Measurement of Spring Constants of Polyacrylamide Chains Bridging Particles to a Solid Surface

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ABSTRACT: Spring constants of high molecular weight polyacrylamide chains have been measured by analyzing the Brownian motion of particles attached to a surface by such chains. The particles used for the measurement are latex particles and hardened spherical red blood cells. The values of the spring constants obtained are of the same order of magnitude as those estimated from the entropy change when the bridging section of the polyacrylamide chain is stretched.

Introduction

When high molecular weight polymers are used for flocculation of small particles into large aggregates, it is believed that the floc formation is a result of macromolecular bridging. For this mechanism to be effective, the polymer has to form bonds between the particles. In papermaking, high molecular weight polymers can improve the retention of fines and fillers in paper. Also here the mechanism for retention is believed to be bridging, the high molecular weight polymers forming bridges between the fines, fillers, and the pulp fibers. Some of the effective high molecular weight retention aids used in the paper industry are cationic polyacrylamides.

During the study of detachment of calcium carbonate particles deposited onto cellophane using cationic polyacrylamide as a retention aid,[1] it was observed that at high flow rates some calcium carbonate particles were observed to undergo an oscillatory or fluctuating motion about a fixed point on the cellophane without being detached. This phenomenon is similar to that observed by van de Ven and co-workers.[2,3] A related observation was made by Pelton and Allen,[4] who observed that latex beads stuck to a glass surface by poly(ethylenimine) moved back and forth when subjected to an oscillating flow. The motion of latex particles attached to a surface by an invisible linkage was recently analyzed by van de Ven *et al.*[5] In their work, they measured the spring constant for the linkage when the tethered particle was undergoing Brownian motion as well as when shear was applied to it. The values of the spring constants obtained were an order of magnitude less than those calculated from a decrease in entropy when a polymeric chain is stretched. It was speculated that the linkage was formed by a bundle of polymer which was pulled out of the latex particle as result of the hydrodynamic force acting on the particle when shear was applied.

In this paper, work is reported on the measurement of spring constants for polymeric tethers formed by polyacrylamide. Polystyrene latex particles as well as hardened spherical red blood cells were coated with cationic polyacrylamide and then deposited on glass. The hardened spherical red blood cells were used since uncoated latex particles form tethers, which casts doubt on the nature of the tether of coated latex particles. Thus it was necessary to test the behavior with other particles as well. The Brownian motion of tethered particles as well as particle displacement due to shear was measured. The spring constants for polyacrylamide obtained by this method were found to be similar to those expected from a decrease in entropy when a section of the polymer chain is stretched.

Our method shows some similarities with the observation of the relaxation behavior of single DNA molecules attached by specific binding to a latex bead. By moving the latex bead by optical tweezers, the relaxation of a single fluorescent DNA molecule (in a concentrated DNA solution) could be followed experimentally.[6]

Theory

Two approaches are available for the calculation of the spring constant for a particle that is undergoing a harmonic oscillation about a fixed point. The first approach involves the measurement of the particle position distribution as a function of time about the fixed point as a result of the particle undergoing Brownian motion. The second approach involves the measurement of particle displacement from the origin when shear is applied to the particle.

For a particle undergoing Brownian motion about a central point and considered to be connected to a surface by an elastic spring, the frequency for the particle to occupy a certain position with a given distance, Δl, from the center is given by the Boltzmann distribution, which is the case of an elastically bound particle, becomes a Gaussian distribution since the elastic energy is proportional to Δl^2:

$$N = A \exp\left[-\frac{k_s \Delta l^2}{2kT}\right] \tag{1}$$

where A is a normalization constant, k_s the spring constant, k the Boltzmann constant, and T the absolute temperature.

From the frequency histogram of particle displacement from the origin (N as a function of Δl), one is able to obtain the spring constant k_s from the best fit to the Gaussian distribution.

