

Colloidal particle interacting with a polymer
brush: a self-consistent field theory.
Supporting Information

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The Scheutens-Fleer SCF numerical method for calculating the immersion of colloidal particles in a polymer brush.

The Scheutens-Fleer numerical method was developed to study the adsorption of polymer chains on a flat surface. Later the method was extended, for example for polymer brushes¹ and membranes.² In our work, we are interested in the two-gradient method² and etc..³ The cylindrical symmetry of the system is assumed (see the schematic figure 1): 1) there is a direction x - distance from the cylinder axis; 2) there is the z direction - the position on the cylinder axis (we take the grafting surface of polymer chains as the origin).

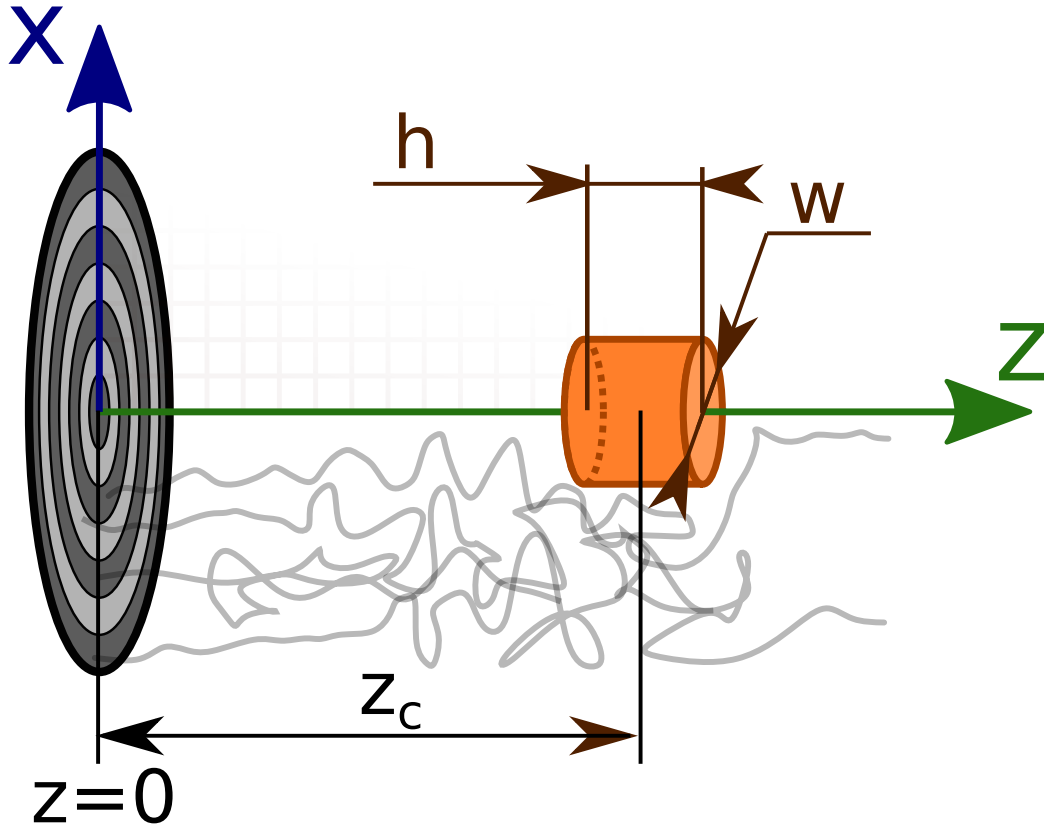


Figure 1: Cylindrical colloidal particle embedded in a polymer brush, schematic representation

The method is based on minimization of the free energy functional, taking

into account the incompressibility condition

$$\begin{aligned}
F[\mathbf{u}, \boldsymbol{\varphi}, \boldsymbol{\alpha}] = & F_{ent}[\mathbf{u}] - \sum_x \sum_z \sum_A u_A(x, z) \varphi_A(x, z) + \\
& + F_{int}[\boldsymbol{\varphi}] + \sum_x \sum_z \alpha(x, z) \left(\sum_A \varphi_A(x, z) - 1 \right)
\end{aligned} \tag{1}$$

where $\varphi_A(x, z)$ is density profile of segment type A (polymer, colloid or solvent), $u_A(x, z)$ is a potential field of segment type A , $\alpha(x, z)$ are the Lagrange multipliers (in this method, their combination is usually called the Lagrange field or self-consistent field). These factors show how much a given cell is filled with segments other than the solvent.

The conditions for the minimum of the functional will be a system of three variations:

$$\begin{cases} \frac{\partial F}{\partial \boldsymbol{\alpha}} = 0 \\ \frac{\partial F}{\partial \boldsymbol{\varphi}} = 0 \\ \frac{\partial F}{\partial \mathbf{u}} = 0 \end{cases} \tag{2}$$

The first condition in eq.2 guarantees the incompressibility of the system. The second condition in eq.2 shows how the potential field is calculated:

$$u_A(x, z) = \sum_B \chi_{A,B} (\varphi_B(x, z) - \varphi_B^b) + \alpha(x, z) \tag{3}$$

where $\chi_{A,B}$ is parameter Flory between segments A and B , and φ_B^b is volume fraction of B in free bulk (equal to 1 for the solvent and zero otherwise). The relationship between the density profiles $\varphi_A(x, z)$ and potential field $u_A(x, z)$ are very useful for building a numerical scheme.

