Rouse Dynamics of Colloids Bound to Polymer Networks

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We present experimental evidence of a transition in the short-time Brownian motion of colloids from diffusive to subdiffusive, Rouse-like. This transition is seen for particles that are bound, through physical adsorption, to transient polymer networks. The characteristic Rouse scaling of the mean square particle displacement with $\sqrt{t}$, found in the experiments, is rationalized using an analytical bead-spring model of a large particle anchored to a set of polymer chains.

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The thermal motion of small particles, first described by botanist Robert Brown in 1828 [1], is strongly influenced by the nature of the surrounding matrix. Albert Einstein derived in 1905 that the mean square displacement $\langle \Delta r^2 \rangle$ of a particle undergoing Brownian motion in a Newtonian fluid must increase linearly with time [2]. In 1908, the concepts of Einstein were expressed in a stochastic differential equation of motion by Paul Langevin [3].

In the 1960s, Mori and Kubo derived the generalized Langevin equation, in which the constant friction coefficient of the traditional Langevin equation is replaced by a memory function that couples the motion of a particle to the history of its velocity [4], thus accounting for the viscoelasticity of the medium that surrounds the particles. This has formed the foundation for a field of investigation known as microrheology. In microrheology the thermal displacement of particles is analyzed in terms of the rheological response of the surrounding material [5,6]. It is now a widely used technique, for example, to study the mechanical properties of biological materials such as actin networks [7] and membranes [8].

In microrheology it is often assumed that the medium that surrounds the particles is continuous and that the particles are inert. In this Letter we will discuss the significant changes observed in the submillisecond Brownian motion of probe particles when the second assumption fails, i.e., when the particles "stick" to their surrounding matrix. Interestingly, we will show that the short-time dynamics of colloidal particles in a polymer network undergoes a transition from diffusive to subdiffusive when the particles get connected to the surrounding network. This characteristic subdiffusive motion shows a strong analogy with the Rouse model that describes the dynamics of individual segments in a polymer chain.

The mean square displacement of monodisperse colloidal particles can be measured using photon correlation spectroscopy. In this technique, fluctuations in the intensity I of light scattered by the probe particles are evaluated in terms of an intensity correlation function, defined as $g^{(2)}(t) = \langle I(\tau)I(\tau + t) \rangle / \langle I(\tau) \rangle^2$, which in turn is related to the normalized field autocorrelation function $g^{(1)}(t)$ with $g^{(2)} = 1 + A[g^{(1)}(t)]^2$, where A is an instrumental constant. From the experiment, under conditions where the scattering of the matrix and particle-particle interactions are negligible, $\langle \Delta r^2 \rangle$ is obtained with

$$\langle \Delta r^2(t) \rangle = -\frac{6}{q^2} \ln[g^{(1)}(t)], \qquad (1)$$

where q is the scattering vector. The experiments are carried out on 2 light scattering setups, with $q = 2.2 \cdot 10^{-2}$ nm^{-1} and $2.6 \cdot 10^{-2}$ nm^{-1}, respectively. $\langle \Delta r^2 \rangle$ was confirmed to be independent of q, indicating that non-Gaussian contributions to the particle displacement are small.

In this Letter we consider two distinct types of transient polymer networks (see Fig. 1), both in water. The first are entangled solutions of flexible homopolymers, here aqueous solutions of polyethylene oxide (PEO) of 35 kg/mol. The entanglement concentration for this polymer was determined to be 25 g/l, from viscosimetry. The second type is associative networks, formed by flexible polymers (PEO, 35 kg/mol) modified with an associating hydrophobic (hexadecyl $C_{16}H_{33}$) group at both ends of the chain. In these networks the junction points are formed by micellar cores interconnected through bridges. The network thresh-
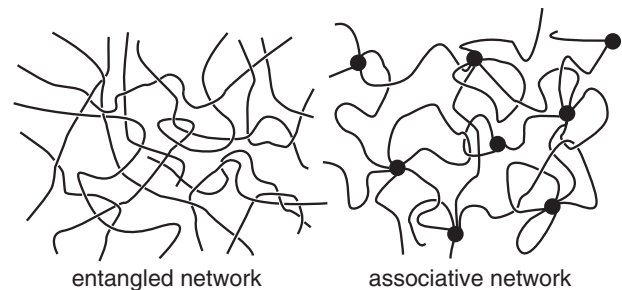

