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Control and Quenching of Electroosmotic Flow with End-Grafted Polymer Chains

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Electroosmotic flow (EOF) refers to a fluid flow induced by an external electric field applied parallel to a solid surface and occurs when a space charge builds up in the fluid near the surface (e.g., the deprotonation of silanol groups at a silica−water interface leaves a net negative surface charge bound to the silica and positive solvated counterions in a diffuse layer near the surface, called the Debye layer). When an external electric field is applied, the mobile counterions are set in motion and, through viscous coupling with the uncharged fluid, eventually drag the bulk of the solution in a uniform flow. EOF is an efficient mode of fluid transport at small scale, and for microfluidic applications it is strongly preferred over Poiseuille flow because (1) it does not require large pressure gradients and (2) it exhibits a flat velocity profile which helps maintain the integrity of material samples transported in solution.[1−3] Ways in which the EOF can be tuned, or eventually quenched, are of immediate pratical relevance,[4−7] to decouple electrosmotic and electrophoretic motion of analytes in order to optimize the separation of biomolecules, to cite one example. Polymer coatings are routinely employed to modulate the EOF or to reduce the adsorption of analytes in capillary electrophoresis, and they exercise their control by either regulating the capillary surface charge or enhancing viscosity near the capillary surface (and therefore reducing the ion mobility in the Debye layer), or both.[8] Despite the wealth of empirical knowledge about the chemistry, processing, and performance of a large number of coatings, a fundamental understanding of the way in which adsorbed (dynamic coatings) or grafted (covalent coatings) polymer molecules modulate the EOF is still lacking. In particular, the relative merit of charge regulation and viscosity enhancement is hardly tractable experimentally. In our opinion, Harden, Long, and Ajdari provided the best theoretical account of the problem to date,[9] extracting insightful scaling laws for the EOF mobility in the presence of end-grafted neutral polymers, as a function of the grafting density and field strength.

The goal of this short communication is straightforward. We report on the first molecular dynamics simulation study of EOF control with grafted polymer chains. We show evidence that momentum absorption by neutral grafted macromolecules is, alone, capable of modulating the EOF strength, eventually to a point of where the bulk flow rate vanishes. The simulations are coarse-grained, typically involve on the order of 10^5 individual particles, and explicitly account for hydrodynamic and electrostatic interactions. Our generic approach is not chemically specific and allows us to model relatively small Debye length systems, thereby extending the scope of our conclusions to the microfluidic regime.

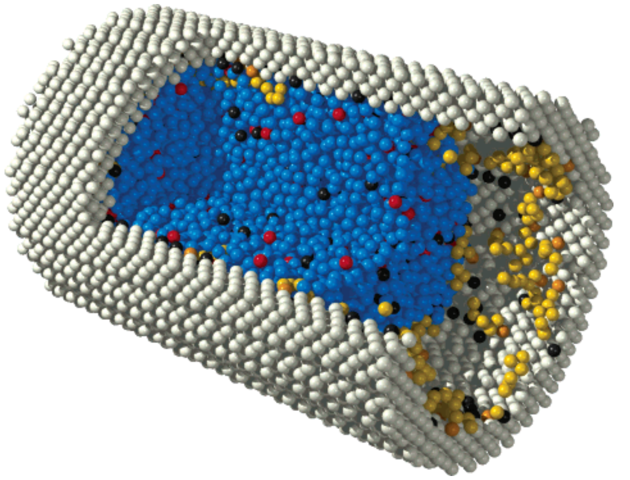

Figure 1. A cut view of a section of the capillary, captured from a simulation of EOF control via end-grafted polymer chains (with some particles removed to reveal the interior of the system). Shown here are the wall (gray), the fluid (blue), positive ions (red), negative ions (black), monomers (yellow), and grafting sites (orange). The diameter of the beads in the figure corresponds to the LJ interaction range, the unit of length in this paper. In this particular picture, the inner capillary wall bears a negative surface charge density $\sigma = -0.1$, the salt density is $n_0 = 0.02$, and the grafted polymer chains have a length $N = 5$ (instead of $N = 10$, for clarity).

