

## Configuration of a polyelectrolyte chain in the Coulombic unscreened limit

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sults for iron are consistent with the weak  $\text{Fe}_2$  bond ( $D^0 \approx 1.1$  eV), thought to be predominantly a  $4s-4s$  interaction.<sup>12</sup> The  $\text{Fe}^+-\text{Fe}$  bond is much stronger ( $D^0 \approx 2.7$  eV)<sup>5,6</sup> although considerably weaker than those in the Nb system. It will be interesting to see whether the observed differences between these clusters are prototypical for metals on the left and right side of the Periodic Table. These differences are very evident in reactivity experiments in progress in our laboratory. Such studies provide considerable qualitative and *quantitative* insight into metal-metal and metal-ligand bonding across the transition metal series.

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## NOTES

# Configuration of a polyelectrolyte chain in the Coulombic unscreened limit

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Recently, the adsorption of a polyelectrolyte chain to a charged surface has been studied using mean field arguments.<sup>1</sup> Here, the polyelectrolyte chain can assume any configuration between those with self-avoiding walk statistics and rod-like structure, depending on the ionic strength of the solution.

The polymer chain was represented as a continuous curve of length  $L$  and had an end to end distance vector  $\mathbf{R}$  whose probability distribution was given by the known Edwards path integral.<sup>2</sup> For a polyelectrolyte chain interacting with a charged surface, the interaction energy contains three contributions: the screened electrostatic interaction between the polymer segments, the popular excluded volume pseudopotential, and the electrostatic interaction between a segment and a surface charged element.

Using a variational procedure, Muthukumar<sup>1</sup> determines analytically the configuration of the chain as an effectively Gaussian chain with an effective step length  $l_1$  such

that the mean square end to end distance is given by  $\langle R^2 \rangle = l_1 L$ . When only the electrostatic interaction between segments are present,  $l_1$  is obtained as a solution of following equation:

$$l_1^{3/2}(l^{-1} - l_1^{-1}) = 4/45(6/\pi)^{1/2}\omega_c L^{3/2} \begin{cases} 1, & \kappa \rightarrow 0 \\ 45/\kappa^2 l_1 L, & \kappa(Ll_1)^{1/2} \rightarrow \infty \end{cases} \quad (1)$$

where  $\kappa^{-1}$  is the Debye screening length,  $l$  is the Kuhn step length, and  $\omega_c = \beta q^2/\epsilon$ . [Here  $\beta = (k_B T)^{-1}$  with  $k_B$  denoting the Boltzmann constant,  $T$  is the absolute temperature,  $\epsilon$  is the dielectric constant of the polyelectrolyte solution, and  $q$  is the charge per repeating unit length of chain.]

In the limit of unscreened interactions ( $\kappa \rightarrow 0$ ), Muthukumar stated that  $l_1$  is proportional to  $L$  so that  $\langle R^2 \rangle$  is proportional to  $L^2$ , corresponding to a rod-like configuration of the polymer. On the other hand, Khandekar, Bhag-

wat, and Wiegel<sup>3</sup> showed recently, by exploiting the analogy between the configuration sum of a polyelectrolyte and the propagator of a polaron in a polar crystal, that for large polymers a weak electrostatic interaction does not change the behavior of  $\langle R^2 \rangle$  from that of a free polymer. Their results support the Gaussian statistics hypothesis assumed by Wiegel<sup>4</sup> in his treatment of the adsorption of a macromolecule to a charged surface. In particular, the critical temperature for adsorption and the probability density function for the end point of the macromolecule are found to be independent of the chain length  $L$ .<sup>4</sup> Nevertheless, for the adsorption problem, Muthukumar claims, in the weak screening limit, for an explicit dependence of both quantities with the chain length  $L$ .<sup>1</sup>

In this work, we show that this discrepancy is only apparent provided that the full solution of Eq. (1) in terms of the relevant adimensional parameter of the model is analyzed.