From the Brownian motion of a tethered particle, one can calculate the mean square displacement of the particle, defined as the average of the square displacements of the particle for various initial positions of the particle. From the solution of the Langevin equation for a harmonically bound particle,[6] it has been shown[7] that the mean square displacement approaches a plateau exponentially with a characteristic time τ, accord-

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ing to

$$\langle\langle \Delta l^2 \rangle\rangle = \frac{kT}{k_s}(1 - e^{-t/\tau}) + \langle \Delta l_0{}^2 \rangle (1 - e^{-t/2\tau})^2 \quad (2)$$

$\langle \Delta l^2 \rangle$ is the mean square displacement from the initial position and $\langle\langle \Delta l^2 \rangle\rangle$ is the mean square displacement averaged over time and initial displacements; $\tau = f/2k_s$, f being the frictional coefficient for tangential motion along the surface. From the best fit of eq 2 to a plot of mean square displacement as a function of time, one is able to obtain the spring constant for the tether of the fluctuating particle.

The drag force acting on a particle due to the application of shear can be equated to the elastic force, in which case the spring constant is given by[5]

$$k_s = \frac{1.7 f_0 a}{\mathrm{d}(\Delta l)/\mathrm{d}G} \quad (3)$$

where 1.7 is the Goldman *et al.*[8] correction factor to the Stokes friction coefficient f_0 and a is the radius of the particle. The value for $\mathrm{d}(\Delta l)/\mathrm{d}G$ is obtained as the slope of a plot of Δl as a function of G in the limit $G \rightarrow 0$.

A polymer in solution can be considered as a random coil. Stretching such a coil results in a decrease in its entropy which is related to an apparent spring constant given by[9]

$$k_s{}^{\mathrm{app}} = \frac{3kT}{N_K L_K{}^2} = \frac{3kT}{C_\infty N L^2} \quad (4)$$

Here N is the number of monomer units in the polymer chain, L is the length of a segment, N_K and L_K are the number of segments and Kuhn length, and C_∞ is the characteristic ratio. Assuming reasonable values of N and L for a given polymeric chain, one is able to make an estimate of the apparent spring constant.

Experimental Section

Materials and Sample Preparation. Polyacrylamide. The cationic polyacrylamide used in this study was a copolymer of acrylamide and (trimethylammonio)ethyl acrylate chloride supplied by Allied Colloids−Canada. The molecular weight of the cationic polyacrylamide was 8 million, it had a charge density of 63%, and it was used without further purification.

Glass Cover Slips. The collectors used in this study were microscope-quality cover slips supplied by Fisher Scientific Co. Ltd., Canada. The glass cover slips used as collectors were cleaned by being kept in chromic acid followed by thorough rinsing with distilled deionized water.

Latex Particles. The latex particles used in this study were polystyrene latex, with a diameter of 2 μm, supplied by Structure Probe Inc., USA. The polystyrene latex particles were cleaned by centrifugation at least three times using distilled deionized water. The latex particles were dispersed in distilled deionized water containing 60% by volume heavy water. The purpose of the heavy water was to increase the density of water so that the latex particles can float. Excess polyacrylamide (more than required to fully coat the particles) was added to the suspension of latex particles in the deposition cell.

Hardened Spherical Red Blood Cells. The purpose of using red blood cells was to eliminate the possibility that the polymeric chain, the spring constant of which was being measured, was a polymer bundle pulled out of the latex by the applied shear as speculated by van de Ven *et al.*[5] The red blood cells used were hardened spherical red blood cells, prepared following the recipe of Tha *et al.*[10] The cells of radius 3 μm were kept in physiological saline solution before being used in the deposition experiments. Prior to placing them in the deposition cell, the cells were dispersed in heavy water and 0.1 mg polyacrylamide was added to the suspension. Heavy water was used to keep the red blood cells floating, as their density is 1.08 kg L^{-1}.[10]

