Nonlinear Elasticity of Single Collapsed Polyelectrolytes

Hirofumi Wada, Yoshihiro Murayama, and Masaki Sano
Department of Physics, University of Tokyo, Hongo, Tokyo, 113-0033, Japan
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Nonlinear elastic responses of short and stiff polyelectrolytes are investigated by dynamic simulations on a single molecule level. When a polyelectrolyte condensate undergoes a mechanical unfolding, two types of force-extension curves, i.e., a force plateau and a stick-release pattern, are observed depending on the strength of the electrostatic interaction. We provide a physical interpretation of such force-extension behavior in terms of intramolecular structures of the condensates. We also describe a charge distribution of condensed counterions onto a highly stretched polyelectrolyte, which clarifies a formation of one-dimensional strongly correlated liquid at large Coulomb coupling regime where a stick-release pattern is observed. These findings may provide significant insights into the relationship between a molecular elasticity and a molecular mechanism of like-charge attractions observed in a wide range of charged biopolymer systems.

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Electrostatic interactions in aqueous media can be controlled by changing temperature, dielectric constant of the solvent, and counterion valency \([1, 2]\). In a strongly charged system, correlations between counterion charge fluctuations that are neglected within the Poisson-Boltzmann (PB) theory give rise to various dramatic phenomena which apparently contradict our understandings based on the PB theory \([3, 4, 5, 6]\). One of the most familiar examples is probably the condensation of a single DNA molecule in the presence of multivalent cations \([7, 8, 9]\), which indicates the counter-intuitive “like-charge attractions” \([10]\). A variety of problems related with electrostatic effects is being of great interest in soft condensed matter physics today \([11]\). Ionic effects also modifies elastic properties of PE chains drastically \([12, 13, 14, 15, 16, 17, 18]\). Recent micromanipulation experiments have shown impressive elastic responses of single collapsed DNA molecules \([19, 20]\), which significantly deviate from those expected from the standard worm-like chain (WLC) model \([22]\). In spite of such experimental evidences, theoretical and numerical studies of this problem have been lacked so far, mainly because of its nonequilibrium nature combined with long-ranged Coulomb interactions.

In this Letter, we report on results of the Brownian Dynamics (BD) simulations on the stretching of single PE condensates. The present simulation covers only a salt-concentration of the added multivalent cations. The struc-

counterions onto a stretched PE reveals a formation of one-dimensional (1D) strongly correlated liquid (SCL) \([4, 5, 6, 7]\) when a \(f-x\) curve shows a stick-release, while such a charge ordering is absent in the case of a force plateau. In order to highlight electrostatic effects on the macroscopic polymer elasticity, we are primarily focusing on systems with very strong Coulomb interactions which is beyond a typical physiological condition. Furthermore the present study deals only with relatively short and stiff polymers and also neglects complicated structures of biopolymers \([23]\), direct comparison with any experiment is therefore impossible at this stage. The primary aim in this Letter is to build bridges between the macroscopic molecular elasticity and the theoretically predicted SCL picture, which may serve as a first step towards microscopic understandings of available experiments.

In our BD simulations, the chain comprises \(N\) harmonically linked beads of radius \(a\), each of which carries a charge \(-qe\). The system also includes \(N\) oppositely charged counterions of the same valency and radius to keep the overall charge neutrality. The charged particles interact via the unscreened Coulomb interaction, where the solvent is replaced by a background with the dielectric constant \(\epsilon\). The system is placed in a cubic box and periodic minimum-image boundary conditions are imposed to keep the monomer/counterion density \(\rho_{\text{mon}} = \rho_{\text{ion}} \approx 1.5 \times 10^{-5}/a^3\) constant \([25, 26]\). Long time dynamics of monomers and counterions are well described by the position Langevin equations \([24]\)

\[
\gamma \frac{dr_i}{dt} = -\nabla_r U[r(t)] + f_i(t),
\]

where \(\gamma\) is the damping constant, \(U\) the potential energy and \(f_i\) the vectorial random force acting on the particle \(i\), which satisfies the correlation property \(\langle f_i(t)f_j(t') \rangle = 2\gamma k_BT \delta_{ij} \delta(t-t')\). Because we are primarily concerned with dense ionic globules, hydrodynamic interactions are not taken into account in this study \([25, 26]\). The particle radius \(a\), the energy scale of the Lennard-Jones potential

*Electronic address: wada@daisy.phys.s.u-tokyo.ac.jp
\( \epsilon \) and \( \tau = \gamma a^2 / \epsilon \) are chosen as the unit of length, energy, and time in our simulations. The potential energy is composed of several kinds of contributions: \( U = U_s + U_b + U_{LJ} + U_r \). The first one \( U_s \) ensures the connectivity of a PE. To maintain small variances of bond lengths around \( b \), i.e., the chain length around \( L = b(N - 1) \), we use a large value of the spring constant \( K = 400 \, \text{e} / a^2 \). The second one \( U_b \) accounts for the intrinsic bending stiffness of a chain:

\[
U_b = \kappa \sum_{i=1}^{N-2} \left( 1 - \frac{(r_{i+1} - r_i) \cdot (r_i - r_{i-1})}{b^2} \right). \tag{2}
\]

