Electric-Field-Induced Friction Reduction and Control

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Friction is always present when surfaces in contact are set in motion. In this work I describe how a precise, active control of the global friction is possible by adjusting the local molecular conformation of a polyelectrolyte coating via the application of an alternating electric field. The intensity of the applied field determines the degree of interpenetration between polymer brushes in contact, regulating chain stretching while sliding, which is the process at the origin of the global friction. The dynamics of the problem is controlled by the relaxation times of the polyelectrolyte.

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Friction is not a fundamental force but a macroscopic quantity that results from different energy dissipation mechanisms. Even in well-controlled experiments with molecularly smooth surfaces, friction forces may be the result of multiple concurrent contributions related to processes independently occurring at molecular scale. For example, the rupture and formation of adhesive nanojunctions [1], the deformation and snapoff of regular nano-asperities in contact [2], and the deformation of interpenetrated polymer brushes [3] are all molecular scale mechanisms behind macroscopic friction: the global friction results of the combined contribution of independently changing domains of submicrometric size. The global friction can then be controlled by tuning the fundamental processes occurring locally. Salinity, radiation, *p*H, and temperature are some variables that can be used to modify the configuration of a responsive lubricant layer. However, molecular response to changes of these parameters is generally slow and they are difficult to control at a local level. Physical strategies have also been proposed to control friction. For example, it has been reported that controlled vibrations may be used for friction tuning (an effect dubbed sonolubrication) [4]. However, it seems difficult to produce a localized mechanical perturbation of interest for specific applications.

There has been considerable progress in understanding the interaction forces between polymer-coated surfaces during the past few decades. It has been shown that polymer coatings in a good solvent can act as very effective lubricants, reducing the friction by 100-fold compared with uncoated surfaces [5]. This has been attributed to the long-range entropic repulsion between the coated surfaces acting to maintain a finite separation with a relatively fluid film. This effect is magnified for the case of two polyelectrolytes (PE) layers: upon compression their hydration sheaths overlap and a film of water remains in the interlayer region. This is probably the reason why charged polymers are often important components of biolubricants (e.g., in tears or synovial fluid). The lubrication properties of PEs are related to the degree of interpenetration between the layers in the rubbing surfaces. Interpenetrated polymer brushes are deformed under shear; friction is due to the dissipation upon sliding of the elastic energy temporarily stocked on the stretched chains. Given that interpenetration is more important at larger compressive loads, PE lubrication properties rapidly worsen when pressure is augmented [6].

In this work it is shown that friction forces can be controlled if brush interpenetration is adjusted by taking advantage of PE responsiveness to external stimuli. PEs are affected by external physical or chemical fields as a consequence of their ionic charge [7–9]. As opposed to chemically induced changes, the molecular response to a changing electric field occurs quickly. This response can be used to tune the magnitude of frictional resistance. I studied the interaction between molecularly smooth mica surfaces coated by PE brushes produced by self-assembly of amphiphilic diblock polystyrene-polyacrylic acid copolymers (PS_{36}-*b*-PAA_{125}) from aqueous solution at *p*H 10. The adsorption of badly solvated hydrophobic PS blocks (anchor) is driven by dispersion forces. On the contrary, the water soluble PAA moieties (buoy) are negatively charged at *p*H above neutral and are electrostatically repelled from the mica surfaces. The surfaces were rinsed and immersed in water at *p*H 10.1 (with NaOH) after overnight adsorption (before the first approach). The density of the self-assembled polymer brush is limited by steric restrictions, as has been described before [10]. However, this can be advantageous for building responsive coatings: if the grafting density is too large, there will not be enough space for molecular conformational changes. It is reasonable to expect the largest response to external stimuli when neighbor polymer chains are barely overlapping, a regime naturally achieved by self-assembly [8]. I have used atomic force microscopy and quartz crystal microbalance with dissipation monitoring (QCMD, Q-sense) in a liquid environment to confirm the adsorption of a *pH*-responsive, nonstructured polymer layer. The normal and lateral interaction forces between identically polymer-coated mica surfaces were measured by using a surface forces apparatus similar to the one designed by Israelachvili *et al.* [11].