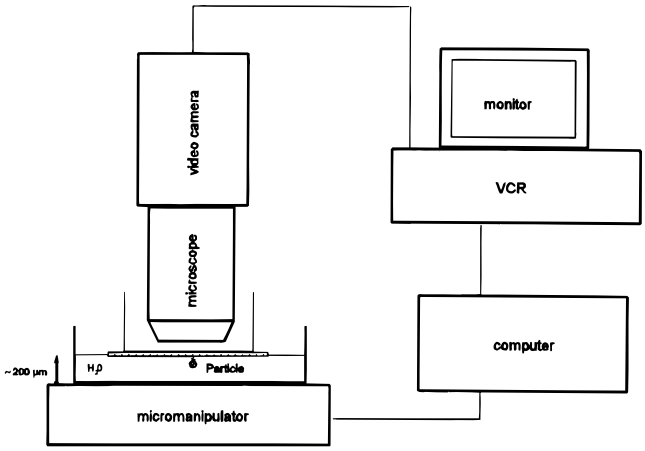

Figure 1. Experimental setup.

Experimental Setup and Procedure

Figure 1 is a schematic of the experimental setup. Its main feature is a deposition cell consisting of two plates 200 μm apart with particles deposited on the upper plate. The Brownian motion of the tethered particles (polystyrene latex and red blood cells) is observed through a microscope equipped with a video camera. The video camera is simultaneously connected to a monitor for visual display and a VCR (video cassette recorder) for recording the images. Shear can be applied to the tethered particles by moving the lower plate of the deposition cell, which was placed on a computer-controlled micromanipulator. When shear was applied to the tethered particle, it was observed to shift in the direction of shear. The particle was observed to return to its original position when the shear was removed. The motions of tethered particles, both Brownian and due to applied shear, were analyzed using a video card. Five minutes after the latex or red cells suspension was placed in the deposition cell, a search for tethered particles was commenced. The search involved applying shear to the deposited particle so as to identify tethered particles. After a tethered particle was identified, its Brownian motion was recorded on video for analysis. In some cases, shear was applied and the motion was recorded as well. We observed four latex particles and two hardened red blood cells.

Results and Discussion

Figure 2 shows examples of the positions of a latex particle and a red blood cell undergoing Brownian motion about a central point. Each point represents a position of a respective particle in time.

Figure 3 shows histograms for the latex particle as well as the red blood cell undergoing Brownian motion about a central point. The points are the experimental observations, and the smooth curves represent the best fit to a Gaussian distribution. The spring constant can be obtained from the variance using eq 1.

Figure 4 is a plot of mean square displacement as a function of time for one example of a latex particle as well as for one example of a red blood cell. The points are the experimental observations, and the smooth curves represent the best fit using eq 2.

Figure 5 is a plot of Δl versus shear rate. The slope of this plot in the limit $G \rightarrow 0$ (cf. eq 3)) was used in the calculation for the spring constant for the polyacrylamide polymeric chain using the latex particle. At a

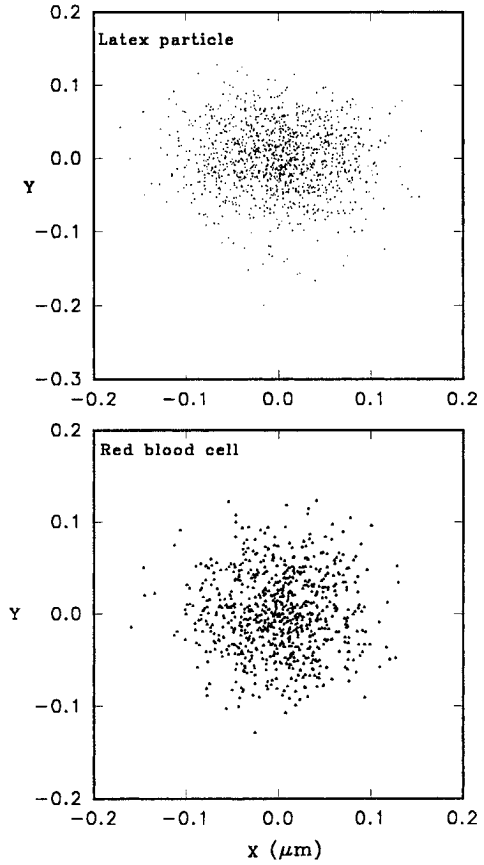

Figure 2. Examples of positions of a latex particle and a hardened spherical red blood cell undergoing Brownian motion. The points are particle positions at some time.