We choose to tackle this problem with united-atom molecular dynamics (MD) simulations,[10,11] an ubiquitous technique for discrete fluid simulation. All particles in our simulations interact with a pairwise purely repulsive (truncated) Lennard-Jones (LJ) potential. We confine the fluid inside a cylindrical shell extruded from an fcc lattice, with periodic boundary conditions along the capillary axis, to model a narrow, infinitely long capillary (see Figure 1). Wall particles differ from fluid ones in that they are anchored to fixed lattice sites via a harmonic potential. We model self-avoiding grafted polymer chains of length N by stringing together N particles with a finitely extensible nonlinear elastic (FENE) potential and further binding the first monomer of the chain to a wall site using the same potential.

To introduce the electrostatic aspect of EOF, we endow some particles (randomly selected in the fluid or on the inner surface of the capillary wall, respecting overall neutrality) with an electric charge and add between all charged pairs a Coulomb interaction, truncated at distances beyond a third of the capillary length. It is generally incorrect in 3 dimensions to impose a cutoff on the long-ranging Coulomb interaction, but in our case the system only extends along one direction so we may consider the interaction as short-ranged[10] for distances larger than twice the capillary radius a. By varying the cutoff length r_c from $1a$ to $8a$, we verified that simulation results are independent of the cutoff value when it is above $3a$, and we chose a safe $r_c \approx 5a$ in producing our final data. We control the temperature of the system by periodically rescaling the velocity of the particles in the outer layers of the capillary wall to keep their mean kinetic energy consistent with the target temperature. We thus effectively only couple the outside of the capillary to a heat sink, ensuring that our thermostat does not bias the net fluid velocity or the hydrodynamic effects during EOF.

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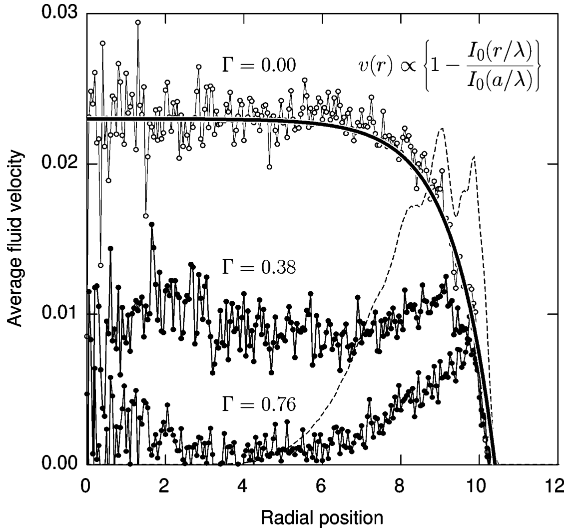

Figure 2. Molecular dynamics EOF velocity profiles in a capillary of radius $a \approx 10.4$, without a polymer coating (open circles) and for two polymer grafting densities $\Gamma = 0.38$ and $\Gamma = 0.76$ (filled circles). The wall charge density is $\sigma = -0.1$, the salt density is $n_0 = 0.02$, and the external field is $E = 1$. The grafted polymers have length $N = 10$, and the normalized monomer distribution is shown as a dashed line (using an arbitrary scale); it is the same for both values of Γ. The thick line is a fit of the polymer-free EOF flow profile to the continuum theory prediction, given in the top right of the figure.

Physical quantities herein are quoted as dimensionless numbers and are understood to be multiplied by an appropriate combination of the natural MD units: the LJ range parameter σ for length, the LJ energy scale ϵ for energy, and the mass m_f of fluid particles. Together these three units determine the natural MD unit of time $\tau = \sqrt{m_f\sigma^2/\epsilon}$. The system is initialized in a random state, and the particle trajectories are integrated using the velocity-Verlet algorithm with a time increment $\Delta\tau = 0.001\tau$, for more than 10^6 steps. All simulations reported here are carried out with the same mean fluid density $\tilde{\rho}_f = 0.8$, mean wall density $\tilde{\rho}_w = 1.0$, temperature $k_BT = 1.0$, capillary radius $a = 10.4$, capillary length $L = 158.7$, Coulomb cutoff length $r_c = 50$, and the same Bjerrum length $\lambda_B = 2$ (corresponding to that of water, a fluid with a high dielectric constant).

