

Theory: PEBrush-3D

General theoretical buildup

As shown in Fig. 1, we consider brushes composed of polyelectrolyte (PE) chains with one end grafted onto a substrate and immersed in a solution of n_s solvent molecules and n_{\pm} mobile ions. The system is treated as a semicanonical ensemble with a fixed number of PE chains n_p whereas solvent and mobile ions are connected to a bulk salt solution of ion concentration c_{\pm}^b that maintains the chemical potentials of the solvent μ_s and ions μ_{\pm} . PEs are assumed to be Gaussian chains of N total segments with Kuhn length b . We adopt the smear charge model with the backbone charge density α . Mobile ions are considered to have valency z_{\pm} .

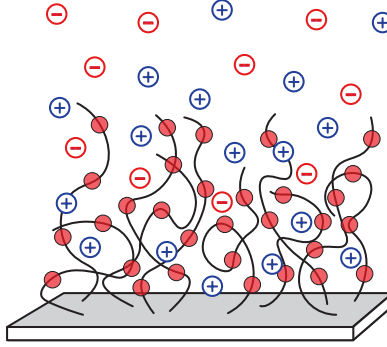


Figure 1: Schematic of a polyelectrolyte brush on a planar substrate immersed in a salt solution.

The semicanonical partition function of the system is

$$\Xi = \frac{1}{n_p! \nu_p^{N n_p}} \prod_{\gamma} \sum_{n_{\gamma}=0}^{\infty} \frac{e^{\mu_{\gamma} n_{\gamma}}}{n_{\gamma}! \nu_{\gamma}^{n_{\gamma}}} \prod_{k=1}^{n_p} \int \mathcal{D}\{\mathbf{R}_k\} \prod_{j=1}^{n_{\gamma}} \int d\mathbf{r}_{\gamma,j} \exp \left\{ -\mathcal{H} \right\} \prod_{\mathbf{r}} \delta[\hat{\phi}_p(\mathbf{r}) + \hat{\phi}_s(\mathbf{r}) - 1] , \quad (1)$$

where small molecules are denoted $\gamma = s, \pm$ for solvent and ions, respectively. ν_p is the volume of PE segments, whereas ν_γ is the volume of small molecules. Here, we assume $\nu_p = \nu_s = \nu$ for simplicity. $\mathcal{D}\{\mathbf{R}_k\}$ denotes the integration over all chain configurations for each chain k . $\hat{\phi}_p(\mathbf{r})$ and $\hat{\phi}_s(\mathbf{r})$ are the local instantaneous volume fractions of the PE and solvent, respectively. The δ function at the end of Eq. 1 accounts for the incompressibility. We only consider the contributions from polymers and solvent in the incompressibility constraint. For the parameter space studied in this work, the volume fractions of ions in the brushes are very low and can thus be neglected.

The Hamiltonian \mathcal{H} is given by

$$\mathcal{H} = \sum_{k=1}^{n_p} \sum_{s=0}^{N-1} \frac{3}{2b^2} [\mathbf{R}_k(s+1) - \mathbf{R}_k(s)]^2 + \frac{1}{\nu} \int d\mathbf{r} \chi \hat{\phi}_p(\mathbf{r}) \hat{\phi}_s(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \hat{\rho}_c(\mathbf{r}) C(\mathbf{r}, \mathbf{r}') \hat{\rho}_c(\mathbf{r}') , \quad (2)$$

