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Supplementary Information:

Structure and Thermodynamics of Grafted Silica/Polystyrene Nanoparticles Investigated Through Self-Consistent Field Theory

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S1.1. Grand canonical partition function and Hamiltonian

We consider a polymer melt within an arbitrarily shaped three-dimensional region $\mathcal{R}$ of volume V at temperature T. The region $\mathcal{R}$ is not necessarily convex. It is partly bounded by one or multiple solid surfaces, which exert an external potential $u_{\mathrm{s}}(\mathbf{r})$ per polymer segment at each position $\mathbf{r} \in \mathcal{R}$. The boundary of the domain $\mathcal{R}$ will be referred to as $\partial\mathcal{R}$. Part of $\partial\mathcal{R}$ may be defined by solid surfaces, while the rest of $\partial\mathcal{R}$ will be characterized by zero-flux Neumann boundary conditions.

The polymer consists of matrix chains of length N_{m} monomers/segments each. In addition, there are chains terminally grafted on the solid surfaces, the length of each grafted chain being N_{g} segments. Both matrix and grafted chains are assumed to be monodisperse, but matrix chains can have different chain length from grafted chains. In the context of the present work, matrix and grafted chains are of the same chemical composition, hence the potential energy field per segment, $u_{\mathrm{s}}(\mathbf{r})$, is applicable to both.

We use the symbols n_{m} and n_{g} to denote the numbers of matrix and grafted chains, respectively. The number n_{g} will be fixed. The number n_{m} is free to fluctuate, subject to the condition that the matrix chains in the interfacial region are in equilibrium with a bulk polymer phase at temperature T, whose density, in segments per unit volume, is $\rho_{\mathrm{seg,bulk}}$. Of course, $\rho_{\mathrm{seg,bulk}}$ can be determined from the temperature T and the pressure P of the bulk polymer phase through an appropriate equation of state. From the same equation of state one can determine the chemical potential μ_{m} per chain segment in the bulk polymer.

In general, the mean segment density of polymer in the considered interfacial region, $\bar{\rho}_{\mathrm{seg}} = \dfrac{n_{\mathrm{m}} N_{\mathrm{m}} + n_{\mathrm{g}} N_{\mathrm{g}}}{V}$, will be different from $\rho_{\mathrm{seg,bulk}}$. The interfacial region and the bulk one will be at equilibrium; the chemical potential μ_{m} of matrix chain segments in $\mathcal{R}$ is the same as in a bulk phase of matrix chains.

The unperturbed mean square radii of gyration of matrix and grafted chains will be denoted as $\left\langle R_{\mathrm{G,g}}{}^{2} \right\rangle$ and $\left\langle R_{\mathrm{G,m}}{}^{2} \right\rangle$, respectively. The grafting points (starts of the grafted chains) will be denoted by $\mathbf{r}_{\mathrm{g},i_{\mathrm{g}}}$, $i_{\mathrm{g}}=1,\ 2,\ \ldots,\ n_{\mathrm{g}}$. They all lie on solid surfaces which belong to $\partial\mathcal{R}$. In practice, the grafting point is located at a finite distance from the solid surface. Technically speaking, it is not possible to attach the end of the chain exactly on the surface, because this would result in a conflict between the grafted chains initial condition and the Dirichlet boundary conditions imposed on the solid boundaries.

The matrix chains in the interfacial region of volume V at temperature T and chemical potential $\mu_\mathrm{m}N_\mathrm{m}$ follow the probability distribution of the grand canonical ensemble. Treating all chains as Gaussian strings and describing the nonbonded interactions by an equation of state in conjunction with a gradient term, $f\left[\hat{\rho}(\mathbf{r}),\nabla\hat{\rho}(\mathbf{r})\right]$, we can write the grand partition function for the polymer contained in $\mathcal{R}$ as:

$$\begin{gathered}\Xi = \sum_{n_\mathrm{m}=0}^{\infty}\frac{1}{n_\mathrm{m}!}\exp\left[\beta\mu_\mathrm{m}N_\mathrm{m}n_\mathrm{m}\right]\mathcal{A}_\mathrm{m}^{n_\mathrm{m}}\mathcal{A}_\mathrm{g}^{n_\mathrm{g}}\int\prod_{i_\mathrm{m}=1}^{n_\mathrm{m}}\mathcal{D}\mathbf{R}_{i_\mathrm{m}}(\bullet)\mathcal{P}_\mathrm{m}\left[\mathbf{R}_{i_\mathrm{m}}(\bullet)\right] \\ \prod_{i_\mathrm{g}=1}^{n_\mathrm{g}}\mathcal{D}\mathbf{R}_{i_\mathrm{g}}(\bullet)\mathcal{P}'_\mathrm{g}\left[\mathbf{R}_{i_\mathrm{g}}(\bullet)\right]\exp\left\{-\beta\int\left(f[\hat{\rho}(\mathbf{r}),\nabla\hat{\rho}(\mathbf{r})]+u_\mathrm{s}(\mathbf{r})\hat{\rho}(\mathbf{r})\right)d\mathbf{r}\right\}\end{gathered} \qquad \text{S1}$$

where $\beta = 1/(k_\mathrm{B}T)$, $\int\mathcal{D}\mathbf{R}_{i_\mathrm{m}}(\bullet)$ symbolizes a functional integral over all paths $\mathbf{R}_{i_\mathrm{m}}(N)$, $0 \le N \le N_\mathrm{m}$, of a matrix chain i_m ($1 \le i_\mathrm{m} \le n_\mathrm{m}$) and $\int\mathcal{D}\mathbf{R}_\mathrm{g}(\bullet)$ symbolizes a functional integral over all paths $\mathbf{R}_{i_\mathrm{g}}(N)$, $0 \le N \le N_\mathrm{g}$, of a grafted chain i_g ($1 \le i_\mathrm{g} \le n_\mathrm{g}$). $\mathcal{A}_\mathrm{m}, \mathcal{A}_\mathrm{g}$ are normalizing factors per matrix and per grafted chain, respectively, appearing in the path integral formulation. They must be the same between the interfacial system and the bulk polymer and render the grand partition function, Ξ, dimensionless.

The functional $f\left[\hat{\rho}(\mathbf{r}),\nabla\hat{\rho}(\mathbf{r})\right]$ is the Helmholtz energy density (Helmholtz energy per unit volume) describing the nonbonded interactions between polymer segments, obtainable from an appropriate equation of state. Herein we identify f with an excess Helmholtz energy, i.e., the Helmholtz energy of a real polymer fluid consisting of a certain number of chains in a given volume minus the Helmholtz energy of an equal number of noninteracting (ideal gas) chains occupying the same volume. $U_\mathrm{s}(\mathbf{r})$ is the total potential energy exerted by the solid on a polymer segment as a function of the position $\mathbf{r}$ of that segment.