The EOF arises naturally in our simulations when we apply an external electric force on all the charged particles. We choose a surface charge density of -0.1 for the inside capillary wall (with compensating positive counterions in the fluid) and a fluid salt density of 0.02. This yields a Debye length $\lambda \approx 1$, and as expected, the flow initially arises in this layer, near the wall, where there is a net charge. However, the bulk of the fluid is rather quickly dragged into a steady-state flow, which exhibits a uniform velocity outside the Debye layer, as shown in Figure 2, where the open circles show simulation results for the steady-state EOF velocity profile when an external field $E = 1$ is applied. The thick solid line corresponds to the velocity profile expected from continuum electrostatics and hydrodynamics: $v(r) \propto [1 - I_0(r/\lambda)/I_0(a/\lambda)]$ (where I_0 is the modified Bessel function of the first kind);[12] the proportionality constant is the only fitted parameter. Our simulation technique thus reproduces the known qualities of EOF faithfully. The measured velocities exhibit relatively large fluctuations because we are limited to small external fields; larger fields generate to much Joule heating inside the fluid for the wall thermostat to regulate the temperature effectively. Note that the magnitude of the EOF is inversely proportional to viscosity and that our fluid, in the bulk, has about a fourth of the viscosity of water (this is not surprising, given the absence of the attractive part in the LJ interaction and the absence of hydrogen bonds).

We now arrive at the central question of this communication: in what measure can neutral polymer chains grafted on the capillary surface reduce the magnitude of the EOF flow, and can they quench it altogether? We consider the impact of chains of length $N = 10$ grafted on the inside surface of the capillary, for two surface grafting densities $\gamma = 0.05$ and $\gamma = 0.10$. It is convenient to cast γ into the dimensionless coverage parameter $\Gamma = \gamma\pi R_g^2$ (where R_g is the radius of gyration of the polymer) to give a sense of whether we are in a "mushroom" regime ($\Gamma < 1$) or a "brush" regime ($\Gamma > 1$).[9] For grafted chains of length $N = 10$, we have extracted $R_g = 1.56 \pm 0.07$, so the two grafting densities studied correspond to $\Gamma \approx 0.38$ and $\Gamma \approx 0.76$; both cases thus correspond to a mushroom regime. The steady-state results for the corresponding flow profiles are shown in Figure 2, where they can be compared to the situation where there is no polymer coating on the capillary wall. The dashed line in Figure 2 gives the shape of the normalized monomer distribution as a function of radial position to show that the coating thickness is commensurate with the Debye length (the distribution is essentially the same for both grafting densities, supporting the idea that we are in a mushroom regime rather than a brush regime).[9,13] The results in Figure 2 clearly indicate that the grafted chains significantly reduce the ability of the drifting ions in the Debye layer to drag the bulk of the fluid into a uniform flow. At $\Gamma = 0.76$, the flow velocity in the central part of the channel has practically vanished, even though the flow generation has not relented in the immediate vicinity of the wall. We should point out that the net charge density is practically unaffected by the presence of the polymers, so the shear plane does not move away from the wall in the coated situation (the zeta potential is the same). We also note that the field is small enough that both the monomer and the net charge distributions are not affected significantly during flow; hence, there is no charge regulation at work here. The only mechanism of EOF control is a transfer of energy from the fluid adrift inside the Debye layer to the grafted chains by collisions, and in turn to the wall particles, where it is evacuated as heat.

To our knowledge, this is the first simulation work that confirms the operation of a viscosity-only quenching of EOF. Although it is not surprising that EOF is reduced by anchored flexible molecules, it is unexpected to find that it is completely quenched at a coverage value well below the brush regime threshold and without any shift in the position of the shear plane. These first results compel us to investigate more closely the dependence of EOF mobility on the chain length N and the coverage parameter Γ. We will report on these simulations in a future, more detailed publication and compare our results directly with the theory of Harden, Long, and Ajdari, valid in the limit of vanishing Debye length.[9] Other critical parameters definitely include the chain stiffness and the field strength (we have implemented a new profile-unbiased thermostat derived from dissipative particle dynamics,[14] which can be applied to the whole fluid, allowing us to study regimes where the conformation of the grafted chains is affected by the flow). Finally, our approach is also geared toward the study of adsorbed polymer coatings, and we think it will provide some fundamental insight into the peculiar mode of operation of adsorbed coatings conjectured from experimental evidence.[7]

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