PRL **94,** 038301 (2005) PHYSICAL REVIEW LETTERS week ending 28 JANUARY 2005

Polymer Bridging Probed by Magnetic Colloids

Laetitia Cohen-Tannoudji,[1] Emanuel Bertrand,[1,*] Lydie Bressy,[1] Cécile Goubault,[1,2] Jean Baudry,[1] Jacob Klein,[3]
Jean-François Joanny,[2] and Jérôme Bibette[1]
[1]*LCMD, ESPCI, CNRS UMR 7612, 10 rue Vauquelin, 75231 Paris CEDEX 05, France*
[2]*PCC, Institut Curie, CNRS UMR 168, 11 rue Pierre et Marie Curie, 75231 Paris CEDEX 05, France*
[3]*PTCL, Oxford University, South Parks Road, Oxford OX1 3QZ, United Kingdom,*
and Weizmann Institute, Rehovot, Israel
(Received 19 May 2004; published 25 January 2005)

Superparamagnetic particles offer a new way to probe the kinetics of adhesive processes. Two different scenarios of physical adhesion are studied. The thermal activation of van der Waals adhesion is well described by an Arrhenius model. In contrast, it is necessary to go beyond the Arrhenius description to understand the thermal activation of bridging between colloidal particles by a polymer at equilibrium adsorbance. We show that polymer bridging requires some removal of adsorbed polymer and is strongly influenced by the proximity of a glass transition within the adsorbed polymer.

DOI: 10.1103/PhysRevLett.94.038301 PACS numbers: 82.70.Dd, 82.35.Gh

The various strategies to stabilize or to destabilize colloids have been extensively studied over the last decades, both for the fundamental understanding of adhesion and for numerous industrial applications. To study the kinetics of adhesive processes, we have developed a new tool based on the self-assembling properties of superparamagnetic beads under field. It consists in following the kinetics of formation of permanents links between self-organized magnetic beads with optical microscopy. Here, we apply this new method to two types of physical adhesion. We first consider van der Waals attraction and study its activation by temperature and by the intensity of the magnetic field. We subsequently show that adhesion by polymer bridging is also activated both by temperature and by the field. However, the thermal activation of polymer bridging can only be understood if the proximity of a glass transition within the adsorbed polymer is taken into account.

To be used in these experiments, the magnetic beads must be spherical, monodisperse, strongly magnetic, and Brownian. In addition, their surfaces must provide very strong colloidal stability. They consist in calibrated emulsion droplets of an organic ferrofluid in water. The ferrofluid used is a suspension in octane of γ-Fe_2O_3 ferrimagnetic nanoparticles stabilized by oleic acid. In the following experiments, we use beads of diameter 800 nm, supplied by Ademtech [1]. Some oleic acid ($pK_a = 5.0$) covers the surfaces of the beads, which are thus negatively charged at neutral pH. Such suspensions are therefore very stable kinetically against flocculation, due to electrostatic repulsions.

Whereas they remain perfectly dispersed when no field is applied, the magnetic beads self-organize under field: a magnetic moment is induced in each bead and an anisotropic dipolar attraction takes place. The conformation of lowest energy consists in chains of beads aligned along the direction of the field [Fig. 1(a)]. If no adhesive process occurs, the beads redisperse immediately once the field is removed. In contrast, if adjacent beads are linked by any adhesive phenomenon, some permanent chains remain [Fig. 1(b)] [2].

Our new method to follow the kinetics of adhesion relies on the formation of magnetic chains that persist after the field removal. A colloidal sample is introduced by capillarity in a square tube of 50 μm. The tube is placed under a given field, at a controlled temperature, during a given incubation time. After the field removal, the sample is observed by optical microscopy with a ×40 objective (Nikon) and six photographs of different parts of the tube are taken. For each photograph, the sum of the lengths of all the chains is determined numerically (Image Pro Plus, MediaCybernetics). The ratio of this total length by the diameter of a bead gives the number N of adhesive links and is averaged over the six photographs. This is repeated for different incubation times, which gives the kinetics of the adhesive process. The field intensity must be sufficiently high so that the time required for the formation of