FIG. 1. Schematic representation of the two types of networks employed in this Letter: solutions of flexible polymers above the overlap concentration (left) and micellar, associative networks of telechelic polymers (right).
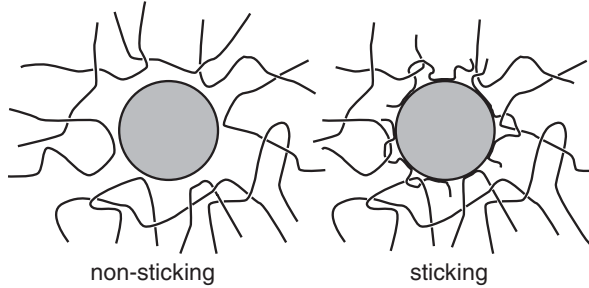
FIG. 2. Illustration of the two boundary conditions at the surface of the particles. On the left, the "nonstick" situation, in which no chains of the matrix adsorb onto the particle. This situation also applies when adsorbed chains are not entangled or associated with the matrix. On the right, "sticking" between particle and matrix as a result of adsorption of polymer chains to the particle surface. These adsorbed chains are connected to the transient network, either through entanglements or through associative interactions.

old for this system is found at 5 g/l. When the concentration of the associative system is further increased, entanglements will become important.

Three types of probe particles were used to illustrate the difference between stick and "nonstick" conditions (see Fig. 2): (i) silica particles with a radius of 70 nm onto which the polymers in the network can adsorb; (ii) silica particles with a radius of 70 nm onto which a layer of high molecular weight PEO (1000 kg/mol) was preadsorbed, such that the network itself cannot adsorb [9] (the loops and tails of the adsorbed polymer layer can however get entangled with constituents of the transient network) and (iii) charge-stabilized latex particles of 100 nm radius, predominantly consisting of polystyrene, onto which the polymer does not adsorb significantly. Particles were employed at 0.01 vol% (silica) or 0.001 vol% (latex), such that particle-particle interaction can be neglected.

Examples of $[g^{(2)}(t) - 1]/A$ obtained from these light scattering experiments are shown in Fig. 3. The sharp, single exponential decay found for the silica particles in pure water (diamonds) indicates that the particles used here are monodisperse. With increasing polymer concentration we observe a large increase in the major decay time, which must be attributed to the strong increase in the long-time diffusion coefficient as a result of the viscosity increase. We also see that at short times, a small, second decay appears in the correlation functions, which results in the nonlinear behavior of $\langle \Delta r^2 \rangle$ with time, as we will discuss below.

In Fig. 4 we see three typical results for $\langle \Delta r^2(t) \rangle$ obtained with Eq. (1). The upper curve shows the diffusive motion of probe particles through pure water. The scaling of the mean square displacement with time,

$$\langle \Delta r^2(t) \rangle \propto t^\alpha, \qquad (2)$$

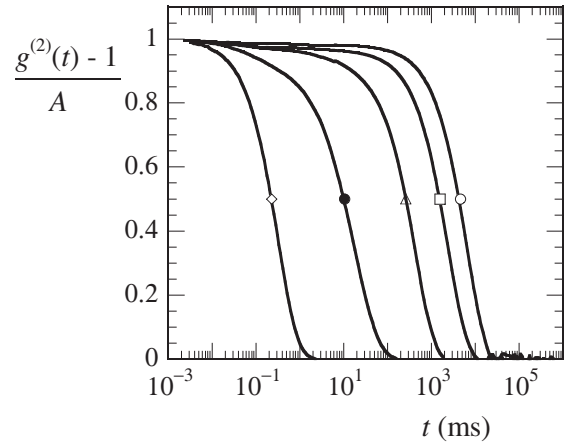is linear for diffusion; hence α is unity. The other curves in

FIG. 3. Autocorrelation functions $[g^{(2)}(t) - 1]/A$ for plain silica probe particles ($R = 70$ nm) in associative polymer networks at various polymer concentrations: 0 ($\diamond$), 9.6 ($\bullet$), 30.1 ($\triangle$), 49.5 ($\square$), and 77.1 g/l ($\bigcirc$). Each curve consists of approximately 250 data points.