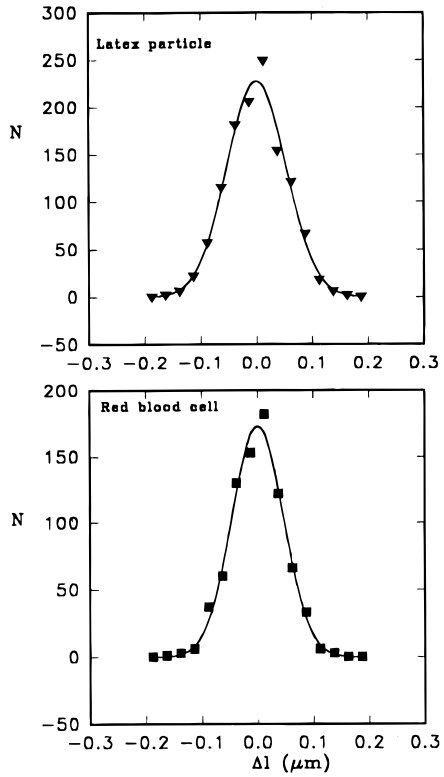

Figure 3. Examples of histograms showing the frequency of particle position with respect to time. The points are the experimental observations, and the smooth curves are the best fit of a Gaussian distribution.

shear rate of 10 s^{-1}, the hydrodynamic force exerted on the sphere is approximately 0.3 pN. This is several

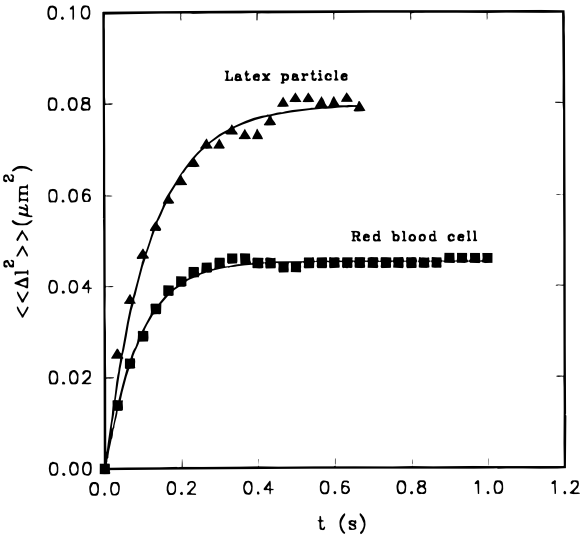

Figure 4. Examples of mean square displacement for the center of the particles as a function of time. The points are experimental observations, and the smooth lines are the best fit to eq 2.

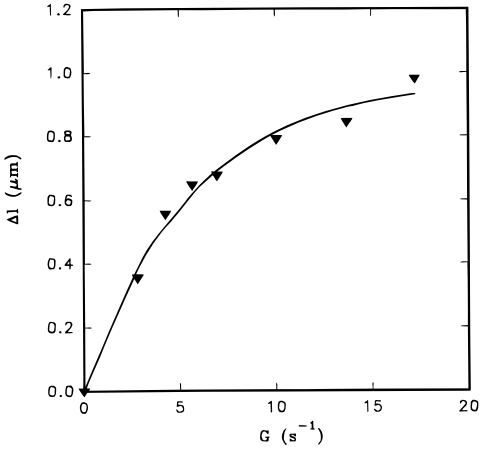

Figure 5. Particle displacement from the origin as a function of shear. The points are experimental observations. The solid line is an exponential fit.

orders of magnitude smaller than the shear forces exerted on the particles observed by Pelton and Allen[4] which were in the range 50 pN to 5 nN. The authors concluded that the tether reached its maximum extension instantaneously and thus behaved non-Hookean. Increasing the force beyond a critical value resulted in the detachment of the sphere.[4] It is likely that the curve in Figure 5 levels off at high shear. At shear rates much larger than 20 s^{-1}, the particle would be seen to move almost instantaneously to its maximum extension of about 1 μm and the Hookean characteristics at low shear rates would be missed. The agreement of the data with the expectations for a harmonically bound particle strongly suggests that at low and zero shear the tether behaves as a spring.

