Bidirectional Transport of Polyelectrolytes Using Self-Modulating Entropic Ratchets

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Asymmetric cavities are shown to induce net transport, for random walkers and polyelectrolytes, upon the application of zero-mean, time-symmetric, fluctuating external fields (and similarly for zero-mean, temporally asymmetric fluctuating fields with symmetric cavities). Entropic trapping is shown to enhance the ratchet effect for polyelectrolytes. Time biasing an ac field can even cause different polymers to migrate in opposite directions. Entropic trapping can thus convert simple steric ratchets into self-modulating ratchets capable of size fractionating polyelectrolytes such as DNA.

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Recently, Magnasco [1] demonstrated that ratchet potentials (i.e., potentials spatially asymmetric with respect to their maxima) can rectify zero-mean, correlated fluctuations and generate net motion (hence the name “correlation ratchet”). Chialvo and Millonas also demonstrated that temporally asymmetric, zero-mean fluctuations can operate a correlation ratchet even when the potential is spatially symmetric [2]. This idea was actually exploited earlier in a process called zero-integrated field gel electrophoresis (ZIFE) which uses unbiased pulsed electric fields to separate chromosomes DNA [3]. According to the pioneering work of Curie [4], spatially asymmetric, periodic structures may act as ratchets for Brownian particles in the presence of dissipation or other sources of time-reversal symmetry breaking. Ajdari and Prost put Curie’s symmetry principle to the test in showing how a simple microstructure could act, in principle, as a ratchet [5]. However, as Leibler remarked [6], the success of future applications for correlation ratchets is still somewhat dubious, especially when compared with well-established separation techniques such as gel electrophoresis. Here, we investigate the possibility of exploiting a new ratchet-like system for DNA electrophoresis. In particular, we show that the internal entropy of long polyelectrolytes (which can be thought of as a series of charged tethered Brownian particles) magnifies the ratchet effect for small steric asymmetries. An efficient ratchet system can thus be built without using an external asymmetric electrostatic potential. Finally, we offer a rough estimate of the specifications for such a ratchet separation device constructed using microolithographic techniques.

When the velocity $V$ is a nonlinear function of the applied force (spatially or temporally), asymmetric systems may exhibit net drift velocities even though the time-averaged force is zero. Consider Magnasco’s example of a pointlike particle in a sawtoothed one-dimensional potential with different uphill slopes on each side of the extrema [1]. Since the critical forces $E_{\pm}$ allowing the ratchet to move in the $\pm$ directions are different, one can obtain net transport by applying an unbiased ac force made of, e.g., square pulses of amplitude $E_{-} < E < E_{+}$ and duration $T_{E}$. Here, the pulse durations $T_{E}$ are assumed to be much longer than the thermally activated jumping times (i.e., we are not dealing with stochastic resonance [7]). For symmetric potentials ($E_{-} = E_{+}$), a net drift can be obtained with alternating (square) pulses of intensity $E_{1}$ and $-E_{2}$ and duration $T_{E1}$ and $T_{E2}$, respectively, with $E_{1}T_{E1} = E_{2}T_{E2}$ (i.e., zero mean) and $E_{1} < E_{2} < E_{1} [2,3]$. We first demonstrate that it is possible, in principle, to build a ratchet system using only steric interactions. Our toy model consists of biased random walkers migrating through a 2D channel with “rough” walls (Fig. 1). We use a square lattice with diagonal periodic boundary conditions. The walkers are $n \times n$ lattice plaquettes. The (dimensionless) scaled field $E$ is directed along the diagonal, i.e., $E_{x} = E_{y} = E/\sqrt{2}$. For each step of duration $\Delta t = \tanh(E_{s})/E_{s}$, a walker must jump along the $\pm x$ or $\pm y$ directions with probabilities $p_{\pm} = [1 + \exp(\mp 2E_{s})]^{-1}/2$ [8]. Jumps that make the particle

![FIG. 1. Our toy model: $1 \times 1$ and $2 \times 2$ plaquettes (black) perform biased random walks on the square lattice between the symmetric rough walls (gray). An asymmetric channel can be created if those wall plaquettes denoted with A’s are removed.](image)
overlap with a wall structure are rejected. The exact dc mobility \( \mu = V/E \) of 1 \( \times \) 1 and 2 \( \times \) 2 walkers (for the same given charge) has been calculated as a function of \( E \) following a method first used to study gel electrophoresis [8]. For a pathway with symmetrically alternating narrow and wide passages (Fig. 1), the mobilities are even functions of \( E_z \); e.g., we find that

\[
\mu_{1 \times 1} = \frac{16 + 12 \text{sech}(2E_z)}{39 + 32 \text{sech}(2E_z) + \text{sech}^2(2E_z)},
\]

\[
\mu_{2 \times 2} = \frac{4}{11 + \text{sech}(2E_z)}.
\]