In the absence of a field, the probability density distribution (statistical weight) of a matrix chain conformation/path, $\mathbf{R}_{i_\mathrm{m}}(N)$, and the corresponding one of a grafted chain, $\mathbf{R}_{i_\mathrm{g}}(N)$, are given by eqs S2 and S3, respectively, in the context of the Gaussian chain model.

$$\mathcal{P}_{\mathrm{m}}\left[\mathbf{R}_{i_{\mathrm{m}}}(\bullet)\right]=\exp\left[-\frac{1}{4{R_{\mathrm{G,m}}}^{2}}\int_{0}^{N_{\mathrm{m}}}\left(\frac{\mathrm{d}\mathbf{R}_{i_{\mathrm{m}}}}{\mathrm{d}N}\right)^{2}\mathrm{d}N\right] \qquad \text{S2}$$

$$\mathcal{P}_{\mathrm{g}}'\left[\mathbf{R}_{i_{\mathrm{g}}}(\bullet)\right]=\exp\left[-\frac{1}{4{R_{\mathrm{G,g}}}^{2}}\int_{0}^{N_{\mathrm{g}}}\left(\frac{\mathrm{d}\mathbf{R}_{i_{\mathrm{g}}}}{\mathrm{d}N}\right)^{2}\mathrm{d}N\right]\delta\left[\mathbf{R}_{i_{\mathrm{g}}}(0)-\mathbf{r}_{\mathrm{g},i_{\mathrm{g}}}\right]=\mathcal{P}_{\mathrm{g}}\left[\mathbf{R}_{i_{\mathrm{g}}}(\bullet)\right]\delta\left[\mathbf{R}_{i_{\mathrm{g}}}(0)-\mathbf{r}_{\mathrm{g},i_{\mathrm{g}}}\right] \qquad \text{S3}$$

The reduced segment density operators $\hat{\varphi}_{\mathrm{m}}(\mathbf{r})$, $\hat{\varphi}_{\mathrm{g}}(\mathbf{r})$ are defined as shown in eqs S4 and S5 respectively.

$$\hat{\varphi}_{\mathrm{m}}(\mathbf{r})\equiv\frac{\hat{\rho}_{\mathrm{m}}(\mathbf{r})}{\rho_{\mathrm{seg,bulk}}}=\frac{\sum_{i_{\mathrm{m}}=1}^{n_{\mathrm{m}}}\int_{0}^{N_{\mathrm{m}}}\delta\left(\mathbf{r}-\mathbf{R}_{i_{\mathrm{m}}}(N)\right)\mathrm{d}N}{\rho_{\mathrm{seg,bulk}}} \qquad \text{S4}$$

$$\hat{\varphi}_{\mathrm{g}}(\mathbf{r})\equiv\frac{\hat{\rho}_{\mathrm{g}}(\mathbf{r})}{\rho_{\mathrm{seg,bulk}}}=\frac{\sum_{i_{\mathrm{g}}=1}^{n_{\mathrm{g}}}\int_{0}^{N_{\mathrm{g}}}\delta\left(\mathbf{r}-\mathbf{R}_{i_{\mathrm{g}}}(N)\right)\mathrm{d}N}{\rho_{\mathrm{seg,bulk}}} \qquad \text{S5}$$

and we set the total reduced segment density operator as $\hat{\varphi}(\mathbf{r})=\hat{\varphi}_{\mathrm{m}}(\mathbf{r})+\hat{\varphi}_{\mathrm{g}}(\mathbf{r})$. Next, we wish to re-express the Boltzmann factor on the right-hand side of eq S1 in terms of a density field, $\rho(\mathbf{r})$, and a chemical potential field, $w(\mathbf{r})$. To begin with, this term can be written as presented in the following eq S6.[1]

$$\exp\left\{-\beta\int\left(f[\hat{\rho}(\mathbf{r}),\nabla\hat{\rho}(\mathbf{r})]+u_{\mathrm{s}}(\mathbf{r})\hat{\rho}(\mathbf{r})\right)\mathrm{d}\mathbf{r}\right\}=\int\mathcal{D}\rho(\mathbf{r})\ \delta[\rho(\mathbf{r})-\hat{\rho}(\mathbf{r})]\ \exp\left\{-\beta\int\left(f[\rho(\mathbf{r}),\nabla\rho(\mathbf{r})]+u_{\mathrm{s}}(\mathbf{r})\rho(\mathbf{r})\right)\mathrm{d}\mathbf{r}\right\} \qquad \text{S6}$$

Next, we write the Dirac delta functional as the inverse Fourier transform of eq S7, which involves the two aforementioned fields.

$$\delta[\rho(\mathbf{r})-\hat{\rho}(\mathbf{r})]=C\int\mathcal{D}\left[\beta w(\mathbf{r})\right]\exp\left\{i\int\mathrm{d}\mathbf{r}\beta w(\mathbf{r})[\rho(\mathbf{r})-\hat{\rho}(\mathbf{r})]\right\} \qquad \text{S7}$$

with C being a normalization constant.[2]

Combining eqs S6 and S7, the following expression is obtained for the Boltzmann factor of the grand partition function of the system.

$$
\begin{aligned}
&\exp\left\{-\beta\int\left(f[\hat{\rho}(\mathbf{r}),\nabla\hat{\rho}(\mathbf{r})]+u_{\mathrm{s}}(\mathbf{r})\hat{\rho}(\mathbf{r})\right)\mathrm{d}\mathbf{r}\right\}= \\
&=C\int\mathcal{D}\rho(\mathbf{r})\int\mathcal{D}\left[\beta w(\mathbf{r})\right]\exp\left\{i\int\mathrm{d}\mathbf{r}\beta w(\mathbf{r})[\rho(\mathbf{r})-\hat{\rho}(\mathbf{r})]\right\}\exp\left\{-\beta\int\left(f[\rho(\mathbf{r}),\nabla\rho(\mathbf{r})]+u_{\mathrm{s}}(\mathbf{r})\rho(\mathbf{r})\right)\mathrm{d}\mathbf{r}\right\}
\end{aligned}
\qquad \text{S8}
$$

Within the functional integral of the right-hand side of eq S8, there is a term incorporating the density operator, $\hat{\rho}(\mathbf{r})$, which is the sum of $\hat{\rho}_{\mathrm{m}}(\mathbf{r})$ and $\hat{\rho}_{\mathrm{g}}(\mathbf{r})$. Introducing the definitions for these operators, eqs S4 and S5 respectively, that term can be written as in the following eq S9.

$$
\begin{aligned}
&\exp\left(-i\int\mathrm{d}\mathbf{r}\beta w(\mathbf{r})\hat{\rho}(\mathbf{r})\right)=\exp\left[-i\int\mathrm{d}\mathbf{r}\beta w(\mathbf{r})\left(\sum_{i_{\mathrm{m}}=1}^{n_{\mathrm{m}}}\int_0^{N_{\mathrm{m}}}\delta\left(\mathbf{r}-\mathbf{R}_{i_{\mathrm{m}}}(N)\right)\mathrm{d}N+\sum_{i_{\mathrm{g}}=1}^{n_{\mathrm{g}}}\int_0^{N_{\mathrm{g}}}\delta\left(\mathbf{r}-\mathbf{R}_{i_{\mathrm{g}}}(N)\right)\mathrm{d}N\right)\right] \\
&=\exp\left[-\sum_{i_{\mathrm{m}}=1}^{n_{\mathrm{m}}}\int\mathrm{d}\mathbf{r}\int_0^{N_{\mathrm{m}}}\mathrm{d}N\delta(\mathbf{r}-\mathbf{R}_{i_{\mathrm{m}}}(N))i\beta w(\mathbf{r})\right]\cdot\exp\left[-\sum_{i_{\mathrm{g}}=1}^{n_{\mathrm{g}}}\int\mathrm{d}\mathbf{r}\int_0^{N_{\mathrm{g}}}\mathrm{d}N\delta(\mathbf{r}-\mathbf{R}_{i_{\mathrm{g}}}(N))i\beta w(\mathbf{r})\right] \\
&=\prod_{i_{\mathrm{m}}=1}^{n_{\mathrm{m}}}\exp\left(-\int\mathrm{d}\mathbf{r}\int_0^{N_{\mathrm{m}}}\mathrm{d}N\delta(\mathbf{r}-\mathbf{R}_{i_{\mathrm{m}}}(N))i\beta w(\mathbf{r})\right)\cdot\prod_{i_{\mathrm{g}}=1}^{n_{\mathrm{g}}}\exp\left(-\int\mathrm{d}\mathbf{r}\int_0^{N_{\mathrm{g}}}\mathrm{d}N\delta(\mathbf{r}-\mathbf{R}_{i_{\mathrm{g}}}(N))i\beta w(\mathbf{r})\right) \\
&=\prod_{i_{\mathrm{m}}=1}^{n_{\mathrm{m}}}\exp\left(-i\beta\int_0^{N_{\mathrm{m}}}\mathrm{d}Nw(\mathbf{R}_{i_{\mathrm{m}}}(N))\right)\cdot\prod_{i_{\mathrm{g}}=1}^{n_{\mathrm{g}}}\exp\left(-i\beta\int_0^{N_{\mathrm{g}}}\mathrm{d}Nw(\mathbf{R}_{i_{\mathrm{g}}}(N))\right)
\end{aligned}
\qquad \text{S9}
$$