The third condition in eq.2 goes into the usual diffusion equation, which shows the rule for calculating back and forward propagators ($G_b(s, x, z)$ and $G_f(s, x, z)$, s is the sequence number of the segment in the chain) for polymer chain.³ In the initial conditions and the equations of the propagator steps, the Boltzmann statistic weights $G(s, x, z)$ are used, which are easy to find by the formula

$$G(s, x, z) = \exp(-u_A(x, z)), \tag{4}$$

where A is type of segment with number s . The static sum of the chain is obtained from the calculated propagators

$$q = \sum_x \sum_z L(x, z) \sum_s \frac{G_f(s, x, z) G_b(s, x, z)}{G(s, x, z)} \tag{5}$$

where $L(x, z)$ is reduced cell volume. Then the density distribution is obtained

$$\varphi(s, x, z) = \frac{\sigma N G_f(s, x, z) G_b(s, x, z)}{q G(s, x, z)} \quad (6)$$

(σ is polymer density and N is length of polymer chain). The most of the numerical algorithms for solving the Scheutens-Fleer system of nonlinear SCF equations are based on the choice of the potential field¹ as an unknown variable.

We used the package SFbox, provided by F.A.M. Leermakers and J. van Male (from Wageningen University, the Netherlands⁴, for our calculations. One of the most powerful methods of unconstrained optimization was chosen - Newton's method⁵ which uses finite-difference formulas to calculate the Hessian H of the minimized functional. The algorithm starts from an initial guess for the potential field (we chose it to be a zero vector). Then, the propagators, density profiles φ , gradient \mathbf{g} , Hessian H are calculated and a new approximation for the potential field is found using Newton's formula $\mathbf{u} = \mathbf{u} - H^{-1}\mathbf{g}$. The method ends its work when the accuracy 1e-8 is achieved.

Analytical density and osmotic pressure profiles calculation details

An in-house python package has been developed to solve aforesaid expressions numerically, as there is no analytical solution in common case. The goal was to obtain functions $\phi(z)$ and $\Pi(z)$ for a given σ , N , χ_{PS} such that it can be used in further calculations. The source code can be found here https://github.com/miklakt/ascf_pb.

Note that the result from this step referred further as 'analytical' even though the actual values has been calculated numerically.

Almost every step is accompanied by root finding. In every case a root is found using Brent's method.

For the root finding routines let us reformulate eq. 3 (main text) to the next equation

$$Z(\phi, d, z) = \Lambda(d)^2 + \frac{3\kappa^2}{2a^2}(\ln(1 - \phi) - 2\chi_{PS}\phi) - z^2 \quad (7)$$

Where d is an arbitrary value as we do not now brush thickness yet. $\Lambda(d)^2$ is found from eq. 7 (main text) taking $D = d$.

Let us define a function $\phi^*(z, d)$, where the value is the root of eq. 7 for a given z, d .

For the root finding we need the sign changing interval. It is not enough to set $\phi \in [0, 1)$ in this case, but more strict $\phi \in [\phi_D^*, \phi_0^*]$ has to be used, where $\phi_0^* \equiv \phi^*(0, d)$ is polymer density near the grafting surface, while $\phi_D^* \equiv \phi^*(d, d)$ is polymer density at the end. The interval has to be strict for two reasons: it ensures convergence and the sanity of the root.

To calculate ϕ_D^* eq. 6 (main text) is used, the interval be $\phi \in [0, 1)$. ϕ_0^* is the root of eq. 8 (main text) for a given d and $z = 0$, the next interval should be used $\phi \in [\phi_D^*, 1)$.

$$R(d) = \int_0^d \phi^*(z, d) dz - \frac{Na^3}{s} \quad (8)$$

the root of this function is brush thickness D ; as $D \ll N$, sign changing interval is $d \in (0, N]$.

The final polymer density profile $\phi(z) = \phi^*(z, d = D)$

References

- (1) Cosgrove, T.; Heath, T.; van Lent, B.; Leermakers, F.; Scheutjens, J. Phys. A 1980, 13, 1811. (19). *P. G. Scaling Concepts in Polymer Physics: Cornell-Thftlca NY* **1987**, 20, 2957.
- (2) Leermakers, F. A.; Scheutjens, J. M.; Lyklema, J. Statistical thermodynamics of association colloids. IV. Inhomogeneous membrane systems. *Biochimica et Biophysica Acta (BBA) - Biomembranes* **1990**, 1024, 139–151.
- (3) Fleer, G.; Stuart, M.; Scheutjens, J.; Cosgrove, T.; Vincent, B., *Polymers at Interfaces*; Springer Netherlands: 1993.
- (4) Male, J. v. Self-consistent-field theory for chain molecules: extensions, computational aspects, and applications, Ph.D. Thesis, 2003.
- (5) Dennis Jr, J. E.; Schnabel, R. B., *Numerical methods for unconstrained optimization and nonlinear equations*; SIAM: 1996, p 395.