The normal force-separation profiles $F(D)$ between coated surfaces were monotonically repulsive and fully reversible, as can be observed in Fig. 1. The onset of repulsion was observed at $D \sim 40$ nm, corresponding to an extension 5 times the radius of gyration of PAA (~ 4 nm) on each surface, but less than 30% of the contour length of the chains. At low compressions, $F(D)$ can be well described by the model derived by Pincus for osmotic brushes [10,12]. In this model the brush height L is determined by the balance between the osmotic pressure of the trapped counterions, $F_{\mathrm{osm}} \approx \alpha N k_B T/L$, and the entropic elastic force of the compressed brush, $F_{\mathrm{elas}} \approx L k_B T/N a^2$, where N is the number of Kuhn monomers of length a of the brush and α is the fraction of noncondensed counterions. This model fails at large compressions ($\beta = L/D > 2$), when the polymer volume fraction ϕ increases considerably. As can be observed in the figure, in this region $F(D)$ can be better described by a term proportional to D^{-3} growth, which may be accounted for by the contribution of many-body interactions [13].

$F(D)$ is not significantly modified by the application of an external electric field. On the contrary, an abrupt friction force F_f reduction is observed when an alternating electric field is applied through the lubricant layer. In the example reported in Fig. 1, F_f decreases below the detection limit of our apparatus triggered by the application of the field, indicating a friction reduction of several orders of magnitude. The effect is very fast and reversible: F_f immediately regains its original level after the alternating field is removed. The applied field facilitates sliding by momentarily reducing local interlayer interpenetration without impairing the global ability of the polymer coating to sustain the applied pressure and keep the surfaces apart. This effect allows a precise control of F_f: as can be observed in Fig. 1(c), F_f is a slowly changing function of the applied voltage, which can be precisely tuned.

The normal load dependence of F_f is presented in Fig. 2. The unperturbed PE layer shows excellent lubricant properties at low loads ($L < 0.25$ mN). It has been proposed that in this ultralow friction regime the brushes get thinner as they are compressed, avoiding interpenetration [6]. On the contrary, for $L > 0.25$ mN, F_f progressively increases. As can be observed in the figure, F_f is substantially reduced by applying an alternating voltage between the surfaces, the effect being more significant at high normal loads. This effect is not due to chemical modifications of the boundary layer: as the coating polymer and the aqueous solution are separated from the silver electrode by a dielectric layer (mica), redox cycles are not taking place. It is due to the perturbation of both the conformation of the PE chains and the configuration of the counterion cloud. The polymer layer is not permanently affected by the process; thousands of friction cycles in the presence and in the absence of the applied field were performed without noticeable change on normal interaction or friction forces.

Several forces related to the application of the field act on the PE brush. The combination of hydrodynamic and electrostatic effects determines the overall response. The applied field acts on the charges of the PE producing an electrostatic