Combining eqs S1, S8 and S9 the following equation is obtained for the grand partition function.

$$
\begin{aligned}
\Xi &= C\sum_{n_{\mathrm{m}}=0}^{\infty}\frac{1}{n_{\mathrm{m}}!}\exp\left[\beta\mu_{\mathrm{m}}N_{\mathrm{m}}n_{\mathrm{m}}\right]\mathcal{A}_{\mathrm{m}}^{n_{\mathrm{m}}}\mathcal{A}_{\mathrm{g}}^{n_{\mathrm{g}}}\int\prod_{i_{\mathrm{m}}=1}^{n_{\mathrm{m}}}\mathcal{D}\mathbf{R}_{i_{\mathrm{m}}}(\bullet)\mathcal{P}_{\mathrm{m}}\left[\mathbf{R}_{i_{\mathrm{m}}}(\bullet)\right]\\
&\times\prod_{i_{\mathrm{g}}=1}^{n_{\mathrm{g}}}\mathcal{D}\mathbf{R}_{i_{\mathrm{g}}}(\bullet)\mathcal{P}'_{\mathrm{g}}\left[\mathbf{R}_{i_{\mathrm{g}}}(\bullet)\right]\Big]\int\mathcal{D}\rho(\mathbf{r})\int\mathcal{D}\left[\beta w(\mathbf{r})\right]\exp\left\{i\int\mathrm{d}\mathbf{r}\beta w(\mathbf{r})[\rho(\mathbf{r})-\hat{\rho}(\mathbf{r})]\right\}\\
&\times\exp\left\{-\beta\int\left(f[\rho(\mathbf{r}),\nabla\rho(\mathbf{r})]+u_{\mathrm{s}}(\mathbf{r})\rho(\mathbf{r})\right)\mathrm{d}\mathbf{r}\right\}\\
&= C\sum_{n_{\mathrm{m}}=0}^{\infty}\frac{1}{n_{\mathrm{m}}!}\exp\left[\beta\mu_{\mathrm{m}}N_{\mathrm{m}}n_{\mathrm{m}}\right]\mathcal{A}_{\mathrm{m}}^{n_{\mathrm{m}}}\mathcal{A}_{\mathrm{g}}^{n_{\mathrm{g}}}\\
&\times\int\mathcal{D}\rho(\mathbf{r})\int\mathcal{D}\left[\beta w(\mathbf{r})\right]\exp\left\{i\int\mathrm{d}\mathbf{r}\beta w(\mathbf{r})\rho(\mathbf{r})\right\}\exp\left\{-\beta\int\left(f[\rho(\mathbf{r}),\nabla\rho(\mathbf{r})]+u_{\mathrm{s}}(\mathbf{r})\rho(\mathbf{r})\right)\mathrm{d}\mathbf{r}\right\}\\
&\times\int\prod_{i_{\mathrm{m}}=1}^{n_{\mathrm{m}}}\mathcal{D}\mathbf{R}_{i_{\mathrm{m}}}(\bullet)\mathcal{P}_{\mathrm{m}}\left[\mathbf{R}_{i_{\mathrm{m}}}(\bullet)\right]\prod_{i_{\mathrm{m}}=1}^{n_{\mathrm{m}}}\exp\left(-i\beta\int_{0}^{N_{\mathrm{m}}}\mathrm{d}Nw(\mathbf{R}_{i_{\mathrm{m}}}(N))\right)\\
&\times\prod_{i_{\mathrm{g}}=1}^{n_{\mathrm{g}}}\mathcal{D}\mathbf{R}_{i_{\mathrm{g}}}(\bullet)\mathcal{P}'_{\mathrm{g}}\left[\mathbf{R}_{i_{\mathrm{g}}}(\bullet)\right]\Big]\prod_{i_{\mathrm{g}}=1}^{n_{\mathrm{g}}}\exp\left(-i\beta\int_{0}^{N_{\mathrm{g}}}\mathrm{d}Nw(\mathbf{R}_{i_{\mathrm{g}}}(N))\right)\\
&= C\sum_{n_{\mathrm{m}}=0}^{\infty}\frac{1}{n_{\mathrm{m}}!}\exp\left[\beta\mu_{\mathrm{m}}N_{\mathrm{m}}n_{\mathrm{m}}\right]\mathcal{A}_{\mathrm{m}}^{n_{\mathrm{m}}}\mathcal{A}_{\mathrm{g}}^{n_{\mathrm{g}}}\\
&\times\int\mathcal{D}\rho(\mathbf{r})\int\mathcal{D}\left[\beta w(\mathbf{r})\right]\exp\left\{i\int\mathrm{d}\mathbf{r}\beta w(\mathbf{r})\rho(\mathbf{r})\right\}\exp\left\{-\beta\int\left(f[\rho(\mathbf{r}),\nabla\rho(\mathbf{r})]+u_{\mathrm{s}}(\mathbf{r})\rho(\mathbf{r})\right)\mathrm{d}\mathbf{r}\right\}\\
&\times\prod_{i_{\mathrm{m}}=1}^{n_{\mathrm{m}}}\int\mathcal{D}\mathbf{R}_{i_{\mathrm{m}}}(\bullet)\mathcal{P}_{\mathrm{m}}\left[\mathbf{R}_{i_{\mathrm{m}}}(\bullet)\right]\prod_{i_{\mathrm{m}}=1}^{n_{\mathrm{m}}}\exp\left(-i\beta\int_{0}^{N_{\mathrm{m}}}\mathrm{d}Nw(\mathbf{R}_{i_{\mathrm{m}}}(N))\right)\\
&\times\prod_{i_{\mathrm{g}}=1}^{n_{\mathrm{g}}}\int\mathcal{D}\mathbf{R}_{i_{\mathrm{g}}}(\bullet)\mathcal{P}_{\mathrm{g}}\left[\mathbf{R}_{i_{\mathrm{g}}}(\bullet)\right]\delta\left[\mathbf{R}_{i_{\mathrm{g}}}(0)-\mathbf{r}_{\mathrm{g},i_{\mathrm{g}}}\right]\prod_{i_{\mathrm{g}}=1}^{n_{\mathrm{g}}}\exp\left(-i\beta\int_{0}^{N_{\mathrm{g}}}\mathrm{d}Nw(\mathbf{R}_{i_{\mathrm{g}}}(N))\right)
\end{aligned}
\tag{S10}
$$

The next step is to define the single chain partition functions (or functionals to be technically accurate) of a matrix and a grafted chain, $Q_{\mathrm{m}}[iw(\mathbf{r})]$ and $Q_{\mathrm{g}}[\mathbf{r}_{\mathrm{g},i_{\mathrm{g}}};iw(\mathbf{r})]$ respectively, in the field $iw(\mathbf{r})$ by the following eqs S11 and S12.