For 1 \( \times \) 1 plaquettes, the asymptotic mobilities for \( E \rightarrow 0 \) and \( E \rightarrow \infty \) are thus \( \mu_0 = \frac{7}{18} \) and \( \mu_\infty = \frac{16}{17} \), respectively, while the critical field \( E_z \), which we define as that value of \( E \) for which \( \mu = (\mu_0 + \mu_\infty)/2 \), is \( E_z = 1.04421 \). For 2 \( \times \) 2 plaquettes, we find \( \mu_0 = \frac{1}{3} \), \( \mu_\infty = \frac{4}{11} \), and \( E_z = 0.967267 \). Using ac square pulses of intensities \( +E \) and \( -E/R \), with \( E = E_z \), and (arbitrarily long) durations \( T_+ \) and \( T_− = RT_+ \), respectively, we can obtain net motion in the “positive” north-east (NE) direction (i.e., if \( R > 1 \)) even though the mean field is zero. Figure 2 depicts the net velocity of these particles vs \( E \) for a ratio \( R = 2 \). The ratchet velocities are a maximum for \( E = 2.4 \).

For a channel with a broken spatial symmetry (same as Fig. 1 after removal of the “A” squares), motion in the negative direction is now easier. Exact solutions for this case have also been obtained but are too unwieldy to be given here. For a 1 \( \times \) 1 particle, we have \( \mu_0 = 0.648113 \) and \( \mu_\infty = 0.655653 \). Again, a net drift ensues (Fig. 3). Maximum ratchet velocities occur for the fields \( E = 0.648113 \) and \( E = 0.769662 \) for the 2 \( \times \) 2 and 1 \( \times \) 1 particles, respectively, which correspond roughly to the lower critical fields for these particles. The inset of Fig. 3 shows the effect of a time bias \( \Delta = (T_+ − T_-)/(T_+ + T_-) \), where \( T_+ \) and \( T_- \) are the pulse durations in the two directions, with \( E = 0.518038 \). When \( \Delta \in [0.00 \, 0.00438 \, 0.00 \, 0.00938 \, 0.00 \, 0.0045 \, 0.00 \, 0.05] \), the \( 2 \times 2 \) particle moves in the negative direction while the \( 1 \times 1 \) particle moves in the positive direction. This is a remarkable result since the two particles have the same charge. In principle, this simple idea may be exploited for the construction of a separation process. However, the range of \( \Delta \)’s over which the effect exists is quite narrow. This is so because steric ratchet barriers are very inefficient for hard objects. However, as we will demonstrate below, such steric barriers are quite efficient for polymers because the internal configurational entropy of a polymer directly modulates the height and the degree of asymmetry of the steric barriers.

Let’s consider a polymer of length \( M \) and radius of gyration \( R_g(M) \) in linear channels having a periodically

![FIG. 2. Net velocity vs applied field \( E \) for 1 \( \times \) 1 and 2 \( \times \) 2 plaquettes in the symmetric tube shown in Fig. 1. Square pulses of intensity \( +E \) and duration \( T_+ \), alternate with pulses of intensity \( -E/R \) and duration \( T_− = RT_+ \), where \( R = 2 \). Although the mean field is zero, the ac field is temporally asymmetric.](image)

![FIG. 3. Absolute value of net velocity vs the applied field \( E \) for 1 \( \times \) 1 and 2 \( \times \) 2 plaquettes in the asymmetric tube shown in Fig. 1 upon removal of the gray squares labeled A. Unbiased ac square pulses of amplitude \( E \) and arbitrarily long durations are applied. Inset: Net velocity of the two particles vs the time bias \( \Delta \) of the square ac pulses of amplitude \( E = 0.518038 \).](image)
varying bore radius $R_f$ [with $(R_f)_{\text{min}} < R_f < (R_f)_{\text{max}}$] and a spatially asymmetric profile (Fig. 4) along the tube axis ($x$). In those stricture regions where $R_f(x) < R_s(M)$, the polymer’s entropy decreases like $\Delta S \sim k_B(R_s/R_f)^{1/\nu}$, where $\nu$ is Flory’s exponent [9–12]. Therefore, the internal entropy of the polymer is a function of the local tube radius, $S = S(R_f(x))$, and the polymer experiences an entropic force $F_S(x) \sim -T(\partial S/\partial x) = -\left(\partial S/\partial R_f \right) \times \left(\partial R_f/\partial x \right)$ wherever the tube radius $R_f(x)$ varies; the strictures thus act like potential barriers. Since the conformational entropy is an extensive variable ($S \sim M$), the entropic force $F_S = F_S(M)$ at any given stricture corresponds to different potential barriers for different polymer sizes $M$.