The intrinsic persistent length is thus given by \( L_p^0 = b s / k_B T \). The Coulomb potential \( U_r \) acts between all charged particles except between bonded ones. In order to prevent a collapse of monomers and counterions, a truncated Lennard-Jones potential \( U_{LJ} \) acting between all particles is also incorporated only for \( |r_i - r_j| < b \). The coupling constant \( \Gamma = q^2 \pi B / a \) controls the relative strength of the electrostatic interaction to the thermal energy at a distance \( a \). (The Bjerrum length \( l_B = e^2 / 4 \pi \varepsilon k_B T \approx 0.7 \, \text{nm} \) in water at room temperature.)

In the beginning of our simulation, a randomly generated initial configuration is allowed to collapse to a globule and equilibrated for \( 5 \times 10^6 \) time steps with \( \Delta t = 10^{-3} \tau \). Then the collapsed chain is stretched by pulling its one end at a constant speed, while the other end is fixed in a position. The stretching speed \( v_s \) is measured by the value \( \mu \) defined as \( \mu = v_s / v_0 \), where \( v_0 = b / \tau_R \) with \( \tau_R = \gamma b^2 N^2 / 3 \pi^2 \epsilon \) the Rouse relaxation time for a flexible polymer with \( N \) monomers at \( k_B T = \epsilon / 2 \). In all simulations presented below, we fix \( N = 32 \), \( b = 2a \), \( L / L_p^0 = 4 \), \( \mu = 0.1 \) and \( k_B T = 0.3 \epsilon \), while \( \Gamma \) is widely changed. To complete single stretch/relax cycle, simulation runs for more than \( 10^8 \) time steps even for \( N = 32 \). Simulations for larger \( N \) is desirable, but it is much more time consuming because the total time steps is proportional to \( L \tau_R \sim N^3 \) in addition to the \( O(N^2) \) computations for Coulomb interactions at every time step.

\( \epsilon / k_B T = 2 \) and \( \mu = 0.1 \) are fixed. The chain remains elongated in this case, and the \( f\)-\( x \) curve obeys the standard WLC formula:

\[
\frac{L_p f}{k_B T} = u + \frac{1}{4(1-u)^2} - \frac{1}{4}, \tag{3}
\]

where \( u = x / \langle L \rangle \) is the fractional extension \( 22 \). Even in this case, the persistence length \( L_p \) differs from \( L_p^0 \) because of the electrostatic contribution \( 13, 14, 15, 16 \). In Fig. 2 we plot the effective \( L_p \) as a function of \( \Gamma \), which are determined by fitting Eq. (3) to the simulated \( f\)-\( x \) curves for \( 0.80 \leq u \leq 0.97 \). For small \( \Gamma \) (roughly less than 3), the electrostatic repulsion between monomers leads to a stretched configuration of the chain, i.e., an increasing stiffness. As the coupling increases, however, it is more and more screened out by the counterion condensation. Far from the onset value of the Manning condensation (\( \Gamma_c \approx 2 \) for infinitely long, stiff chain \( 23 \)), the electrostatic interactions are significantly reduced, and \( L_p \) again decreases to \( L_p^0 \). Such behavior is also consistent with that of the radius of gyration \( R_g \) observed in other simulations \( 22, 26 \), if one recalls that the persistent length is related to the radius of gyration.

**FIG. 1:** The force-extension curves of a PE for three different values of the coupling parameter (a) \( \Gamma = 0.1 \) (WLC), (b) \( \Gamma = 40 \) (force plateau), and (c) \( \Gamma = 110 \) (stick-release). The dashed line in (a) is the best fit of Eq. (3) to the simulation data. Arrows indicate stretching/relaxing.

**FIG. 2:** The effective persistence length of a PE deduced from its force-extension curve as a function of \( \Gamma \). Inset is the same plot on a semi-log scale.
as $R_g^2 \sim L_p L$ for a semiflexible polymer. The sudden drop of $L$ at $\Gamma = 35$ may be the sign of intramolecular collapse [25].

For $\Gamma = 40$ [Fig. 1 (b)], a distinct force plateau is emerged in the $f$-$x$ curve, reflecting intramolecular attractions which are purely electrostatic origin. To evaluate the magnitude of the condensation force between monomers, we calculate the excess work $\Delta W = \int_{x_1}^{x_2} \left( f - f_0 \right) dx = \bar{f} \left( x_2 - x_1 \right)$ from the data, where $f_0$ is the WLC force calculated by Eq. (3), and $x_1$ and $x_2$ are chosen as 0.3$(L)$ and 0.8$(L)$. We obtain $\Delta W \sim 0.8k_BT/a$, which roughly corresponds to $\bar{f} \sim 1.6k_BT/a$. Taking into account that $\bar{f}$ is a certain increasing function of $\Gamma$, let us tentatively compare our $\bar{f}$ with that of available experiments. Assuming DNA’s linear charge density $\nu = q/(2a)$ and the charge valency $q = 4$ in our model, we have $a \sim 0.34$ nm (1bp), which gives $f/\Gamma \sim 0.04k_BT/bp$ for $\Gamma = 40$. On the other hand, for DNA with trivalent cation ($q = 3$) at room temperature, one finds $\Gamma = 2 \nu k_BT/a \cong 24$. Using the experimental value $\Delta W = 0.33k_BT/bp$ for trivalent cation Co-Hex obtained by Baumann et al. [19], one would obtain $f/\Gamma \sim 0.01k_BT/bp$ for $\Gamma = 24$, which agrees with our value.