$$
Q_{\mathrm{m}}[iw(\mathbf{r})]=\frac{\int\mathcal{D}\mathbf{R}_{i_{\mathrm{m}}}(\bullet)\mathcal{P}_{\mathrm{m}}\left[\mathbf{R}_{i_{\mathrm{m}}}(\bullet)\right]\exp\left[-i\beta\int_{0}^{N_{\mathrm{m}}}\mathrm{d}Nw(\mathbf{R}_{i_{\mathrm{m}}}(N))\right]}{\int\mathcal{D}\mathbf{R}_{i_{\mathrm{m}}}(\bullet)\mathcal{P}_{\mathrm{m}}\left[\mathbf{R}_{i_{\mathrm{m}}}(\bullet)\right]}
\tag{S11}
$$

$$
Q_{\mathrm{g}}[\mathbf{r}_{\mathrm{g},i_{\mathrm{g}}};iw(\mathbf{r})]=\frac{\int\mathcal{D}\mathbf{R}_{i_{\mathrm{g}}}(\bullet)\mathcal{P}_{\mathrm{g}}\left[\mathbf{R}_{i_{\mathrm{g}}}(\bullet)\right]\delta\left[\mathbf{R}_{i_{\mathrm{g}}}(0)-\mathbf{r}_{\mathrm{g},i_{\mathrm{g}}}\right]\exp\left[-i\beta\int_{0}^{N_{\mathrm{g}}}\mathrm{d}Nw(\mathbf{R}_{i_{\mathrm{g}}}(N))\right]}{\int\mathcal{D}\mathbf{R}_{i_{\mathrm{g}}}(\bullet)\mathcal{P}_{\mathrm{g}}\left[\mathbf{R}_{i_{\mathrm{g}}}(\bullet)\right]\delta\left[\mathbf{R}_{i_{\mathrm{g}}}(0)-\mathbf{r}_{\mathrm{g},i_{\mathrm{g}}}\right]}
\tag{S12}
$$

where, $\int \mathcal{D}\mathbf{R}_{i_\mathrm{m}}(\bullet)\mathcal{P}_\mathrm{m}\left[\mathbf{R}_{i_\mathrm{m}}(\bullet)\right] = Z_{\mathrm{m,free}}V$ is the configurational integral of a field-free matrix chain and $\int \mathcal{D}\mathbf{R}_{i_\mathrm{g}}(\bullet)\mathcal{P}_\mathrm{g}\left[\mathbf{R}_{i_\mathrm{g}}(\bullet)\right]\delta\left[\mathbf{R}_{i_\mathrm{g}}(0) - \mathbf{r}_{\mathrm{g},i_\mathrm{g}}\right] = Z_{\mathrm{g,free}}$ is the configuration integral of a field-free grafted chain. $Q_\mathrm{m}[iw(\mathbf{r})]$ is the configurational integral or partition function of a single matrix chain of length N_m, whose segments are subject to the field $iw(\mathbf{r})$, relative to the corresponding partition function of a field-free chain (i.e., Gaussian string performing a random-walk) and is dimensionless by definition. In like manner, $Q_\mathrm{g}[\mathbf{r}_{\mathrm{g},i_\mathrm{g}};iw(\mathbf{r})]$ is the partition function of a grafted chain of length N_g, which starts at $\mathbf{r}_{\mathrm{g},i_\mathrm{g}}$ and whose segments are subject to the field $iw(\mathbf{r})$, relative to the partition function of a field-free chain of the same length starting at $\mathbf{r}_{\mathrm{g},i_\mathrm{g}}$. It is dimensionless as well.

Combining eqs S10, S11 and S12 the grand partition function becomes:

$$\begin{aligned}
\Xi &= C\sum_{n_\mathrm{m}=0}^{\infty}\frac{1}{n_\mathrm{m}!}\exp\left[\beta\mu_\mathrm{m}N_\mathrm{m}n_\mathrm{m}\right]\mathcal{A}_\mathrm{m}^{n_\mathrm{m}}\mathcal{A}_\mathrm{g}^{n_\mathrm{g}} \\
&\times\int\mathcal{D}\rho(\mathbf{r})\int\mathcal{D}\left[\beta w(\mathbf{r})\right]\exp\left\{i\int \mathrm{d}\mathbf{r}\beta w(\mathbf{r})\rho(\mathbf{r})\right\}\exp\left\{-\beta\int\left(f[\rho(\mathbf{r}),\nabla\rho(\mathbf{r})]+u_\mathrm{s}(\mathbf{r})\rho(\mathbf{r})\right)\mathrm{d}\mathbf{r}\right\} \\
&\times\left(Z_{\mathrm{m,free}}V\right)^{n_\mathrm{m}}\left(Q_\mathrm{m}[iw(\mathbf{r})]\right)^{n_\mathrm{m}}Z_{\mathrm{g,free}}^{n_\mathrm{g}}\left(\prod_{i_\mathrm{g}=1}^{n_g}Q_\mathrm{g}[\mathbf{r}_{g,i_\mathrm{g}};iw(\mathbf{r})]\right) \\
&= C\int\mathcal{D}\rho(\mathbf{r})\int\mathcal{D}\left[\beta w(\mathbf{r})\right]\exp\left\{i\int \mathrm{d}\mathbf{r}\beta w(\mathbf{r})\rho(\mathbf{r})\right\}\exp\left\{-\beta\int\left(f[\rho(\mathbf{r}),\nabla\rho(\mathbf{r})]+u_\mathrm{s}(\mathbf{r})\rho(\mathbf{r})\right)\mathrm{d}\mathbf{r}\right\} \\
&\times\sum_{n_\mathrm{m}=0}^{\infty}\frac{1}{n_\mathrm{m}!}\exp\left[\beta\mu_\mathrm{m}N_\mathrm{m}n_\mathrm{m}\right]\left(\mathcal{A}_\mathrm{m}Z_{\mathrm{m,free}}V\right)^{n_\mathrm{m}}\left(Q_\mathrm{m}[iw(\mathbf{r})]\right)^{n_\mathrm{m}}\left(\mathcal{A}_\mathrm{g}Z_{\mathrm{g,free}}\right)^{n_\mathrm{g}}\left(Q_\mathrm{g}[iw(\mathbf{r})]\right)^{n_\mathrm{g}} \qquad \text{S13} \\
&= C\int\mathcal{D}\rho(\mathbf{r})\int\mathcal{D}\left[\beta w(\mathbf{r})\right]\exp\left(\int \mathrm{d}\mathbf{r}\beta\left\{iw(\mathbf{r})\rho(\mathbf{r})-f[\rho(\mathbf{r}),\nabla\rho(\mathbf{r})]-u_\mathrm{s}(\mathbf{r})\rho(\mathbf{r})\right\}\right) \\
&\times\exp\left\{\exp\left[\beta\mu_\mathrm{m}N_\mathrm{m}\right]\mathcal{A}_\mathrm{m}Z_{\mathrm{m,free}}VQ_\mathrm{m}[iw(\mathbf{r})]\right\}\prod_{i_\mathrm{g}=1}^{n_g}\left(\mathcal{A}_\mathrm{g}Z_{\mathrm{g,free}}Q_\mathrm{g}[\mathbf{r}_{g,i_\mathrm{g}};iw(\mathbf{r})]\right)
\end{aligned}$$

We set the grand partition function to be equal to:

$$\Xi = C\int\mathcal{D}\left[\rho(\mathbf{r})\right]\int\mathcal{D}\left[\beta w(\mathbf{r})\right]\exp\left(-\beta H\left[\rho(\mathbf{r}),\nabla\rho(\mathbf{r}),w(\mathbf{r})\right]\right) \qquad \text{S14}$$

where the Hamiltonian of the system, H, is a functional of the segment density, $\rho(\mathbf{r})$, of its spatial gradient, and of the chemical potential field, $w(\mathbf{r})$. Finally, using eqs S13 and S14, the general form of the Hamiltonian is given by eq S15.

$$\begin{aligned} H\left[\rho(\mathbf{r}),\nabla\rho(\mathbf{r}),w(\mathbf{r})\right] &= \int \mathrm{d}\mathbf{r}\left\{-iw(\mathbf{r})\rho(\mathbf{r})+f[\rho(\mathbf{r}),\nabla\rho(\mathbf{r})]+u_{\mathrm{s}}(\mathbf{r})\rho(\mathbf{r})\right\} \\ &-\frac{1}{\beta}\exp(\beta\mu_{\mathrm{m}}N_{\mathrm{m}})\mathcal{A}_{\mathrm{m}}Z_{\mathrm{m,free}}VQ_{\mathrm{m}}[iw(\mathbf{r})]-\frac{1}{\beta}\sum_{j=1}^{n_{\mathrm{g}}}\ln\left(\mathcal{A}_{\mathrm{g}}Z_{\mathrm{g,free}}Q_{\mathrm{g}}[\mathbf{r}_{\mathrm{g},i_{\mathrm{g}}};iw(\mathbf{r})]\right) \end{aligned} \qquad \mathrm{S15}$$