Fig. 4 show the motion of similar particles through a viscoelastic polymer network. For nonsticking particles (open circles) the motion is diffusive at short time scales (with $\alpha = 1$). This is followed by a caging plateau ($\alpha \approx 0$) where the particles are trapped in elastic cages formed by the polymer chains. At longer time scales diffusive motion is observed again, due to the reversible nature of the cross-links. For sticking particles (filled triangles) both the caging plateau and the long-time diffusive regime are qualitatively reproduced. However, we see a clear difference in the short-time behavior, which has changed from diffusive ($\alpha = 1$) [10] to subdiffusive, with $\alpha \approx \frac{1}{2}$.

This change in the short-time motion is observed for sticking boundary conditions (BCs) in both types of networks. This is illustrated in Fig. 5 where the exponent α
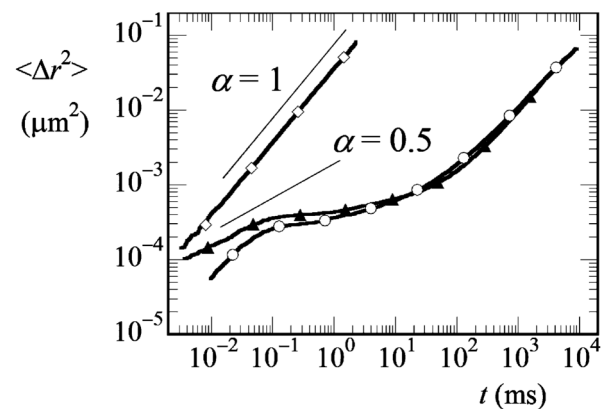

FIG. 4. Three typical examples of $\langle \Delta r^2(t) \rangle$ for silica probe particles: (i) purely diffusive motion in water ($\diamond$), (ii) motion of the particles in an associative polymer network, $c = 30.1$ g/l, under sticking conditions ($\blacktriangle$), (iii) motion of particles pretreated with a high molecular weight polymer (nonstick conditions), in an associative polymer network with $c = 30.1$ g/l, ($\bigcirc$).
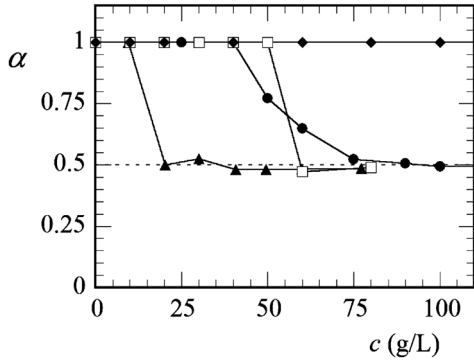
FIG. 5.   Effect of polymer concentration c on the exponent α
[Eq. (2)] at short time scales. Four combinations of probe
particles and polymer are shown: silica particles (sticking BC)
in solutions of unmodified PEO (●), silica particles (sticking
BC) in solutions of associative polymers (▲), silica particles
with a polymer layer preadsorbed (special BC, see text) in
associative polymer solutions (□), and nonsticking latex parti-
cles in regular PEO solutions (◆). The dotted line indicates $\alpha =$
0.5, for Rouse-like motion.

