Electronic Supplementary Material (ESI) for Soft Matter.
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Journal Name

ARTICLE TYPE

Polyelectrolyte brushes in external fields: Molecular dynamics simulations and mean-field theory (supplementary material)

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In this supplementary section, we compare the results presented in the main text with an older self-consistent field (SCF) theory of weakly charged brushes[1]. The model-polymers used for this approach are Gaussian chains without volumetric interactions. A parabolic SCF potential is then applied to arrive at their eq. (33),

$$\zeta = h + \frac{\sqrt{\pi}}{2} h^2 e^{h^2} \mathrm{erf}(h) \ , \tag{1}$$

which is evaluated numerically to yield the reduced brush height $h = H/H_0$, where

$$H_0 = \sqrt{\frac{8}{3\pi^2}}\, f^{1/2} N \tag{2}$$

denotes the characteristic length scale of the ion-distribution inside the (osmotic) brush, $\zeta = H_0/\lambda$ its ratio with the Gouy-Chapmann length, and f the charge fraction of monomers.

Once the height is determined, the (Gaussian) vertical monomer density distribution is derived as

$$c(\xi) = \frac{p_0}{f\zeta}\left(1 + h^2 e^{h^2-\xi^2}\right) \ , \tag{3}$$

which is truncated at h. Here, $\xi = z/H_0$ is the reduced vertical coordinate, and the factor $p_0 = f\sigma N/H_0$ contains the grafting density σ. Similarly, the distribution of free ends is derived as

$$g(\xi) = \frac{\xi}{H_0\zeta}\left(\frac{1+h^2}{\sqrt{h^2-\xi^2}} + \sqrt{\pi} h^2 e^{h^2-\xi^2} \mathrm{erf}(\sqrt{h^2-\xi^2})\right) \ . \tag{4}$$

This function diverges at the brush height h.

The Fig. 1 compares the scaled results of our MD simulations of charged brushes (in the absence of external fields) with the corresponding SCF predictions. The monomer density profiles (upper panel) show qualitative similarities at higher grafting densities, with increasing deviations at lower densities. The end-monomer distributions (lower panel) display more significant differences, and appear to deviate even on a qualitative scale. Obviously, some of the simplifications that went into the formulation of the SCF model must have led to profiles which only partially reproduce the outcome of our MD simulations.

The authors of the SCF approach have observed similar qualitative differences before, during their comparisons with a rather accurate numerical SCF method[2] and attributed the observed differences to the finite length of the polymers under consideration (the numerical SCF used polymers of $N = 200$), and the corresponding influence of fluctuations. However, a later SCF approach by Biesheuvel et al. has been demonstrated to yield density profiles in rather close agreement with MD-simulations[3,4], even though the latter applied far shorter chains of $N = 32$. Among the main improvements of that SCF approach over its predecessors appears to be the introduction of a non-parabolic SCF-potential, which may have led to its rather realistic profiles. On the other hand, the latter SCF method requires the local charge neutrality condition, which excludes the treatment of weakly charged brushes.

The former SCF formalism has also been applied to charged brushes inside external electric fields, using a suitable re-scaling of the grafting density[5]. Its performance regarding the prediction of the resulting brush heights has been demonstrated in Fig. 5 of the main text of this paper. It may be argued that the application of a free fit parameter α for the elasticity of chains in our box model might lead to an unfair contest, because the SCF has to perform without any empirical fit. The Fig. 2 therefore displays the mean-field result once again, this time prior to any optimization of the chain elasticity, i.e. using $\alpha = 1$ (red curve). The brush heights still deviate by less than 10% from the MD simulations, thus remaining semi-quantitative, compared to a roughly 50% deviation of the SCF model.

The same SCF model does also predict the fraction of counterions inside the brush and yields[1]

$$\kappa = 1 - h/\zeta \ , \tag{5}$$

where h is the solution of eq. (1). It is plotted in Fig. 3, along with the result of our box-model and the MD simulations. Here, the SCF prediction (blue curve) is in fact somewhat closer to the simulated data, particularly at high densities, but the transition to the weak charge regime appears sharper than observed in the simulations. The box model (black curve), though consistently

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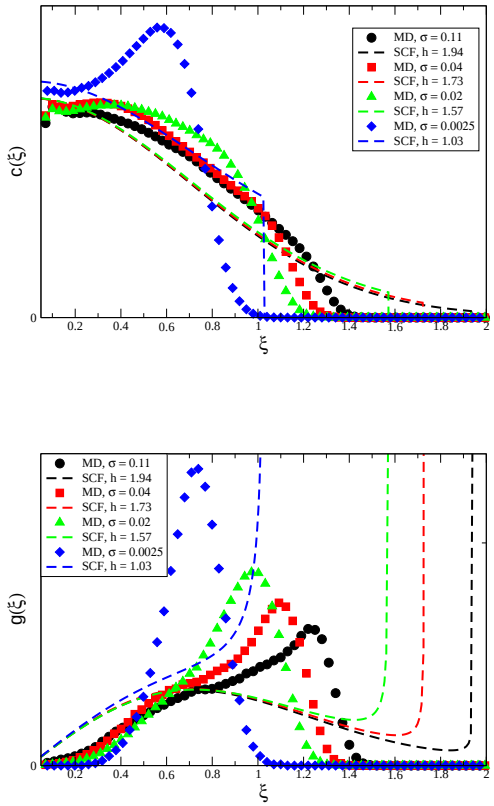

Fig. 1 Upper panel: Normalized monomer density distributions of MD simulations (symbols), with SCF predictions of Eq. (3). Lower panel: Normalized end-monomer distributions; SCF predictions from Eq. (4).

underestimating the number of counterions inside the brush, appears to reproduce that gradual crossover between the osmotic and the weak charge regime better. The somewhat low fraction of counterions inside the brush can be explained as a result of the neglect of explicit electrostatic interactions between the counterions (outside the brush) and the residual brush charge in our model.