S1.2. Grand canonical partition function after implementing the saddle-point approximation

In the context of self-consistent field theory, we need to replace the functional integral of eq S15 with its dominant term, i.e., the density and field configurations which have the highest probability and thus the maximum contribution to the Hamiltonian of the system. In order to determine those configurations, we need to perform a so-called saddle-point approximation, i.e., find the stationary point of the Hamiltonian functional with respect to $\rho(\mathbf{r})$ and $w(\mathbf{r})$. To this end, we first set the functional derivative of the Hamiltonian with respect to $w(\mathbf{r})$ equal to zero, as shown in eq S16.

$$\frac{\delta H}{\delta w}=0\Leftrightarrow -i\rho(\mathbf{r})-\frac{1}{\beta}\exp(\beta\mu_{\mathrm{m}})\mathcal{A}_{\mathrm{m}}Z_{\mathrm{m,free}}V\frac{\delta Q_{\mathrm{m}}[iw(\mathbf{r})]}{\delta w}-\frac{1}{\beta}\sum_{i_{\mathrm{g}}=1}^{n_{\mathrm{g}}}\frac{\delta\ln Q_{\mathrm{g}}[\mathbf{r}_{\mathrm{g},i_{\mathrm{g}}};iw(\mathbf{r})]}{\delta w}=0 \qquad \mathrm{S16}$$

Following eq S11, we write:

$$\begin{aligned} \frac{\delta Q_{\mathrm{m}}[iw(\mathbf{r})]}{\delta w} &= \frac{\int \mathcal{D}\mathbf{R}_{i_{\mathrm{m}}}(\boldsymbol{\cdot})\mathcal{P}_{\mathrm{m}}\left[\mathbf{R}_{i_{\mathrm{m}}}(\boldsymbol{\cdot})\right]\left(-i\beta\int_0^{N_{\mathrm{m}}}\mathrm{d}N\delta(\mathbf{r}-\mathbf{R}_{i_{\mathrm{m}}}(N))\right)\exp\left[-\int\mathrm{d}\mathbf{r}\int_0^{N_{\mathrm{m}}}\mathrm{d}N\delta(\mathbf{r}-\mathbf{R}_{i_{\mathrm{m}}}(N))i\beta w(\mathbf{r})\right]}{\int \mathcal{D}\mathbf{R}_{i_{\mathrm{m}}}(\boldsymbol{\cdot})\mathcal{P}_{\mathrm{m}}\left[\mathbf{R}_{i_{\mathrm{m}}}(\boldsymbol{\cdot})\right]} \\ &= -\beta iQ_{\mathrm{m}}[iw(\mathbf{r})]\frac{\int \mathcal{D}\mathbf{R}_{i_{\mathrm{m}}}(\boldsymbol{\cdot})\mathcal{P}_{\mathrm{m}}\left[\mathbf{R}_{i_{\mathrm{m}}}(\boldsymbol{\cdot})\right]\left(\int_0^{N_{\mathrm{m}}}\mathrm{d}N\delta(\mathbf{r}-\mathbf{R}_{i_{\mathrm{m}}}(N))\right)\exp\left[-\int\mathrm{d}\mathbf{r}\int_0^{N_{\mathrm{m}}}\mathrm{d}N\delta(\mathbf{r}-\mathbf{R}_{i_{\mathrm{m}}}(N))i\beta w(\mathbf{r})\right]}{\int \mathcal{D}\mathbf{R}_{i_{\mathrm{m}}}(\boldsymbol{\cdot})\mathcal{P}_{\mathrm{m}}\left[\mathbf{R}_{i_{\mathrm{m}}}(\boldsymbol{\cdot})\right]\exp\left[-\int\mathrm{d}\mathbf{r}\int_0^{N_{\mathrm{m}}}\mathrm{d}N\delta(\mathbf{r}-\mathbf{R}_{i_{\mathrm{m}}}(N))i\beta w(\mathbf{r})\right]} \\ &= -\beta iQ_{\mathrm{m}}[iw(\mathbf{r})]\left\langle\int_0^{N_{\mathrm{m}}}\mathrm{d}N\delta(\mathbf{r}-\mathbf{R}_{i_{\mathrm{m}}}(N))\right\rangle \\ &= -\frac{\beta i\rho_{\mathrm{seg,bulk}}Q_{\mathrm{m}}[iw(\mathbf{r})]}{\overline{n}_{\mathrm{m}}}\left\langle\frac{\sum_{i_{\mathrm{m}}=1}^{\overline{n}_{\mathrm{m}}}\int_0^{N_{\mathrm{m}}}\mathrm{d}N\delta(\mathbf{r}-\mathbf{R}_{i_{\mathrm{m}}}(N))}{\rho_{\mathrm{seg,bulk}}}\right\rangle = -\frac{\beta i\rho_{\mathrm{seg,bulk}}Q_{\mathrm{m}}[iw(\mathbf{r})]}{\overline{n}_{\mathrm{m}}}\left\langle\hat{\varphi}_{\mathrm{m}}(\mathbf{r})\right\rangle = -\frac{\beta i\rho_{\mathrm{seg,bulk}}Q_{\mathrm{m}}[iw(\mathbf{r})]}{\overline{n}_{\mathrm{m}}}\varphi_{\mathrm{m}}(\mathbf{r}) \end{aligned} \qquad \mathrm{S17}$$

Likewise, following equation S12, we can write:

$$\begin{aligned}
\frac{\delta \ln Q_{\mathrm{g}}[\mathbf{r}_{\mathrm{g},i_{\mathrm{g}}};iw(\mathbf{r})]}{\delta w} &= \frac{1}{Q_{\mathrm{g}}[\mathbf{r}_{\mathrm{g},i_{\mathrm{g}}};iw(\mathbf{r})]}\frac{\delta Q_{\mathrm{g}}[\mathbf{r}_{\mathrm{g},i_{\mathrm{g}}};iw(\mathbf{r})]}{\delta w} \\
&= \frac{1}{Q_{\mathrm{g}}[\mathbf{r}_{\mathrm{g},i_{\mathrm{g}}};iw(\mathbf{r})]}\frac{\int \mathcal{D}\mathbf{R}_{i_{\mathrm{g}}}(\cdot)\mathcal{P}'_{\mathrm{g}}\left[\mathbf{R}_{i_{\mathrm{g}}}(\cdot)\right]\left(-i\beta\int_0^{N_{\mathrm{g}}}\mathrm{d}N\delta(\mathbf{r}-\mathbf{R}_{i_{\mathrm{g}}}(N))\right)\exp\left[-\int\mathrm{d}\mathbf{r}\int_0^{N_{\mathrm{g}}}\mathrm{d}N\delta(\mathbf{r}-\mathbf{R}_{i_{\mathrm{g}}}(N))i\beta w(\mathbf{r})\right]}{\int \mathcal{D}\mathbf{R}_{i_{\mathrm{g}}}(\cdot)\mathcal{P}'_{\mathrm{g}}\left[\mathbf{R}_{i_{\mathrm{g}}}(\cdot)\right]} \\
&= -\beta i\frac{\int \mathcal{D}\mathbf{R}_{i_{\mathrm{g}}}(\cdot)\mathcal{P}'_{\mathrm{g}}\left[\mathbf{R}_{i_{\mathrm{g}}}(\cdot)\right]\left(\int_0^{N_{\mathrm{g}}}\mathrm{d}N\delta(\mathbf{r}-\mathbf{R}_{i_{\mathrm{g}}}(N))\right)\exp\left[-\int\mathrm{d}\mathbf{r}\int_0^{N_{\mathrm{g}}}\mathrm{d}N\delta(\mathbf{r}-\mathbf{R}_{i_{\mathrm{g}}}(N))i\beta w(\mathbf{r})\right]}{\int \mathcal{D}\mathbf{R}_{i_{\mathrm{g}}}(\cdot)\mathcal{P}'_{\mathrm{g}}\left[\mathbf{R}_{i_{\mathrm{g}}}(\cdot)\right]\exp\left[-\int\mathrm{d}\mathbf{r}\int_0^{N_{\mathrm{g}}}dN\delta(\mathbf{r}-\mathbf{R}_{i_{\mathrm{g}}}(N))i\beta w(\mathbf{r})\right]} \\
&= -\beta i\left\langle\int_0^{N_{\mathrm{g}}}\mathrm{d}N\delta(\mathbf{r}-\mathbf{R}_{i_{\mathrm{g}}}(N))\right\rangle
\end{aligned} \tag{S18}$$