which contains the elastic energy governed by Gaussian chain statistics, the short-range hydrophobic interactions between polymer segments and solvent molecules, and the long-range Coulomb interactions between all charged species. The hydrophobic interaction is manifested by the Flory–Huggins χ parameter. $\hat{\rho}_c(\mathbf{r}) = z_+ \hat{c}_+(\mathbf{r}) - z_- \hat{c}_-(\mathbf{r}) + \alpha \hat{\phi}_p(\mathbf{r})/\nu$ is the local charge density with $\hat{c}_\pm(\mathbf{r})$ as the instantaneous number density of ions. $C(\mathbf{r}, \mathbf{r}')$ is the Coulomb operator satisfying $-\nabla \cdot [\epsilon(\mathbf{r}) \nabla C(\mathbf{r}, \mathbf{r}')] = \delta(\mathbf{r} - \mathbf{r}')$. The scaled permittivity is $\epsilon(\mathbf{r}) = kT\epsilon_0\epsilon_r(\mathbf{r})/e^2$, where ϵ_0 is the vacuum permittivity, e is the elementary charge, and $\epsilon_r(\mathbf{r})$ is the local dielectric constant dependent on the local composition of the system.^{1–4}

We follow the standard self-consistent field procedure.⁵ The final partition function is

$$\Xi = \int \mathcal{D}\phi_p \mathcal{D}w_p \mathcal{D}\phi_s \mathcal{D}w_s \mathcal{D}\eta \mathcal{D}\psi \exp(e^{\beta\mu_s} Q_s^{n_s}) \frac{Q_p^{n_p}}{n_p!} \exp \left\{ \frac{1}{\nu} \int d\mathbf{r} \left[\chi \phi_p \phi_s + i w_p \phi_p + i w_s \phi_s + i \eta (\phi_p + \phi_s - 1) \right] \right\} \exp \left\{ \frac{1}{\nu} \int d\mathbf{r} \left[\frac{\epsilon}{2} |i\psi|^2 + \lambda_\pm \exp(\mp z_\pm i\psi) + i\psi \frac{\alpha}{\nu} \phi_p \right] \right\} , \quad (3)$$

where $\lambda_\pm = e^{\mu_\pm}/\nu_\pm$ is the fugacity of the ions.

The single-particle solvent partition function Q_s and the single-chain polymer partition function Q_p are obtained from grouping solvent- and polymer-specific terms:

$$Q_s = \frac{1}{\nu} \int d\mathbf{r}_s \exp(-w_s(\mathbf{r}_s)) \quad (4)$$

$$Q_p = \ln q_c(\mathbf{r}_\perp; 0) , \quad (5)$$

where the forward propagator $q(\mathbf{r}; s)$ and backward propagator $q_c(\mathbf{r}; s)$ originating from the grafted end in the final line satisfies recursion relations:

$$q(\mathbf{r}; s) = (\nu e^{w_p(\mathbf{r})})^{-1} \int d\mathbf{r}' \Phi(\mathbf{r}, \mathbf{r}') q(\mathbf{r}'; s-1) \quad (6a)$$

$$q_c(\mathbf{r}; s) = (\nu e^{w_p(\mathbf{r})})^{-1} \int d\mathbf{r}' \Phi(\mathbf{r}, \mathbf{r}') q_c(\mathbf{r}'; s+1) , \quad (6b)$$

where $\Phi(\mathbf{r}, \mathbf{r}') = \exp[-3(\mathbf{r} - \mathbf{r}')^2/2b^2]$. The initial condition for the propagator beginning at the free end of the chain is $q_c(\mathbf{r}; N) = \exp(-w_p(\mathbf{r}))$, whereas that for the propagator beginning at the tethered end is $q(\mathbf{r}; 0) = \sigma \nu \delta(z - z^*)/q_c(\mathbf{r}; 0)$. $z^* \rightarrow 0_+$ is the grafting plane.

After applying the saddle-point approximation and replacing $i\Psi \rightarrow \Psi$ for the purely imaginary saddle-point values in the fields $\Psi = \phi_p, w_p, \phi_s, w_s, \eta, \psi$, we arrive at the equilibrium free energy in excess to the reference bulk salt solution:

$$F = -e^{\mu_s} Q_s - \sigma \int d\mathbf{r}_\perp \ln Q_p + \frac{1}{\nu} \int d\mathbf{r} \left(\chi \phi_p \phi_s - w_p \phi_p - w_s \phi_s \right) \quad (7)$$

$$- \int d\mathbf{r} \left(\frac{1}{2} \psi \nabla \cdot (\epsilon \nabla \psi) - \frac{\alpha}{\nu} \phi_p \psi + c_+ + c_- - c_+^b - c_-^b \right) .$$