The spring constants and diffusion coefficients for latex particles and hardened spherical red blood cells are shown in Table 1. As can be seen in Table 1, all values of the spring constants obtained from the Brownian motion data are of a comparable magnitude. The values of the spring constants obtained from the shear experiment are lower than those obtained from the Brownian motion data. This suggests that the application of shear might be able to cause detachment of the shortest linkage; bringing longer linkages into play, the

Table 1. Spring Constants for Polyacrylamide Chain and Diffusion Coefficients for Tethered and Free Particles

parameter	latex particles	spherical red blood cells
$k_{s(b)}$ (10^{-6} N m^{-1})[a]	1.5 ± 0.4	2.0 ± 0.1
$k_{s(\Delta l^2)}$ (10^{-6} N m^{-1})[b]	1.7 ± 0.4	1.9 ± 0.1
$k_{s(shr)}$ (10^{-6} N m^{-1})[c]	0.16[d]	
τ (s)	0.011 ± 0.001	0.043 ± 0.002
D (10^{-14} m^2 s^{-1})	11 ± 1	2.5 ± 0.3
D_{Stokes}(10^{-14} m^2 s^{-1})	24	8.2

[a] $k_{s(b)}$ is the spring constant obtained from Brownian motion. [b] $k_{s(\Delta l^2)}$ is the spring constant obtained using eq 2. [c] $k_{s(shr)}$ the spring constant obtained as a result of the applied shear. [d] This point has no error estimates since only one particle was observed due to experimental difficulties.

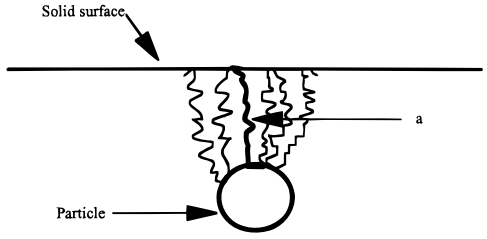

Figure 6. Attachment model. Segment "a" determines the maximum extension of the polymeric linkage.

longer linkages now determine the value of a spring constant which is smaller.

The spring constant using the latex particles coated with polyacrylamide are an order of magnitude larger than those obtained by van de Ven *et al*.[5] for bare latex particles. This indicates that the chains are not made of the same material. Also it is noted that the spring constants obtained using polyacrylamide-coated latex particles are the same as those obtained using polyacrylamide-coated red blood cells. As mentioned earlier, a polymer chain in solution can be taken to be a random coil. The force required to stretch the chain is proportional to the extension of the polymer, and the proportionality constant is determined by the decrease in entropy of the polymer chain. For the calculation of the apparent spring constant for the polymeric chain using eq 4, the number of segments N and the length of each segment were calculated from the structure and the molecular weight of the polyacrylamide. The molecular weight of the polymeric chain was 8×10^6. The molecular weight of a monomer unit is 200, the length of such a unit $l \simeq 3$ Å, and the value for the characteristic ratio for polyacrylamide is 15.[11] Inserting these values into eq 4 for the calculation of the apparent spring constant yields $k_2 = 2 \times 10^{-7}$ N m^{-1}. This value is an order of magnitude less than the values obtained from the Brownian motion data. The maximum extension of the chain is about 1.2 μm, is much larger than the maximum extension of about 0.2−0.3 μm. Hence it is more likely that the particles are attached to the surface by multiple polymeric linkages (cf. Figure 6) and that the shortest linkage determines the value of the spring constant. Assuming an effective connection of 0.2 μm results in a spring constant of 3×10^{-6} N m^{-1}, in fair agreement with experiment. Thus the particle is probably linked to the surface by multiple links. When shear is applied, some bonds could break and the length of the tether could increase, resulting in the reduction of the spring constant.

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