and thus

$$\sum_{i_{\mathrm{g}}=1}^{n_{\mathrm{g}}}\frac{\delta \ln Q_{\mathrm{g}}[\mathbf{r}_{\mathrm{g},i_{\mathrm{g}}};iw(\mathbf{r})]}{\delta w} = -\beta i\rho_{\mathrm{seg,bulk}}\left\langle\frac{\sum_{i=1}^{n_{\mathrm{g}}}\int_0^{N_{\mathrm{g}}}\mathrm{d}N\delta(\mathbf{r}-\mathbf{R}_{i_{\mathrm{g}}}(N))}{\rho_{\mathrm{seg,bulk}}}\right\rangle = -\beta i\rho_{\mathrm{seg,bulk}}\left\langle\hat{\varphi}_{\mathrm{g}}(\mathbf{r})\right\rangle = -\beta i\rho_{\mathrm{seg,bulk}}\varphi_{\mathrm{g}}(\mathbf{r}) \tag{S19}$$

Combining eqs S16, S17 and S19, the following eq S20 is obtained for the density field, $\rho(\mathbf{r})$.

$$\rho(\mathbf{r}) = \exp(\beta\mu_{\mathrm{m}})\mathcal{A}_{\mathrm{m}}Z_{\mathrm{m,free}}V\frac{Q_{\mathrm{m}}[iw(\mathbf{r})]}{\bar{n}_{\mathrm{m}}}\rho_{\mathrm{seg,bulk}}\varphi_{\mathrm{m}}(\mathbf{r}) + \rho_{\mathrm{seg,bulk}}\varphi_{\mathrm{g}}(\mathbf{r}) \tag{S20}$$

The saddle point approximation requires that the functional derivative of the Hamiltonian with respect to the density field, $\rho(\mathbf{r})$, be also equal to zero:

$$\begin{aligned}
&\frac{\delta H}{\delta\rho(\mathbf{r})} = 0 \Leftrightarrow -iw(\mathbf{r}) + u_{\mathrm{s}}(\mathbf{r}) + \left[\frac{\partial f}{\partial\rho} - \nabla\cdot\frac{\partial f}{\partial\nabla\rho}\right]\Bigg|_{\rho=\rho(\mathbf{r})} = 0 \\
&\Leftrightarrow w(\mathbf{r}) = -i\left(\left[\frac{\partial f}{\partial\rho} - \nabla\cdot\frac{\partial f}{\partial\nabla\rho}\right]\Bigg|_{\rho=\rho(\mathbf{r})} + u_{\mathrm{s}}(\mathbf{r})\right)
\end{aligned} \tag{S21}$$

After the saddle point approximation, the Hamiltonian of the system, from eq S15, is given by eq S22.

$$\begin{aligned}\bar{H} = \int \mathrm{d}\mathbf{r} \left\{ f\left[\rho(\mathbf{r}), \nabla\rho(\mathbf{r})\right] - \rho(\mathbf{r}) \left.\frac{\partial f}{\partial \rho}\right|_{\rho=\rho(\mathbf{r})} + \rho(\mathbf{r}) \nabla \cdot \left.\frac{\partial f}{\partial \nabla\rho}\right|_{\rho=\rho(\mathbf{r})} \right\} \\ - \frac{1}{\beta} \exp(\beta\mu_{\mathrm{m}}) \mathcal{A}_{\mathrm{m}} Z_{\mathrm{m,free}} V Q_{\mathrm{m}}[iw(\mathbf{r})] - \frac{1}{\beta} \sum_{i_{\mathrm{g}}=1}^{n_{\mathrm{g}}} \ln\left(\mathcal{A}_{\mathrm{g}} Z_{\mathrm{g,free\text{-}}} Q_{\mathrm{g}}[\mathbf{r}_{\mathrm{g},i_{\mathrm{g}}}; iw(\mathbf{r})]\right)\end{aligned} \qquad \text{S22}$$

S1.3. Thermodynamic properties

According to the saddle point approximation considerations which were developed in the previous section, the grand potential of our interfacial polymer system, occupying volume V at temperature T and chain chemical potential $\mu_{\mathrm{m}} N_{\mathrm{m}}$ is given by eq S23.

$$\Omega(\mu_{\mathrm{m}}, n_{\mathrm{g}}, V, T) = -\frac{1}{\beta} \ln \Xi = -\frac{1}{\beta} \ln\left[\exp(-\beta \bar{H})\right] = \bar{H} \qquad \text{S23}$$

Any multiplicative factor arising in Ξ upon introduction of the saddle point approximation contributes an additive constant to Ω, which will cancel upon referring Ω to an equal amount of polymer in the bulk. Ω is an extensive—system size-dependent—thermodynamic property. It is convenient to express the system thermodynamics with reference to a bulk phase of matrix chains occupying volume V at temperature T and chemical potential $\mu_{\mathrm{m}} N_{\mathrm{m}}$, a set of n_{g} isolated end-pinned unperturbed chains of length N_{g} at temperature T, and an isolated bare nanoparticle, as described below.

The grand potential of an amount of bulk polymer occupying volume V at temperature T and chemical potential $N_{\mathrm{m}} \mu_{\mathrm{m}}$ is:

$$\Omega_{\mathrm{bulk}}(\mu_{\mathrm{m}}, V, T) = -\frac{1}{\beta} \ln \Xi_{\mathrm{bulk}} = \bar{H}_{\mathrm{bulk}} \qquad \text{S24}$$

with $\bar{H}_{\mathrm{bulk}}$ being the effective Hamiltonian of eq S21 applied to bulk polymer:

$$\bar{H}_{\mathrm{bulk}} = \int \mathrm{d}\mathbf{r} \left.\left\{ f[\rho, 0] - \rho \frac{\partial f}{\partial \rho} \right\}\right|_{\rho=\rho_{\mathrm{seg,bulk}}} - \frac{1}{\beta} \exp(\beta\mu_{\mathrm{m}}) \mathcal{A}_{\mathrm{m}} Z_{\mathrm{m,free}} V Q_{\mathrm{m}}[iw_{\mathrm{bulk}}] \qquad \text{S25}$$

Note that, for all forms of the local free energy density f considered here, $\frac{\partial f}{\partial \nabla \rho} = \mathbf{0}$ in the bulk polymer phase.