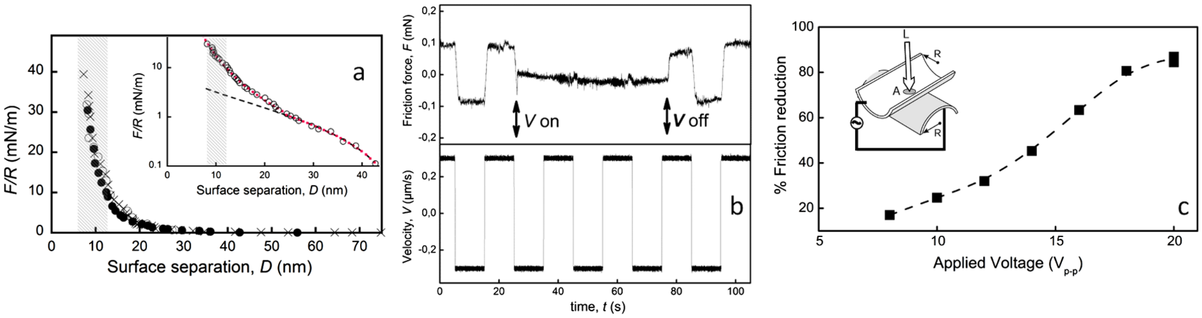

FIG. 1 (color online). Interaction forces between mica surfaces (thickness 4.018 μm) coated with a brush layer of $\mathrm{PS}_{36}\mathrm{PAA}_{125}$ immersed in water pH 10.1 (a) Normal force F (normalized by the radius of curvature of the surfaces R) vs surface separation D. The force profiles were measured during quasistatic approach (closed circles) and separation (open circles) of the surfaces, and upon application of an alternating voltage (crosses, 450 Hz, 20 $\mathrm{V}_{p\text{-}p}$), measured 30 min after the application of the potential difference was started. For compressions outside the hatched zone, friction was below the detection limit of our instrument. Inset: Log-linear representation. The model described in the text (dashed line) fails to fit the data at high compressions. Adding a term proportional to D^{-3} (red dotted line) provides an accurate description of the data. (b) Friction forces. A dramatic reversible reduction in F_f is immediately observed upon the application of a potential difference between silver electrodes deposited in the back side of the surfaces (square wave, 450 Hz, 20 $\mathrm{V}_{p\text{-}p}$). $V = 0.3$ μm/s, $L = 1.85$ mN. Lower panel: Relative velocity between the surfaces in contact. Reciprocating motion (responsible for the alternating sign of the friction signal) is necessary due to the finite displacement range. (c) Voltage dependence of F_f reduction. Fine control of friction can be achieved by changing the magnitude of the applied voltage. $L = 5.56$ mN, $V = 0.3$ μm/s. Dashed line is a guide to the eye. Inset: Crossed-cylinder geometry used in the surface forces apparatus.

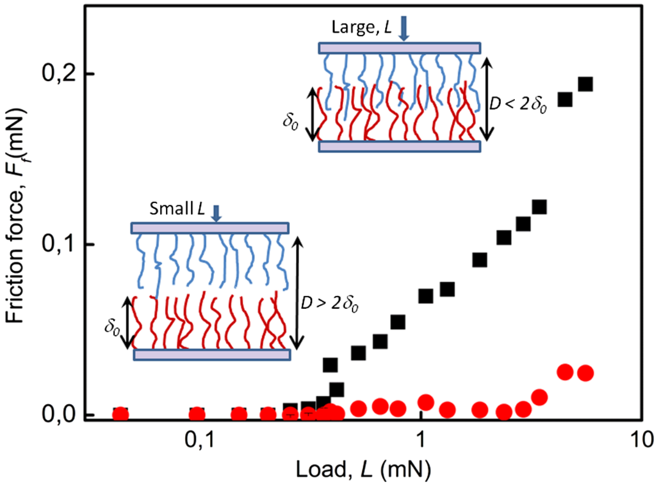

FIG. 2 (color online). Load dependence of F_f between mica surfaces coated with a layer of PS_{36}-PAA_{125} with (circles) and without (squares) an externally applied electric field. At low L the PE layers oppose very small resistance to shear because of the limited layer interpenetration. Lubrication is substantially worsened at larger loads. F_f is greatly reduced when the external field is applied (alternating square wave voltage, 450 Hz, 20 $V_{p\text{-}p}$). $V = 0.3\ \mu$m/s. Mica thickness 4.018 μm

force F_E of magnitude QE (Q is the total effective charge on chain). Analogously, the counterions of charge q feel a force qE. The movement of the counterions deforms the ionic cloud [14] changing the counterion-related osmotic pressure, which may have dramatic effects on the PE chain conformation. This effect is more significant for the case of weakly charged PEs, such as the one discussed here. The combination of the mentioned forces can be strong enough to induce a substantial deformation of the PE chains, which is opposed by F_{elas}. Yamamoto and Pincus theoretically described how the application of a field can produce the local collapse of a PE brush [15]. Substantial PE brush deformation has also been predicted by Migliorini from a mean-field study of the static problem [16].

The dynamic case of a changing applied field (e.g., alternating field of frequency $\nu > 0$) is much more involved; additional hydrodynamic forces need to be considered. First, the continuous deformation of the chains is opposed by a conformation-dependent viscous drag force F_ν proportional to the chain speed and the viscosity of the surrounding media. Second, the hydrated counterions will move in the opposite direction of the chains inducing a shear drag force F_d on them, as has been described before [14,17]. Even though the magnitude of the electrostatic force on the ions and PE chains is identical (because of electroneutrality), there is a net effect on the PE: as F_d is mediated by the presence of the solvent and depends on the spatial charge distribution and the charge density of the PE chains, it must be smaller than the electrostatic force on the counterions [17]. It is then reasonable to expect that $F_E > F_d$ under all conditions.