In fact, Eq. (1) is written, when  $\kappa \rightarrow 0$ , as

$$x^3 + rx + s = 0, \quad (2)$$

where

$$x = l_1 + 2l/3, \quad r = -l^2/3, \quad s = -\hat{\omega}_c^2 l^2 L^3 + 2l^3/27$$

with

$$\hat{\omega}_c = 4/45(6/\pi)^{1/2}\omega_c.$$

The roots of Eq. (2) depend on the sign of the discriminant  $\Delta$ :

$$\begin{aligned} \Delta = s^2/4 + r^3/27 &= (\hat{\omega}_c l)^4 L^6/4 - (\hat{\omega}_c l)^2 (Ll/3)^3 \\ &= \langle R^2 \rangle_0 L \lambda^2 N^{-1} (1 - 4\lambda^2 N^{-1}/27)/2, \end{aligned} \quad (3)$$

where  $\langle R^2 \rangle_0 = lL$  is the mean square end to end distance of the free chain,  $\lambda = k_B T \epsilon / q^2 L$  and  $N = L/l$  is the number of segments.

We can determine all the roots of Eq. (2) by tuning the adimensional parameter  $z = (4/27)\lambda^2 N^{-1}$  below and above one. [An alternative expression is  $z = (4/27)(\langle R^2 \rangle_0 / Q^2 N_e^4)$  where  $Q$  is the Bjerrum length ( $= e^2 / k_B T \epsilon$ ) and  $N_e$  is the total number of elementary charges  $e$  on the chain.]

Case A:  $z < 1$ . The real root adopts here a simple analytical expression in the limit  $z \ll 1$  and reads

$$l_1 = (\hat{\omega}_c l)^{2/3} L \quad (4)$$

corresponding to the rod-like configuration of the polymer, as pointed out by Muthukumar.<sup>1</sup>

Case B:  $z \geq 1$ . Here the root is given by

$$l_1 = 2l/3 [\cos(\vartheta/3) + 1] \quad (5a)$$

with

$$\cos \vartheta = 2z^{-1} - 1. \quad (5b)$$

In the limit  $z \gg 1$ , we recover the Gaussian configuration ( $l_1 = l$ ) as reported by Khandekar *et al.*<sup>3</sup> when the charge is weak and the polyelectrolyte is not too long. As  $z = 1$ , the root is simply  $l_1 = 4/3l$  and the chain is moderately expanded.

In terms of the adimensional parameter  $z$ , we find a smooth crossover between a rod-like configuration, as  $z \rightarrow 0$ , and a Gaussian statistics as  $z \rightarrow \infty$ , in the absence of excluded volume effects.

The generalization of Wiegel's theory of the adsorption of a polyelectrolyte to a charged planar surface developed by Muthukumar<sup>1</sup> gives the critical temperature of adsorption as

$$k_B T_c = 48\pi |q\sigma| / j_{0,1}^2 \epsilon \kappa^3 l l_1. \quad (6)$$

Here  $\sigma$  is the uniform charge density of the surface,  $j_{0,1} = 2.4041\dots$  and  $q$  is now the charge per repeating unit. When  $l_1$ , given by Eqs. (4) and (5), is replaced in the above equation we recover the limiting behaviors:  $T_c \sim \kappa^{-3} L^{-1}$  and  $T_c \sim \kappa^{-3}$  for  $z \ll 1$  and  $z \gg 1$ , respectively. The same conclusion holds for the probability density function of the end point of the macromolecule chain. Again, no discrepancy appears between the results of Refs. 1 and 4 due to the fact that they belong to different regimes of the coupling constant  $z$ .

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## Time domain reflectometry study of fast-ionic-conducting glasses

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The dielectric behavior of fast-ionic-conducting (FIC) glasses at frequencies from dc to the far infrared can give valuable information about the cation-network interactions, but attempts to synthesize relevant data suffer from the lack of experimental information between  $10^6$  and  $10^{10}$  Hz.<sup>1</sup> Time

domain reflectometry (TDR) techniques, employing fast rising pulse generating and sampling devices, are known from studies of liquids to provide accurate dielectric information in this range by Laplace transformation of the system's pulse response.<sup>2</sup> In a previous communication we first