Application of eq S20 for the density to the bulk polymer gives

$$\rho_{\text{seg,bulk}} = \exp(\beta\mu_{\text{m}})\mathcal{A}_{\text{m}} Z_{\text{m,free}} V \frac{Q_{\text{m}}[iw_{\text{bulk}}]}{n_{\text{m,bulk}}}\rho_{\text{seg,bulk}} \Leftrightarrow \exp(\beta\mu_{\text{m}})\mathcal{A}_{\text{m}} Z_{\text{m,free}} V Q_{\text{m}}[iw_{\text{bulk}}] = \frac{\rho_{\text{seg,bulk}} V}{N_{\text{m}}} \tag{S26}$$

Combining eqs S25 and S26,

$$\bar{H}_{\text{bulk}} = \int d\mathbf{r} \left\{ f\left[\rho, 0\right] - \rho \frac{\partial f}{\partial \rho} \right\}\Bigg|_{\rho=\rho_{\text{seg,bulk}}} - \frac{\rho_{\text{seg,bulk}} V}{\beta N_{\text{m}}} \tag{S27}$$

In the bulk melt, the self-consistent field from eq S21 becomes

$$w_{\text{bulk}} = -i \frac{\partial f}{\partial \rho}\bigg|_{\rho=\rho_{\text{seg,bulk}}} \tag{S28}$$

and thus the matrix chain partition function from eq S11 takes the form

$$Q_{\text{m}}\left[iw_{\text{bulk}}\right] = \exp\left(-\beta N_{\text{m}} \frac{\partial f}{\partial \rho}\bigg|_{\rho=\rho_{\text{seg,bulk}}} \right) \tag{S29}$$

On the other hand, for a set of isolated end-pinned unperturbed chains of length N_{g} at temperature T, which are identical in length and chemical composition to our grafted chains, the total Helmholtz energy in the context of our model is given by eq S30.

$$A_{\text{g}}^{\text{isol}}(T, n_{\text{g}}) = -\frac{1}{\beta} \sum_{i_{\text{g}}=1}^{n_{\text{g}}} \ln\left(\mathcal{A}_{\text{g}} Z_{\text{g,free}} Q_{\text{g}}\left[\mathbf{r}_{\text{g},i_{\text{g}}}; iw_{\text{bulk}} \right] \right) \tag{S30}$$

Subtracting eqs S27 and S30 from eq S22:

$$\begin{aligned}
\Delta\Omega &= \Omega(\mu,V,T)-\Omega_{\mathrm{bulk}}(\mu,V,T)-A_{\mathrm{g}}^{\mathrm{isol}}(T,n_{\mathrm{g}})\\
&=\int \mathrm{d}\mathbf{r}\left\{ f\left[\rho(\mathbf{r}),\nabla\rho(\mathbf{r})\right]-\rho(\mathbf{r})\left.\frac{\partial f}{\partial\rho}\right|_{\rho=\rho(\mathbf{r})}+\rho(\mathbf{r})\nabla\cdot\left.\frac{\partial f}{\partial\nabla\rho}\right|_{\rho=\rho(\mathbf{r})}\right\}\\
&-\int \mathrm{d}\mathbf{r}\left.\left\{ f\left[\rho,\mathbf{0}\right]-\rho\frac{\partial f}{\partial\rho}\right\}\right|_{\rho=\rho_{\mathrm{seg,bulk}}}\\
&+\frac{\rho_{\mathrm{seg,bulk}}V}{\beta N_{\mathrm{m}}}\left(1-Q_{\mathrm{m}}\left[w'(\mathbf{r})-w'_{\mathrm{bulk}}\right]\right)\\
&-\frac{1}{\beta}\sum_{i_{\mathrm{g}}=1}^{n_{\mathrm{g}}}\ln Q_{\mathrm{g}}\left[\mathbf{r}_{\mathrm{g},i_{\mathrm{g}}};w'(\mathbf{r})-w'_{\mathrm{bulk}}\right]
\end{aligned} \qquad \text{S31}$$

In eq S31 we have made the substitution

$$iw(\mathbf{r})=w'(\mathbf{r}),\ \text{a real field.} \qquad \text{S32}$$

The second integral in eq S31, referring to a homogeneous bulk phase of matrix chains, can be performed immediately, yielding a factor of V times the integrand.

By expressing eq S21 in terms of the real field from eq S32, $\partial f/\partial\rho = w'(\mathbf{r})+\nabla\cdot\partial f/\partial\nabla\rho-u_{\mathrm{s}}(\mathbf{r})$, and by substituting it to eq S31, the latter can be expressed as follows:

$$\begin{aligned}
\Delta\Omega &= \int \mathrm{d}\mathbf{r}\left\{ f\left[\rho(\mathbf{r}),\nabla\rho(\mathbf{r})\right]-f\left[\rho_{\mathrm{seg,bulk}},\mathbf{0}\right]\right\}\\
&-\int \mathrm{d}\mathbf{r}\left\{\rho(\mathbf{r})w'(\mathbf{r})-\rho_{\mathrm{seg,bulk}}w'_{\mathrm{bulk}}\right\}\\
&+\int \mathrm{d}\mathbf{r}\left\{\rho(\mathbf{r})u_{\mathrm{s}}(\mathbf{r})\right\}\\
&+\frac{\rho_{\mathrm{seg,bulk}}V}{\beta N_{\mathrm{m}}}\left(1-Q_{\mathrm{m}}\left[w'(\mathbf{r})-w'_{\mathrm{bulk}}\right]\right)\\
&-\frac{1}{\beta}\sum_{i_{\mathrm{g}}=1}^{n_{\mathrm{g}}}\ln Q_{\mathrm{g}}\left[\mathbf{r}_{\mathrm{g},i_{\mathrm{g}}};w'(\mathbf{r})-w'_{\mathrm{bulk}}\right]
\end{aligned} \qquad \text{S33}$$

wherein the *first term* is the contribution of the cohesive interactions, the *second term* is the interaction energy between the density field and the chemical potential field, the third term describes the polymer-solid interactions, the *fourth term* describes the translational and conformational entropy (relative to the bulk melt) of the matrix chains, and the *fifth term* is associated with the conformational entropy of the n_{g} grafted chains subject to the field w'.

S1.4. Derivation of the segment balance equations

To deal with the grafted and the matrix chains in the presence of the field w', we introduce the propagator $G(\mathbf{r}_{\text{start}}, \mathbf{r}, s)$ following Edwards[3]:

$$G(\mathbf{r}_{\text{start}},\mathbf{r},N)=\frac{\int\limits_{\mathbf{R}(0)=\mathbf{r}_{\text{start}}}^{\mathbf{R}(N)=\mathbf{r}} \mathcal{D}\left[\mathbf{R}(\bullet)\right]\mathcal{P}\left[\mathbf{R}(\bullet)\right]\exp\left\{-\beta\int\limits_{0}^{N}\mathrm{d}N'w'\left(\mathbf{R}(N')\right)\right\}}{\int \mathrm{d}\mathbf{r}\int\limits_{\mathbf{R}(0)=\mathbf{r}_{\text{start}}}^{\mathbf{R}(N)=\mathbf{r}} \mathcal{D}\left[\mathbf{R}(\bullet)\right]\mathcal{P}\left[\mathbf{R}(\bullet)\right]} \qquad \text{S34}$$

$G(\mathbf{r}_{\text{start}},\mathbf{r},N)$ has dimensions of inverse volume. It is proportional to the conditional probability that a chain, which has started at $\mathbf{r}_{\text{start}}$ and is subject to the field $w'(\mathbf{r})$ on its segments, finds itself at position $\mathbf{r}$ at contour length N, as depicted in Fig. **S1**. The denominator in eq S34 is a partition function for a field-free chain, represented as a Gaussian string, which has started at $\mathbf{r}_{\text{start}}$ and may end anywhere in the system. The denominator is independent of $\mathbf{r}_{\text{start}}$ and $\mathbf{r}$; it depends only on N.

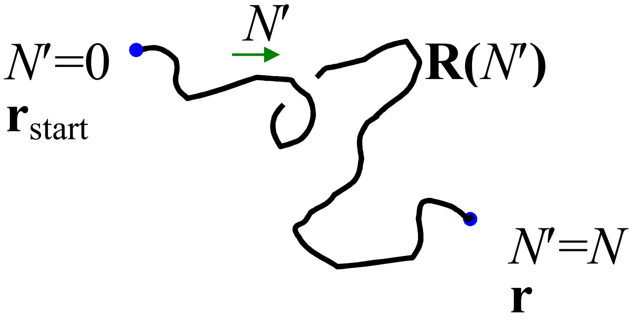

Figure S1. Schematic representation of a Gaussian string starting at $N'=0$ and ending at $N'=N$.