The second term represents a quenched average along the grafting plane as $n_p \rightarrow \infty$.⁵ $c_\pm = \lambda_\pm \exp(\mp z_\pm \psi)$ is the ion concentration. $\sigma = n_p/A$ is the grafting density of chains on the substrate, where A is the total area of the substrate. After functional minimization of F with respect to all the fields (i.e., $\phi_p, \phi_s, w_p, w_s, \eta, \psi$) in addition to assuming that $\epsilon(\mathbf{r})$ can be expressed as a function of $\phi_p(\mathbf{r})$, we obtain the following coupled, self-consistent field equations:

$$w_p(\mathbf{r}) = \chi \phi_s(\mathbf{r}) + \alpha \psi(\mathbf{r}) - \frac{\partial \epsilon(\mathbf{r})}{\partial \phi_p} \frac{|\nabla \psi(\mathbf{r})|^2}{2} \nu - \eta(\mathbf{r}) \quad (8a)$$

$$w_s(\mathbf{r}) = \chi \phi_p(\mathbf{r}) + \frac{\partial \epsilon(\mathbf{r})}{\partial \phi_p} \frac{|\nabla \psi(\mathbf{r})|^2}{2} \nu - \eta(\mathbf{r}) \quad (8b)$$

$$\phi_p(\mathbf{r}) = e^{w_p(\mathbf{r})} \sum_{s=0}^N q(\mathbf{r}; s) q_c(\mathbf{r}; s) \quad (8c)$$

$$\phi_s(\mathbf{r}) = e^{\mu_s} \exp(-w_s(\mathbf{r})) \quad (8d)$$

$$-\nabla \cdot (\epsilon(\mathbf{r}) \nabla \psi(\mathbf{r})) = z_+ c_+(\mathbf{r}) - z_- c_-(\mathbf{r}) + \frac{\alpha}{\nu} \phi_p(\mathbf{r}) , \quad (8e)$$

Here, we consider the substrate to be impenetrable and charge neutral, which is reflected by setting the boundary conditions $\phi_p = 0$ and $d\psi/dz = 0$ at the surface ($z = 0$).

Numerical methods

The C codes used in this work are publicly available and documented at github.com/tyokokur. The Poisson–Boltzmann equation (Eq. 8e) is solved using an iterative, centered finite difference scheme.⁶ The integral for the polymer density distribution (Eq. 8c) can be computed using an open-quadrature which omits the endpoints, avoiding the potential singularity in $q(\mathbf{r}; s)$ at $s = 0$.⁷

$$\int_0^1 ds f(s) = \Delta s \left[\frac{55}{24} f(s_1) - \frac{1}{6} f(s_2) + \frac{11}{8} f(s_3) + \sum_{s=4}^{N_s-4} f(s) + \frac{11}{8} f(s_{N_s-3}) - \frac{1}{6} f(s_{N_s-2}) + \frac{55}{24} f(s_{N_s-1}) \right]. \quad (9)$$

The system of equations (Eq. 8) is solved iteratively until self-consistency is achieved and the equilibrium PE brush density distribution, electrostatic potential, and ion distribution can be obtained. Anderson acceleration is employed to update the polymer and solvent conjugate fields. For the n th iteration, $\bar{w}_{k,m}^{(n)}$ is calculated from Eq. 8 for $k = (p, s)$ fields using the current value $w_{k,m}^{(n)}$. m is the discretization index in space. $\eta_m^{(n)}$ can be computed from Eqs. 8a and 8b:

$$\eta_m^{(n)} = \frac{1}{2} (\chi + \alpha \psi_m^{(n)} - w_{p,m}^{(n)} - w_{s,m}^{(n)}) . \quad (10)$$