In other words, the internal configurational entropy of the polymer modulates the nature of the potential barrier. A previous study of the electrophoretic dynamics of long polyelectrolytes in a tube with symmetric strictures [13] has demonstrated that strictures indeed act as entropic potential barriers. When those strictures are spatially asymmetric, however, the entropic force $F_S$ is dependent on the direction of motion (because we have two different slopes $\partial R_f/\partial x$), and thus, in this sense, the system is similar to Magnasco’s [1]. In Fig. 4, the two slopes differ by a factor of 3, thus rendering our steric ratchet potential very asymmetric. However, unlike previous ratchet potentials, which were modulated via an externally applied field, it is the conformational entropy of the polymer itself which determines the height (and the degree of asymmetry) of our ratchet potential. We call such a system an entropic ratchet (an expression used in a different context in Ref. [14]).

Our computer simulations of this polymer system use the bond-fluctuation algorithm on a square lattice [15]. The field biases the monomer jumps in the field direction according to a Metropolis probability. A polymer molecule is made of $M$ charged monomers which are $1 \times 1$ plaquettes. The scaled field intensity being set at $E = 0.003$, the mean Metropolis rejection probability is about 0.3%. The narrow channels are of length 45 and radius $(R_f)_{\text{min}} = 7$, the maximum radius of the channel is $(R_f)_{\text{max}} = 30$, and the periodicity of the system is 182.

One expects only small entropic effects when $R_s(M) < (R_f)_{\text{min}}$. In contrast, larger molecules (Fig. 4) lose a lot of entropy in the narrow channels. Note, however, that very large molecules can occupy the narrow channel and both adjacent “pores” simultaneously; such qualitatively different scenarios are not treated here. The longer funnel tapers in the negative direction, and the dc mobility is substantially larger for motion in that direction. Figure 5 depicts the net mobility $\mu = V/E$ vs size $M$ for an applied ac field made up of unbiased long square pulses of amplitude $E = 0.003$. The vertical line indicates where $R_s(M) = (R_f)_{\text{min}} = 7$. Large mobilities are indeed observed only for large molecules [$R_s(M) > 7$] which suffer important entropic losses in the narrow channel. This clearly demonstrates a large amplification of the ratchet effect due to conformational entropy (and thus molecular size). Note also that the direction of net transport would remain unchanged under a sign reversal of the molecular charges. The inset of Fig. 5 depicts a case where we have temporally biased the ratchet with longer positive pulses. The three positively charge molecules exhibit very distinctive behaviors. The small one ($M = 8$) migrates in the positive direction since its net drift simply follows the net bias of the applied field. The largest ($M = 30$) molecule, which exhibits very strong ratchet motion for

![FIG. 4. Two polymers moving in a channel with asymmetric strictures. The smaller one has $M = 25$ monomers and must lose entropy in order to cross the narrow passage channel. The larger $M = 40$ polymer maximizes its internal entropy in the widest part of the channel.](image-url)
unbiased pulse conditions, is still characterized by a negative velocity. Finally, the applied time bias exactly cancels the ratchet drift for the intermediate time-asymmetric ratchet using symmetric strictures. The vertical line at \( M = 14 \) denotes that molecular size for which \( R_g(M) = \langle R_T \rangle_{\text{min}} = 7 \). Inset: Position vs time for molecular sizes \( M = 8, 14, \) and \( 30 \). Square pulses of intensity \( E = 0.003 \) and duration \( 4 \times 500000 \) alternate with square pulses of intensity \( E = -0.003 \) and duration \( 2.85 \times 500000 \).

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\text{FIG. 5. Net velocity of the polyelectrolyte vs molecular size } M \text{ for unbiased (zero-mean) ac square pulses of amplitude } E = 0.003 \text{ and arbitrarily long durations. The vertical line at } M = 14 \text{ denotes that molecular size for which } R_g(M) = \langle R_T \rangle_{\text{min}} = 7. \text{ Inset: Position vs time for molecular sizes } M = 8, 14, \text{ and } 30. \text{ Square pulses of intensity } E = 0.003 \text{ and duration } 4 \times 500000 \text{ alternate with square pulses of intensity } E = -0.003 \text{ and duration } 2.85 \times 500000.
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