[Eq. (2)] for the short-time Brownian motion is plotted
versus polymer concentration. Several interesting observa-
tions can be made: (i) the transition from $\alpha = 1$ to $\frac{1}{2}$ occurs
beyond the network formation threshold for the corre-
sponding system, both for the associative polymer net-
works (>5 g/l, triangles in Fig. 5) and for the entangled
polymer solutions (>25 g/l, circles in Fig. 5) (below this
threshold the short-time motion is diffusive); (ii) for parti-
cles that do not bind to the network (diamonds) this tran-
sition is absent; their motion remains diffusive even at
concentrations far above the network formation threshold.
    There is one special situation, also shown in Fig. 5
(squares), for particles that do not bind to the network
themselves, as prevented by a preadsorbed polymer layer
on their surface. For these particles in an associative poly-
mer network, we see that the transition is delayed from the
network threshold for the associative polymer to the over-
lap concentration of the equivalent, unmodified polymer.
This indicates that, although the network itself cannot
adsorb, the polymer layer at the surface of the particles
takes part in entanglements.
    It is striking that $\alpha \approx \frac{1}{2}$, for the short-time motion, is
found for all cases where particles are bound to their
surrounding polymer network irrespective of the nature
of the junction points in the network. For a single case,
Gittes *et al.* [11] have shown with a microscopic particle
tracking technique that the viscoelastic moduli of a flexible
polymer network increase with the square root of the
deformation frequency, at relatively high frequencies.
This result is in agreement with the $\sqrt{t}$ dependence of
$\langle \Delta r^2 \rangle$ at short time scales, as presented here.
    The scaling of the mean square displacement with the
square root of time is also found in the Rouse dynamics of a
single segment in a polymer chain [12]. There is a strong

analogy between the motion of a polymer segment, fixed
between 2 chain parts, and the motion of a colloidal
particle, bound to several chains. To confirm this statement,
we develop an analytical bead-spring model of a colloidal
particle, connected to a polymer network (see Fig. 6).
    We consider a particle connected to f adsorbed polymer
chains. The first segment in every chain m is connected to
the particle, and the last segment N_m is fixed in a crosslink.
For simplicity, we assume that $N_m = N$ is constant for all
chains. The equation of motion for a polymer segment in
one of the adsorbed chains reads, neglecting inertia [13],

$$\zeta_0 \frac{dr_{m,n}}{dt} = -k(2r_{m,n} - r_{m,n-1} - r_{m,n+1}) + f_{m,n}, \quad (3)$$

where ζ_0 is the friction coefficient of a polymer segment, k
is the spring constant of a bond between two monomers
(related to the Kuhn length), $r_{m,n}$ denotes the position of
segment n in chain m, and $f_{m,n}$ is the random force acting
on that segment due to collisions with the solvent mole-
cules. The colloidal particle is connected to f chains, so
that its motion is described by

$$\zeta_P \frac{dr_P}{dt} = -k \sum_{m=1}^{f} (r_P - r_{m,1}) + f_P, \quad (4)$$

where $\zeta_P \gg \zeta_0$ is the friction coefficient of the particle and
r_P its position. We assume that the chain ends can be con-
sidered fixed in space at the short time scales that we are
interested in here: $dr_{m,N}/dt = 0$. The random forces acting
on the polymer segments and on the particle are assumed to
be Gaussian and uncorrelated in time: $\langle f_{m,n}(t) \rangle = 0$ and
$\langle f_{m,n}(t)f_{m',n'}(t') \rangle = 2k_B T \zeta_{m,n} \delta_{mm'} \delta_{nn'} \delta(t - t')$ according
to the fluctuation-dissipation theorem [13]. Equations (3)
and (4) constitute a set of coupled differential equations
that can be written in matrix form: $\dot{\mathbf{R}} = -\mathbf{A} \cdot \mathbf{R} + \mathbf{F}$. The
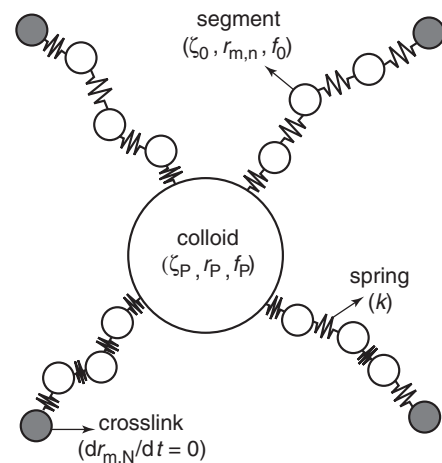