Several snapshots of the PE during stretching are displayed in Fig. 3 (a). When the tension is applied externally, the ionic condensate (the PE-counterions complex) can change its overall structure to a more energetically stable one, because intramolecular attractions are not so strong (typically a few $k_BT$ as inferred above) for the present moderate $\Gamma$. Therefore, the PE can change its configuration continuously to minimise the stored elastic energy during stretching/relaxing, which we consider leads to the appearance of the force plateau.

In Fig. 1 (c), we show the $f$-$x$ curve for the largest coupling parameter: $\Gamma = 110$. The curve exhibits a pronounced sawtooth pattern, which may reflect intermittent plastic deformations of the glass-like ionic condensate [22]. (As will be described below, the condensed counterions are still in a liquid phase, but their individual motions are extremely slow). Figure 1 (b) shows a series of the corresponding snapshots of the PE, which clearly demonstrates the coil-globule coexistence within the single PE under the imposed extension [25]. This is a noticeable difference with the case in an external electric field where an unfolding of a PE is rather abrupt [26]. For sufficiently large $\Gamma$, the electrostatic attractions are so strong that the PE condensate cannot alter its structure easily. Then the elastic energy is more and more stored in the chain as the extension increases, until the PE condensate is locally unravelled in rather abrupt way.

It is important to note that there is marked hysteresis in the $f$-$x$ curve [Fig. 1 (c)] during stretching and relaxing. This suggests that folding and unfolding transitions of the complex are first-order-like, namely, they do not take place at the same extension [25]. This feature is more distinctive in the $f$-$x$ curve [Fig. 1 (c)], which again indicates that each stick-release response is caused by a nonequilibrium configurational change of a PE condensate. Averaging over a large number of single-pass $f$-$x$ curves, one would obtain a smooth $f$-$x$ curve with vanishing peaks. However a hysteresis would remain even in that limit, as long as a time scale of $\nu \sim 10^7$ time steps. It is also important to note that the stored elastic energy during stretching/relaxing, which we consider leads to the appearance of the force plateau.

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FIG. 5: 1D structure factor $S(q)$ of counterions condensed onto a stretched PE with its fractional extension $u$ kept nearly 0.9 for $\Gamma = 40$ (broken line) and for $\Gamma = 110$ (solid line). Inset: The self-diffusion of a single condensed counterion for $\Gamma = 110$, which exhibits sub-diffusive behavior given by $\langle \delta x^2(t) \rangle \propto t^{\alpha}$ with $\alpha = 0.85$ for $t/\tau > 10^4$.

The condensed counterions therefore form a 1D SCL at the surface of a PE. We now expect as follows. A long-ranged attraction mediated by long-ranged charge fluctuations [11, 28] gives rise to the force plateau in $f_x$ curve; on the other hand, the highly nonequilibrium elasticity such as the stick-release for large $\Gamma$ mainly comes from the short-ranged strong attraction created by the structural correlations of 1D SCL. This attraction is predicted to dominate over the long-ranged one at a very short distance that is typically within the inter-particle distance $b$ [31]. Because the counterions are much more strongly bound to the PE for $\Gamma = 110$ than for $\Gamma = 40$ (see fig. 3), it is reasonable to consider that different mechanisms of a net attraction between similarly charged monomers are underlying for $\Gamma = 40$ and 110. To verify this idea, however, fine data for larger $N$ systems are required because we have to diminish finite-size effects and influences of system-size dependent duration time of metastable states as much as possible.

We expect that a sufficiently large $\Gamma$ regime is theoretically accessible from the first principle using the recently developed strong-coupling theory [6, 32], while for intermediate $\Gamma$ regime, a phenomenological approach which postulates a “short-ranged” intramolecular attraction can be still useful to understand a macroscopic elasticity of a long PE [32]. (Note that the intramolecular attraction for moderate $\Gamma$ is long-ranged, as mentioned, compared with a length scale $a$, but is still significantly “short-ranged” compared with an overall polymer contour length which often extends up to several $\mu$m for biopolymers such as DNA.)

In summary, we have studied force responses of collapsed short PE strands by the dynamic simulations in a wide range of $\Gamma$. The simulation results are consistent with the experimental trends, and the idea is proposed by analysing the simulation data that the SCL state of the counterion may be responsible for the stick-release response. To unambiguously conclude these findings, more work for larger $N$ systems will be required.

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