The effect of ν on the observed F_f reduction is very revealing. As shown in Fig. 3, a nonmonotonic F_f vs ν dependence is observed. Substantial F_f reduction is observed for ν lower than 1 kHz, but no effect is detected at larger frequencies. In addition, the friction reduction effect is considerably lessened in a narrow frequency window around 500 Hz. Below this frequency the effect is quite substantial; at larger frequencies it is progressively diminished. It is reasonable to expect that PE chains will fail to respond to the oscillating field at large ν, when the field variation is faster than the characteristic time of chain stretching. The longest relaxation time of a polymer in the unperturbed brush can be roughly estimated as $\tau_{\text{teth}} \approx \eta_0 h^3/k_B T$, [18] where η_0 is the viscosity of the media and h the polymer layer thickness. A relaxation frequency of

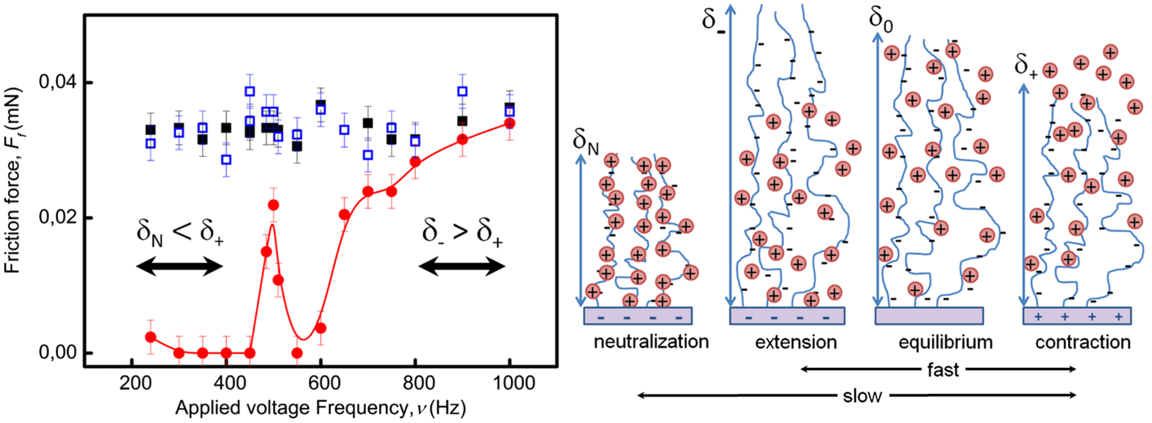

FIG. 3 (color online). F_f variation with the frequency of the applied field ν (red circles). F_f is similar before (open squares) and after (closed squares) application of the field (alternating square wave voltage, 20 $V_{p\text{-}p}$, $V = 0.3\ \mu$m/s, $L = 0.62$ mN). Continuous line is a guide to the eye. The schematic on the right illustrates the variation of polymer configuration with surface charge. At low ν the brush alternates between the neutralized δ_N (negatively charged electrode) and contracted δ_+ (positively charged electrode) states. At high ν slow neutralization does not occur, and the PE oscillates between the contracted, δ_+ and the stretched δ_- states.