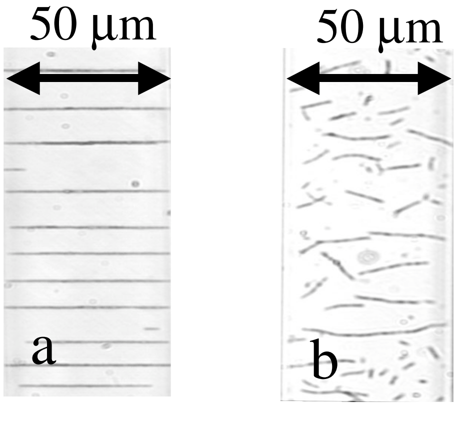

FIG. 1. Superparamagnetic beads (optical microscope, ×40 objective): (a) under $B = 10$ mT; (b) after field removal.

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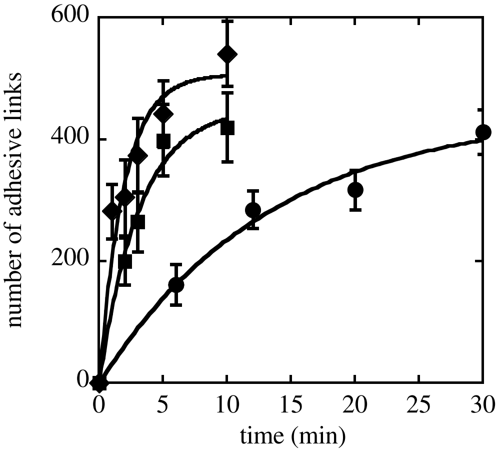

FIG. 2. $N(t)$ for $B = 23$ mT, in the case of van der Waals attraction, at 25 °C (●), 45 °C (■), and 55 °C (◆); curves are fits to Eq. (1).

the chains is negligible compared with the characteristic time of adhesion.

To prove the validity of this method, we have considered a pure Derjaguin-Landau-Verwey-Overbeek (DLVO) system where the only interactions are electrostatic repulsions and van der Waals attractions. A zeta potential of -31.5 mV for the beads has been measured at $p\mathrm{H} = 10$ with a Beckman Coulter zetameter. We thus have a very stable suspension of negatively charged beads. Nevertheless, applying a magnetic field, at $p\mathrm{H} = 10$, with 1 mM of NaCl, enables one to observe adhesion induced by van der Waals attraction. Figure 2 shows the number N of adhesive links as a function of the incubation time t under $B = 23$ mT, for three different temperatures. We observe a monoexponential growth of $N(t)$, well modeled by a first-order kinetics:

$$N(t) = N_0[1 - \exp(-t/\tau)], \qquad (1)$$

where N_0 is the averaged total number of particles in the volume captured by a photograph and τ is the characteristic time of the kinetics. $N_0 = 490$ particles is determined and kept fixed while fitting the experimental points with Eq. (1). The only fitting parameter is thus the characteristic time τ. The relevance of a first-order kinetics is not surprising since the chains are formed very rapidly (after a few seconds under field) and since the appearances of links between particles can be regarded as independent events.

The van der Waals adhesion is found to be thermally activated, and the dependence of τ with T [Fig. 3(a)] is well fitted to an Arrhenius law: $1/\tau = 1/\tau_0 \cdot \exp[-E_a(B)/(k_B T)]$, where k_B is Boltzmann's constant, $E_a(B)$ is the activation energy for a field intensity B, and $1/\tau_0$ is the attempt frequency. $E_a(B)$ can be interpreted as the height of the energy barrier to overcome to go from a metastable redispersible chain to a stable permanent chain. This barrier is due to electrostatic repulsions. Figure 3(b) shows that E_a decreases when B increases. This adhesion is thus also activated by the magnetic field as it adds an attractive interaction between the beads, the magnitude of which increases with B. In addition, as the three points of Fig. 3(b) are aligned, one can extrapolate to zero field to estimate the activation energy of the intrinsic adhesive phenomenon without field. We find $E_a \approx 60 k_B T$, i.e., much higher than the thermal energy, which is in line with the kinetic stability of the corresponding suspension without field. Moreover, $E_a(B)$ can be obtained theoretically from the DLVO theory and the expression of the magnetic attraction [3]. An almost linear variation with B and $E_a \approx 100 k_B T$ is found [Fig. 3(b)], in a rather good agreement with the above extrapolation. The attempt frequency can also be estimated from the DLVO energy-distance profile, according to Kramers' theory [4]: we find approximately 10^5 Hz. Experimentally, only an order of magnitude can be obtained, due to the very narrow temperature experimental window. We find frequencies between 10^5 and 10^9 Hz, which is coherent with the previous estimation. Let us mention that the chains formed here have an "almost infinite" lifetime (more than months), which was expected since they correspond to a thermodynamically stable state.

