2mk_BT\Gamma(|t|)$, can be checked directly. The memory effects and correlations in $F(t)$ come from the interaction between the rest of the chain and the fluid. According to theory [6], the random mean square width of the observed particle's displacement scales at long time as $W^2 \sim t^{1-\alpha}$ if $\hat{\Gamma}(\omega) \sim \omega^{-\alpha}$ in the limit $\omega \sim 0$. Here, the asymptotic behavior of the response function corresponds to $\alpha = 0$ for finite chains and $t > \tau_1$, and to $\alpha = 1/2$ for times below τ_1 ($\tau_1 \to \infty$ when $N \to \infty$). The observed behavior $W^2 \sim t^{1/2}$ for $t \ll \tau_1$ is then in agreement with this theory.

For chains in an unbounded medium, the Zimm model predicts $W \simeq t^{1/3}$ [2], and experiments carried on various magnetorheological fluids report $W \simeq t^{0.35\pm0.05}$ [1]. This behavior is attributed to either hydrodynamic or long-range dipolar interactions. In our system hydrodynamic interactions are suppressed by the walls. This may be understood by noting that the flow in our system is described by a simple Darcy law $v \sim -\nabla P$ at length scales above d, along with $\nabla^2 P = 0$. This implies that a local flow perturbation decays as $1/r^2$ which is faster than the $1/r$ decay, given by the Oseen tensor in an unbounded medium [2]. Since the chain length is typically much larger than d, hydrodynamic interactions are local and do not affect the longer wavelengths of our chain motion. On the other hand, we note that if our experimental and simulation data were truncated as $\log_{10}(H^2t/N^2) \leq -1$ they could support the $W \simeq t^{3/8}$ interpretation made by Furst and Gast [1]. As these authors attribute their exponent 3/8 to long-range dipolar interactions, our results may indicate that such interactions do play a role, but only in a crossover regime to the $W \simeq t^{1/4}$ behavior.

In conclusion, we have established the scaling behavior of confined dipolar chains over 5 orders of magnitude by matching experiments, theory, and Brownian dynamics simulations. We have also related this system to nearby theories of both polymer models, kinetic interface growth, and non-Markovian formulations of anomalous diffusion. This allowed us to show that the quasi-two-dimensional nature of this system reduces it to a Rouse behavior and that this system experimentally validates this recent non-Markovian theory of anomalous diffusion. These results are attractive, in particular, because of the versatility and easy control of the experiments.

[1] E. M. Furst and A. P. Gast, Phys. Rev. E **62**, 6916 (2000); **58**, 3372 (1998); S. Cutillas and J. Liu, Phys. Rev. E **64**, 011506 (2001); A. S. Silva, R. Bond, F. Plouraboué, and D. Wirtz, Phys. Rev. E **54**, 5502 (1996).

[2] A. Y. Grosberg and A. R. Khokhlov, *Statistical Physics of Macromolecules* (AIP Press, New York, 1994).

[3] A. Skjeltorp, Phys. Rev. Lett. **51**, 2306 (1983).

[4] R. Toussaint *et al.*, Phys. Rev. E **69**, 011407 (2004).

[5] A. Skjeltorp and G. Helgesen, Physica (Amsterdam) **176A**, 37 (1991).

[6] R. Morgado, F. A. Oliveira, G. G. Batrouni, and A. Hansen, Phys. Rev. Lett. **89**, 100601 (2002).

[7] *Proceedings of the 5th International Conference on Electro-rheological Fluids, Magneto-rheological Suspensions and Associated Technology*, edited by W. A. Bullough (World Scientific, Singapore, 1996).

[8] T. C. Halsey and W. Toor, J. Stat. Phys. **61**, 1257 (1990); Phys. Rev. Lett. **65**, 2820 (1990); W. R. Toor, J. Colloid Interface Sci. **156**, 335 (1993); J. E. Martin, J. Odinek, and T. C. Halsey, Phys. Rev. Lett. **69**, 1524 (1992).

[9] J. E. Martin, K. M. Hill, and C. P. Tigges, Phys. Rev. E **59**, 5676 (1999); J. Liu *et al.*, Phys. Rev. Lett. **74**, 2828 (1995); M. Fermigier and A. P. Gast, J. Colloid Interface Sci. **154**, 522 (1992); G. Helgesen *et al.*, Phys. Rev. Lett. **61**, 1736 (1988).

[10] S. Fraden, A. J. Hurd, and R. B. Meyer, Phys. Rev. Lett. **63**, 2373 (1989); J. E. Martin, J. Odinek, T. C. Halsey, and R. Kamien, Phys. Rev. E **57**, 756 (1998).

[11] J. Cernak, G. Helgesen, and A. T. Skjeltorp, Phys. Rev. E (to be published).

[12] D. Wirtz, Phys. Rev. Lett. **75**, 2436 (1995).

[13] J. Ugelstad *et al.*, Adv. Colloid Interface Sci. **13**, 101 (1980).

[14] Type EMG 909, produced by FerroTec, 40 Simon Street, Nashua, NH 03060-3075.

[15] B. Bleaney and B. Bleaney, *Electricity and Magnetism* (Oxford University Press, Oxford, 1978).

[16] P. G. De Gennes and P. A. Pincus, Phys. Kondens. Mater. **11**, 189 (1970).

[17] E. G. Flekkøy and D. H. Rothman, Phys. Rev. E **53**, 1622 (1996); Phys. Rev. Lett. **75**, 260 (1995).

[18] F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, Singapore, 1965).

[19] S. F. Edwards and D. R. Wilkinson, Proc. R. Soc. London A **381**, 17 (1982).

[20] L. P. Faucheux and A. J. Libchaber, Phys. Rev. E **49**, 5158 (1994).

[21] R. Toussaint, E. G. Flekkøy, and G. Helgesen, report.