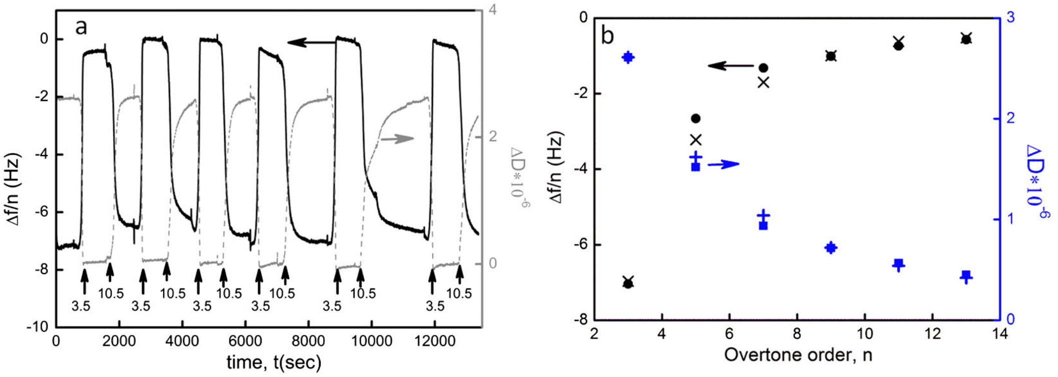

FIG. 4 (color online). (a) Variation of resonance frequency Δf (solid line) and "dissipation factor" ΔD (dashed line) for the third harmonic ($n = 3$) of a silica-coated quartz crystal covered by a polymer brush of $PS_{36}PAA_{125}$ when the pH of the media is switched between 10.5 and 3.5, as indicated. The zero values are chosen at pH 3.5. $D \equiv Q^{-1} = 2\Gamma/f$, where Q is the quality factor and Γ the bandwidth of the resonance peak of frequency f. Similar qualitative response was observed for the different odd overtones ($n = 1$ to $n = 13$). (b) Shift of resonance frequencies (circles) and dissipation (squares) upon pH changes between 3.5 and 10.5 for the different overtones, and corresponding fits (crosses) obtained by viscoelastic modeling of the adsorbed polymer brush. The best possible fit was obtained for a thickness difference of 2.9 ± 0.2 nm (assuming film density 1 g/ml) between the neutralized and charged states. The calculated viscosity and overtone-dependent shear modulus of the layer in the charged state are $\eta = (1.32 \pm 0.02) \times 10^{-3}$ Pa s and $\mu = (0.156 \pm 0.003)$ MPa $\times\, n^{-0.66 \pm 0.02}$, respectively.

the order of 500 kHz can be estimated using this expression, a value substantially larger than the few kHz observed experimentally. This discrepancy is by no means surprising: this scaling corresponds to an unconfined Rouse chain of Zimm blobs, valid for free brushes. At high compressions (large β) the relaxation time of tethered polymers τ_{teth} (occurring by chain retraction) increases substantially. Based on scaling arguments advanced by de Gennes [19], Klein and co-workers [20] proposed that $\tau_{\mathrm{teth}} \sim D^{-3/2} \exp(\mathrm{const} \times N\phi^{5/4})$. As τ_{teth} grows exponentially with ϕ, decreasing D leads to an important slowing down of the confined PE brushes.

The observed absence of F_f reduction in a narrow ν window is more puzzling. At first sight, it could be interpreted as a delicate balance between the different forces described above, canceling their influence at some frequency range. Nevertheless, a closer analysis reveals that this assumption is probably erroneous. Given that F_{elas} and F_v are just reactions to the deformation of the chains, the balance of forces that determines this deformation is governed by $F_E - F_d$, which is independent of frequency for the low frequencies studied here. The reasons for the observed behavior are probably more subtle. Detailed theoretical models describing the configuration of PE chains grafted to surfaces have been reported [12,21]. It has been argued that it is necessary to distinguish between permanently charged, strong (quenched) PEs and weak (annealed) PEs. The latter case corresponds to weak polyions (like PAA) whose degree of ionization depends on the local electrostatic potential. The application of the electric field described in this work produces ionic migration, constantly changing the pH and ionic concentration nearby the grafted polymer chains shifting its degree of ionization, as represented in Fig. 3. Counterintuitively, at low frequencies the configuration of the grafted PE may be shortest when the surfaces are negatively charged, if the chains are partially or totally neutralized. A significant change of effective brush height (~ 2.9 nm) upon neutralization is indeed observed by QCMD (Fig. 4). The difference between δ_N and δ_+ ($\delta_N < \delta_+ < \delta_-$) may be at the origin of the large friction reduction effect at low frequencies (this must be understood in average terms, as contracted and extended chains coexist when a grafted PE is in contact with an oppositely charged substrate [22]). On the contrary, at large ν the slow neutralization process is not completed and the grafted chains act as quenched PEs: the smallest size of the PE brush is now achieved when the surfaces are positively charged (Fig. 3), as expected from the partial shrinking of the chain due to electrostatic interactions ($\delta_+ < \delta_-$) [15]. The change from a scenario of reduced size when the surface is negatively charged to the opposite case of smaller height when the surface is positively charged explains the absence of F_f reduction at intermediate ν. Few studies have addressed the dynamic of PE ionization; characteristic neutralization times of the order of 1 ms have been reported, which is consistent with the change of regime reported in this work [23].

Many applications can be envisaged for the process described here, as electrical signals are relatively easy to produce and control. Friction and wear reduction in water-based environments, surface patterning, and real-time control of tactile sensations are just some examples. This method can also be used to investigate *in situ* molecular structure and relaxation process under confinement.

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