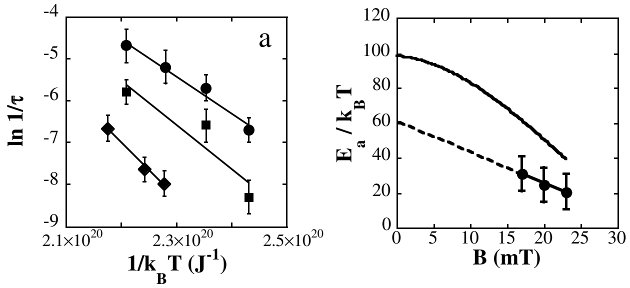

FIG. 3. (a) $\ln(1/\tau)$ as a function of $1/k_B T$ for $B = 17$ mT (◆), 20 mT (■), and 23 mT (●); lines are Arrhenius fits (see text); (b) $E_a/k_B T$ as a function of B (●); the solid line is a theoretical prediction (see text); the dotted line is a linear extrapolation to $B = 0$.

Having proved that our method is valid, we apply it to a more complex non-DLVO system where polymers are adsorbed on the beads and can bridge them. Adsorbed polymers have a strong influence on the stability of colloids. At subequilibrium adsorbance, they may destabilize colloids due to net attractions between particles originating in the formation of bridges between them [5,6], as schematically depicted in Fig. 4. In contrast, at equilibrium adsorbance, polymers are used to stabilize colloids, since the osmotic repulsions exceed the bridging attractions at all separations. Reducing the adsorbance to less than its equilibrium value can therefore change the net osmotic repulsion to a net bridging attraction. The polymer used here is a polyacrylic acid (PAA, Aldrich) of average molecular weight 250 000. It has a pK_a of 5.8, so that in the conditions of our experiments, at $p\mathrm{H} \approx 3.5$, it may be consid-

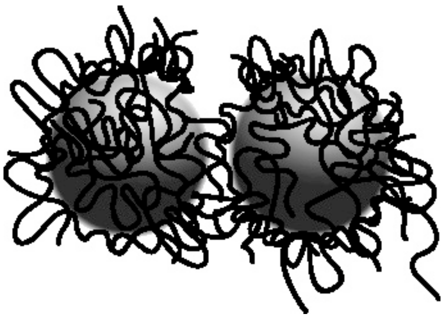

FIG. 4. Schematic picture of polymer bridging: adsorption of the same polymeric chains on both beads.

ered essentially neutral. At this pH the beads are poorly charged and form aggregates very rapidly, whereas if PAA (0.1 wt % solution) is first adsorbed onto the beads, they remain perfectly dispersed. Colloidal stability is thus conferred on the suspension by osmotic repulsions [7]. To ensure that equilibrium adsorbance was attained, we let the beads incubate for 20 h in the PAA solution prior to applying any field [7]. However, when subjected to a magnetic field for a sufficient time, the beads covered by PAA form permanent chains. Contrary to the previous case (DLVO), these chains start breaking apart after a few days, which proves that they do not correspond to a DLVO-like adhesion induced by van der Waals attractions. Moreover, the distance between the beads in a magnetic chain formed with PAA is of approximately 10 nm [8], whereas this distance would be less than 2 nm in a van der Waals potential well.