Finally, Fig. 4 compares the brush heights at different strengths of the electrostatic interaction, the Bjerrum-length. While the mean-field model remains of quantitative accuracy over a wide range of Bjerrum-lengths, and semi-quantitative without any parameter optimization, the predictions of the SCF approach for the brush heights show both qualitative and quantitative deviations from the simulation data.

We may summarize that a simple theoretical approach that describes the physics of charged brushes in electric fields at full accurracy does not yet exist. While the SCF theory presented in ref. [1,2,5] is rigorous in principle, and representing a valuable tool to analyze general scaling laws of the brushes, it does not yield quantitative predictions for basic properties like brush height or monomer density. Its assumption of a parabolic potential may, in particular in combination with the Poisson Boltzmann approach, be responsible for these shortcomings. The box-like mean-field model presented in our paper offers a complementary, rather simple approach that may be further extended to include properties like volumetric interactions, solvent effects and finite extensibility.

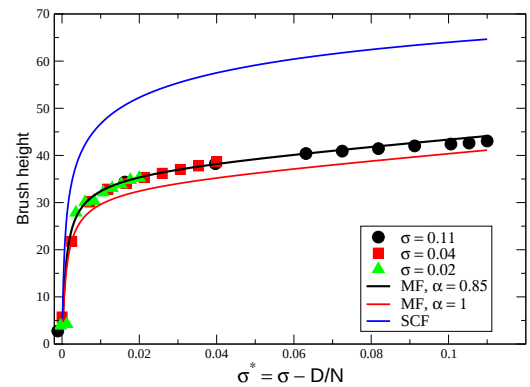

Fig. 2 Brush heights as a function of the re-scaled grafting density (MD simulations, solid symbols). The black curve is the solution of Eqs. (13) - (15) of the main text, with the optimized parameter $\alpha = 0.85$, while the red curve shows the result without optimization. In blue: the SCF result of Eq. (1) of this supplementary part.

References

1 E. Zhulina and O. Borisov, *J. Chem. Phys.*, 1997, **107**, 5952.

2 E. Zhulina, O. Borisov, J. van Male and F. Leermakers, *Langmuir*, 2001, **17**, 1277.

3 P. M. Biesheuvel, W. M. de Vos and V. M. Amoskov, *Macromolecules*, 2008, **41**, 6254–6259.

4 S.-Z. He, H. Merlitz, L. Chen, C.-X. Wu and J.-U. Sommer, *Macromolecules*, 2010, **43**, 7845.

5 E. Zhulina and O. Borisov, *Macromolecules*, 1998, **31**, 7413–7422.

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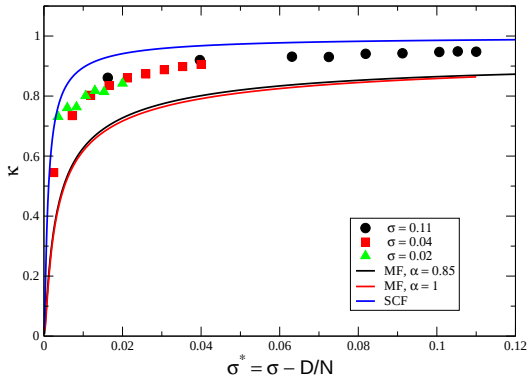

Fig. 3 Fraction of counterions inside the brush, as a function of the re-scaled grafting density (MD simulations, solid symbols). The mean-field results (black and red curves) are the solutions of Eq. (11) of the main text, the SCF (blue curve) is Eq. (5) of this supplementary part.

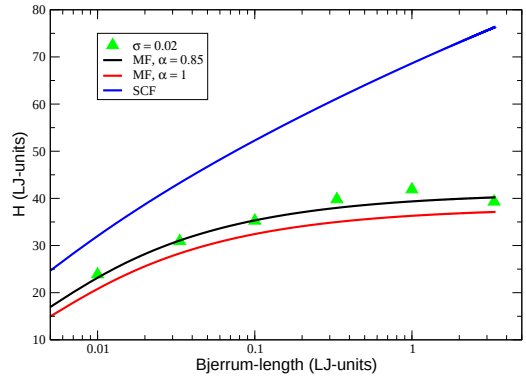

Fig. 4 Brush height as a function of the Bjerrum-length, at grafting density $\sigma = 0.02$. Symbols are simulations, the black curve is the exact solution of Eq. (13)-(15) of the main text, using the fit-parameter $\alpha = 0.85$ for the chain-elasticity. The red curve uses no fit ($\alpha = 1$), and the blue curve is the SCF result, the Eq. (1) of this supplementary.