FIG. 6.   Impression of the bead-spring model of a colloid (the
large central bead) bound to a surrounding polymer network (the
bead-spring chains attached to the particle). In this illustration
$f = 4$ and $N = 4$. The gray beads at the end of each chain
represent the cross-links.

solution is obtained by determining the eigenvalues and eigenvectors of the Rouse connectivity matrix **A**. These can be obtained analytically by taking a continuum limit [13,14]. This gives for the eigenvalue equations:

$$\frac{d^2R_m(n)}{dn^2} = -\lambda R_m(n) \tag{5}$$

with the boundary condition at the particle:

$$\chi \sum_{m=1}^{f} \frac{dR_m}{dn}(0) = -\lambda R_m(0), \tag{6}$$

where $\chi = \zeta_0/\zeta_P < 1$ is the size ratio between a polymer segment and the colloidal particle. The second boundary condition is $R_m(N) = 0$ (i.e., the ends of the chains are fixed). There are two different types of solutions (normal modes). Antisymmetric modes ($R(n) = \sin(p\pi n/N)$ with $p = 1, 2, \ldots N - 1$) have a node at $n = 0$, so that the particle is stationary [14]. Hence, these modes do not contribute to the mean square displacement of the particle. For the other modes we have $R_m(n) = \sin[\omega_p(n - N)]$ with $\omega_p = \lambda_p^{1/2}$ given by the characteristic equation

$$\omega_p \tan(\omega_p N) = \chi f. \tag{7}$$

The mean square displacement of the particle then becomes (details will be published elsewhere)

$$\langle \Delta r^2(t) \rangle = \frac{12k_BT\chi^2 f}{k} \sum_{p=1}^{N} \frac{1 - \exp[-(\omega_p^2 k/\zeta_0)t]}{\omega_p^2(N\omega_p^2 + N\chi^2 f^2 + \chi f)}. \tag{8}$$

For $N\chi f \ll 1$, the motion is dominated by the particle friction and the motion is diffusive until a plateau is reached. On the other hand, for $N\chi f > 1$, the connection with the polymer becomes important, and the particle mean square displacement shows three different regimes. At short times ($t < \zeta_P^2/\zeta_0 kf^2$) the particle friction dominates and the mean square displacement is diffusive: $\langle \Delta r^2(t) \rangle = 6D_P t$ with $D_P = k_BT/\zeta_P$. Interestingly, at intermediate time scales the particle motion is Rouse-like, as observed in the experiments:

$$\langle \Delta r^2(t) \rangle = \frac{12k_BT}{f(\zeta_0 k\pi)^{1/2}} t^{1/2}. \tag{9}$$

Note that the prefactor does not depend on the friction coefficient of the particle. Hence, the bead just follows the motion of the polymer segments. For $f = 2$, Eq. (9) reduces to the classical result for segment motion in a Rouse chain [13]. At very long time scales $t \gg N\zeta_P/fk$, the mean square displacement reaches a plateau, which depends on the number of adsorbed chains f and their length N:

$$\langle \Delta r^2(t) \rangle = \frac{6k_BTN}{fk}. \tag{10}$$

Note that in our model the cross-links were assumed to be fixed, so that the long-time diffusive regime is not accounted for.

Apparently, Rouse dynamics, with $\alpha = \frac{1}{2}$, is not limited to individual components of a chain of equally large segments. In this Letter we have shown, both experimentally and theoretically, that the Rouse model also applies to situations where a strong size asymmetry is present between the particle of interest and the other components in the system and when the particle of interest is connected to a number of chains ≥ 2. The occurrence of Rouse dynamics in colloidal systems significantly changes the short-time motion of the particles. The general assumption made in microrheology, that specific particle-matrix interactions do not influence the observed motion of the particles, must therefore be made with caution.

In conclusion, we pose that analysis of the short-time Brownian motion of colloids in complex fluids can be a sensitive probe to obtain information about the interactions between particles and their matrix.

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