We thus attribute the chain formation to a net attraction between the beads arising from bridging by the polymers. This net attraction can arise only through reduction of the adsorbance to subequilibrium levels by removal of polymer from the region of closest approach. Polymers may be squeezed out of the gap by the lateral force $F_S(r)$ on each chain arising from the lateral pressure gradient $(\partial\Pi/\partial r)$ acting between the curved surfaces, which results from the decrease in osmotic pressure $\Pi(r)$ a distance r away from the point of closest approach D. Writing $\Pi(r) \approx (k_BT/a^3)\phi^2$ [9], where a is a monomer size and the monomer volume fraction $\phi = 2\Gamma/(D + r^2/R)$, R being the bead radius and Γ the polymer adsorbance, we may roughly estimate $F_S(r) \approx$ (volume of polymer chain)$(\partial\Pi/\partial r)$. This gives $F_S(r) \approx (n^{3/2}k_BT\Gamma^2 r/RD^3)$ ($n =$ degree of polymerization ≈ 3500 for the PAA used), which for typical values of the parameters give $F_S(r) \approx 10^{-11}N$. The typical net monomer adsorption energy is $\varepsilon \approx 0.02$–$0.1k_BT$ [6], requiring a tension of order $(\varepsilon/1\ \text{Å}) \approx (1$–$5) \times 10^{-12}N$ to detach. The outward lateral force on each chain is thus comparable with that required to detach the adsorbed monomers, enabling the creep of chains along the surface and their squeezeout to take place, and therefore bridging to become dominant.

The kinetics of adhesion for beads covered with PAA is presented in Fig. 5. A monoexponential fits well the experimental points: Equation (1) is used with $N_0 = 660$ links in the present experimental conditions. The process of polymer creep and relaxation along the surfaces is complex. Since it occurs by the detachment of monomers from the surface, it is likely to be an activated process but will depend also on the dynamics of the near-surface layer. Using an Arrhenius law to fit the evolution of τ with T leads to an estimated activation energy without field of about $150k_BT$ (fits not shown). As in the DLVO system, the rate at which bridging is attained will depend on the magnetic field through its effect on D, which affects the lateral squeezing force $F_S(\propto 1/D^3)$. The value of $150k_BT$ may reflect the need for cooperativity in detachment of polymer segments. Surprisingly, we find attempt frequencies of order 10^{30} Hz, which is much too high for a molecular phenomenon and cannot have any physical meaning. Evidently, the Arrhenius law is thus unable to model the activation of polymer bridging, and another approach has to be considered that takes into account the existence of a glass transition in the system [10–14]. The relevance of this relies on the approach to a glassy state of the near-surface layers [15]. This so-called Vogel-Tamman-Fulcher (VTF) model reads

$$\frac{1}{\tau} = \frac{1}{\tau_0}\exp\left[-\frac{A}{k_B(T - T_0)}\right], \tag{2}$$

where $1/\tau_0$ is still an attempt frequency, A is an energetic parameter, T_0 is the empirical Vogel temperature, and $T > T_0$. T_0 is the temperature at which all the relaxation times of the system diverge [14] and is a few tens of degrees below the glass transition temperature T_g [13]. For a given polymer at a given concentration, T_0 can be determined empirically by fitting dielectric or viscoelastic relaxation data to Eq. (2) [14]. It is still possible to define an apparent activation energy, which depends on temperature [14], and

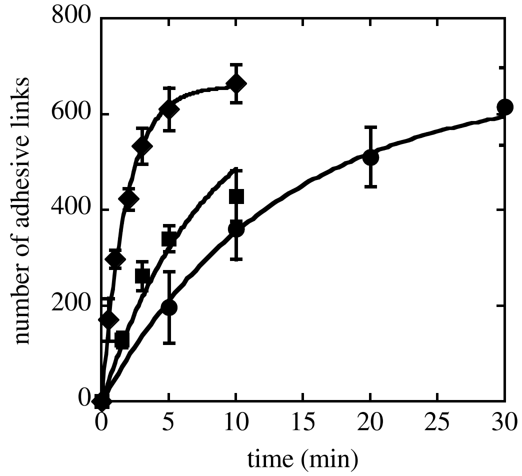

FIG. 5. $N(t)$ for $B = 12$ mT, in the case of adsorbed PAA, at 35 °C (●), 40 °C (■), and 45 °C (◆); curves are fits to Eq. (1).