The deviation from the self-consistent solution is $d_{k,m}^{(n)} = \bar{w}_{k,m}^{(n)} - w_{k,m}^{(n)}$, which can be used to define an overall error:

$$\epsilon_A = \left[\frac{\sum_{k,m} (d_{k,m}^{(n)})^2}{\sum_{k,m} (w_{k,m}^{(n)})^2} \right]^{1/2} . \quad (11)$$

Threshold values can be set to determine numerical self-consistency (e.g., 10^{-5}). If the criterion is not met, $w_{k,m}^{(n+1)}$ is computed by mixing histories of the past n_A iterations. First, deviations from previous iterations are used to calculate a vector of coefficients C_q :

$$U_{qr} = \sum_{k,m} (d_{k,m}^{(n)} - d_{k,m}^{(n-q)}) (d_{k,m}^{(n)} - d_{k,m}^{(n-r)}) \quad (12a)$$

$$V_q = \sum_{k,m} (d_{k,m}^{(n)} - d_{k,m}^{(n-q)}) d_{k,m}^{(n)} \quad (12b)$$

$$C_q = \sum_{r=1}^{n_A} (U^{-1})_{qr} V_q , \quad (12c)$$

where $q, r = 1, 2, \dots, n_A$. The coefficients are used to inform the updated value for the fields

$w_{k,m}^{(n+1)}$ using the deviations from previous field values $w_{k,m}^{(n-q)}$:

$$W_{k,m}^{(n)} = w_{k,m}^{(n)} + \sum_{q=1}^{n_A} C_q (w_{k,m}^{(n-q)} - w_{k,m}^{(n)}) \quad (13a)$$

$$D_{k,m}^{(n)} = d_{k,m}^{(n)} + \sum_{q=1}^{n_A} C_q (d_{k,m}^{(n-q)} - d_{k,m}^{(n)}) \quad (13b)$$

$$w_{k,m}^{(n+1)} = (1 - \sigma_1)w_{k,m}^{(n)} + \sigma_1 [W_{k,m}^{(n)} + \lambda D_{k,m}^{(n)} - (\sigma_2(1 - \phi_{p,m}^{(n)} - \phi_{s,m}^{(n)}))] , \quad (13c)$$

where the gradually increasing mixing parameter $\lambda = 1 - 0.9^n$ in Eq. 13c is taken from Matsen.⁸ σ_1 and σ_2 are mixing parameters which provide additional stability to the traditional Anderson acceleration algorithm. For computations of systems with particularly simple morphologies and sufficiently good initial seeds for the fields, $\sigma_1 = 0.3$ and $\sigma_2 = 0.05$. When stability is prioritized in converging Eq. 8, $\sigma_1 = 0.2$ and $\sigma_2 = 0.1$ can be used instead at the cost of convergence speed. Generally, $n_A = 3$ is sufficient to consistently improve ϵ_A . While higher n_A can be used, there is a higher risk for instabilities and the cost of holding n_A histories of previous fields in memory can become prohibitive for very large systems.

The convolutions in Eq. 6 can be computed using discrete Fourier transforms. In this work, we employ the FFTW package to calculate the xy convolutions using discrete cosine transforms (REDFT-00). The integral in the z direction is computed using Riemann sums. The Poisson–Boltzmann equation (Eq. 8e) can also be computed using discrete Fourier transforms; however, the electrostatic potential should be scaled by an arbitrary constant to avoid dividing by the zeroth wave number. In this work, the squared inverse Debye length is used, $\kappa_D^{-2} = [4\pi l_B(z_+c_+^b + z_-c_-^b)]^{-1}$. When using even discrete Fourier transforms, the computation domain becomes xy -periodic after reflection, requiring the boxes to be relaxed by monitoring the intensive (per chain) free energy.⁵ Parallel processing is particularly useful for computing the convolutions. While consecutive instances of Eq. 6 must be computed sequentially, the convolutions in the xy and z directions within each iteration are independent, and thus straightforward to parallelize.

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