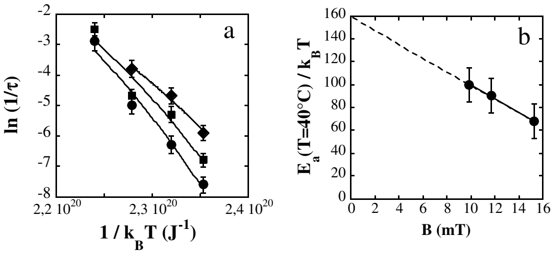

FIG. 6. (a) $\ln(1/\tau)$ as a function of $1/k_BT$ for $B = 10$ mT (◆), 12 mT (■), and 15 mT (●); lines are fits to Eq. (2) with $T_0 = -30\,°\mathrm{C}$; (b) $E_a(T = 40\,°\mathrm{C})/k_BT$ as a function of B; the dotted line is a linear extrapolation to $B = 0$.

is simply the slope of the "$\ln(t)$ versus $1/k_BT$" curve: $E_a(T) = k_Bd[\ln(\tau)]/d(1/T) = A[T/(T - T_0)]^2$.

Figure 6(a) shows the good fit of the experimental points to the VTF model for three field intensities. T_0 and T_g are increasing functions of the polymer concentration [13], and it is known that the local concentration of polymer near the surface on which it is adsorbed is much higher than the bulk concentration [16]. As it is impossible to determine the polymer local concentration in our case, we cannot have any precision on the values of T_g or T_0. $T_0 \approx -120\,°\mathrm{C}$ for dilute solutions of PAA in water (less than 1 wt %) [17] and $T_0 \approx 0\,°\mathrm{C}$ for 75% wt % PAA in water [18]. The adsorbed polymers involved in the bridging should thus have a Vogel temperature ranging roughly between $-70\,°\mathrm{C}$ and $0\,°\mathrm{C}$. We have checked that the choice of T_0 has almost no influence on the apparent activation energy deduced from the fit. T_0 has been arbitrarily fixed at $-30\,°\mathrm{C}$ for Fig. 6, and we find $160k_BT$ for $E_a(40\,°\mathrm{C})$ at zero field [Fig. 6(b)], which compares very well with the value of $150k_BT$ found with the Arrhenius law (i.e., for $T_0 = -273\,°\mathrm{C}$). In contrast, the frequency $1/\tau_0$ determined by the VTF fit is very sensitive to T_0. It ranges from 100 Hz for $T_0 = 0\,°\mathrm{C}$ to 10^{10} Hz for $T_0 = -70\,°\mathrm{C}$, which is physically reasonable. This proves that the VTF model for the thermal activation of polymer bridging is a much better description than the Arrhenius law.

As already mentioned, our interpretation of polymer bridging is the following. The equilibrium adsorption of PAA on the beads being reached, bridging requires that polymer be squeezed away from the near-contact region, which leads to bridging at subequilibrium adsorbance [5]. The surface creep by which this removal of polymer occurs is strongly influenced, namely, slowed, by the proximity of a glassy state within the adsorbed polymer of the near-surface layer [15]. As mentioned above, the squeezing away of the polymer is due to the osmotic outward lateral force F_S, which is an increasing function of the degree n of polymerization of the considered polymer. Experimentally, this implies that the bridging phenomenon should be faster when the adsorbed polymer is longer. We did experiments at 45 °C under $B = 11$ mT with three PAA of different average n. For n of about 28, 1400, and 3500, we found characteristic times τ equal to 1800, 74, and 54 s, respectively. This confirms the role of the squeezing out of polymer in the bridging process. Our interpretation of polymer bridging is also confirmed by the following experiments. We did measurements at 25 °C under $B = 12$ mT after different equilibration times of the beads with the polymer. Whereas a characteristic time $\tau \approx 12$ min is found if the adsorption equilibrium is reached (after 20 h), the kinetics is much more rapid ($\tau \approx 0.9$ min) if the PAA has only 10 min to adsorb prior to applying the field. When the time is insufficient for the polymer to be completely adsorbed, bridging dominance requires less polymer to be squeezed away.

We have presented a new general method based on magnetic colloids to study adhesive processes. With this new tool, we have shown that polymer bridging is activated by temperature but that it cannot be simply understood in terms of an Arrhenius model. Indeed, a more precise approach is required that takes into account the necessary removal of adsorbed polymer from the near-contact region and the slowdown of the dynamics in the near-surface layer, due to the proximity of a surface glassy state. This difficulty to induce bridging at equilibrium adsorbance explains the efficiency of adsorbing polymers at the surface of colloids to improve their kinetic stability.

We thank the French Ministry of Research for financial support.

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*Corresponding author.
Electronic address: emanuel.bertrand@espci.fr

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