We also define the restricted partition function of a matrix chain in the presence of the field $w'(\mathbf{r})$ by the following eq S35.

$$q_{\text{m}}(\mathbf{r},N)=\int\limits_{V}\mathrm{d}\mathbf{r}_{\text{start}}G(\mathbf{r}_{\text{start}},\mathbf{r},N) \qquad \text{S35}$$

This quantity is dimensionless and proportional to the probability that the segment at contour length N of a matrix chain subject to the field finds itself at position $\mathbf{r}$, regardless of where in the system the particular matrix chain may have started. It is reduced by the corresponding probability of a field-free chain. Thus, it equals unity for a field-free chain. The partition function of a matrix chain, Q_{m}, is related to the corresponding restricted one by the equation: $Q_{\mathrm{m}}\left[w'(\mathbf{r})\right]=\frac{1}{V}\int_V \mathrm{d}\mathbf{r}\; q_{\mathrm{m}}(\mathbf{r},N_{\mathrm{m}})$. It is also dimensionless and normalized such that it would be unity for a field-free chain in volume V.

The partition function, Q_{g}, of a chain which is grafted at $\mathbf{r}_{\mathrm{g}}$, relative to a field-free chain of equal length, is given by eq S36.

$$Q_{\mathrm{g}}\left[\mathbf{r}_{\mathrm{g}};w'(\mathbf{r})\right]=\int_V \mathrm{d}\mathbf{r}\; G(\mathbf{r}_{\mathrm{g}},\mathbf{r},N_{\mathrm{g}}) \qquad \text{S36}$$

But, by definition, $G(\mathbf{r}_{\mathrm{g}},\mathbf{r},N_{\mathrm{g}})=G(\mathbf{r},\mathbf{r}_{\mathrm{g}},N_{\mathrm{g}})$, so:

$$Q_{\mathrm{g}}\left[\mathbf{r}_{\mathrm{g}};w'(\mathbf{r})\right]=\int_V \mathrm{d}\mathbf{r}\; G(\mathbf{r},\mathbf{r}_{\mathrm{g}},N_{\mathrm{g}})=q_{\mathrm{m}}(\mathbf{r}_{\mathrm{g}},N_{\mathrm{g}}) \qquad \text{S37}$$

Following eq S34, the propagator of a grafted chain, whose grafted end lies at coordinates $\mathbf{r}_{\mathrm{g}}$, can be written as:

$$\begin{aligned} G(\mathbf{r}_{\mathrm{g}},\mathbf{r},N) &= \frac{\int \mathcal{D}\left[\mathbf{R}'(\bullet)\right]\mathcal{P}\left[\mathbf{R}'(\bullet)\right]\delta\left(\mathbf{R}'(0)-\mathbf{r}_{\mathrm{g}}\right)\delta\left(\mathbf{R}'(N)-\mathbf{r}\right)\exp\left\{-\beta\int_0^N \mathrm{d}N' w'\left(\mathbf{R}'(N')\right)\right\}}{\int \mathcal{D}\left[\mathbf{R}'(\bullet)\right]\mathcal{P}\left[\mathbf{R}'(\bullet)\right]\delta\left(\mathbf{R}'(0)-\mathbf{r}_{\mathrm{g}}\right)} \\ &= \frac{\int \mathcal{D}\left[\mathbf{R}'(\bullet)\right]\mathcal{P}\left[\mathbf{R}'(\bullet)\right]\delta\left(\mathbf{R}'(0)-\mathbf{r}_{\mathrm{g}}\right)\delta\left(\mathbf{R}'(N)-\mathbf{r}\right)\exp\left\{-\beta\int_0^N \mathrm{d}N' w'\left(\mathbf{R}'(N')\right)\right\}}{\frac{1}{V}\int \mathcal{D}\left[\mathbf{R}'(\bullet)\right]\mathcal{P}\left[\mathbf{R}'(\bullet)\right]} \end{aligned} \qquad \text{S38}$$

So far, we denote by $\mathbf{R}'(\bullet)$ the curve in three-dimensional space, which is followed by a Gaussian thread of length N. At this point, we introduce the symbol $\mathbf{R}''(\bullet)$, which represents the curve in three-dimensional space, which is followed by a Gaussian thread of length N_{g}–N. Using these definitions and combining eqs S34 and S35, the restricted partition function of a matrix chain can be written as follows.

$$q_{\mathrm{m}}(\mathbf{r},N_{\mathrm{g}}-N)=\frac{\int\limits_{V}\mathrm{d}\mathbf{r}_{\mathrm{start}}\int\mathcal{D}\left[\mathbf{R}''(\cdot)\right]\mathcal{P}\left[\mathbf{R}''(\cdot)\right]\delta\left(\mathbf{R}''(0)-\mathbf{r}_{\mathrm{start}}\right)\delta\left(\mathbf{R}''(N_{\mathrm{g}}-N)-\mathbf{r}\right)\exp\left\{-\beta\int\limits_{0}^{N_{\mathrm{g}}-N}\mathrm{d}N'w'\left(\mathbf{R}''(N')\right)\right\}}{\frac{1}{V}\int\mathcal{D}\left[\mathbf{R}''(\cdot)\right]\mathcal{P}\left[\mathbf{R}''(\cdot)\right]} \qquad \text{S39}$$

Next, we consider the product $G(\mathbf{r}_{\mathrm{g}},\mathbf{r},N)\;q_{\mathrm{m}}(\mathbf{r},N_{\mathrm{g}}-N)$. By eqs S38 and S39, the numerator of this product will be equal to the following expression.

$$\begin{aligned}numer=&\int\mathcal{D}\left[\mathbf{R}'(\bullet)\right]\mathcal{P}\left[\mathbf{R}'(\bullet)\right]\delta\left(\mathbf{R}'(0)-\mathbf{r}_{\mathrm{g}}\right)\delta\left(\mathbf{R}'(N)-\mathbf{r}\right)\exp\left\{-\beta\int\limits_{0}^{N}\mathrm{d}N'w'\left(\mathbf{R}'(N')\right)\right\}\\ \times&\int\limits_{V}\mathrm{d}\mathbf{r}_{\mathbf{start}}\int\mathcal{D}\left[\mathbf{R}''(\bullet)\right]\mathcal{P}\left[\mathbf{R}''(\bullet)\right]\delta\left(\mathbf{R}''(0)-\mathbf{r}_{\mathrm{start}}\right)\delta\left(\mathbf{R}''(N_{\mathrm{g}}-N)-\mathbf{r}\right)\exp\left\{-\beta\int\limits_{0}^{N_{\mathrm{g}}-N}\mathrm{d}N'w'\left(\mathbf{R}''(N')\right)\right\}\end{aligned} \qquad \text{S40}$$

Changing the integration variable from N' to $N_{\mathrm{g}}-N'$ in the second line, eq S40 is modified to:

$$\begin{aligned}numer=&\int\mathcal{D}\left[\mathbf{R}'(\bullet)\right]\mathcal{P}\left[\mathbf{R}'(\bullet)\right]\delta\left(\mathbf{R}'(0)-\mathbf{r}_{\mathrm{g}}\right)\delta\left(\mathbf{R}'(N)-\mathbf{r}\right)\exp\left\{-\beta\int\limits_{0}^{N}dN'w'\left[\mathbf{R}'(N')\right]\right\}\\ \times&\int\limits_{V}d^{3}r_{\mathrm{start}}\int\mathcal{D}\left[\mathbf{R}''(\bullet)\right]\mathcal{P}\left[\mathbf{R}''(\bullet)\right]\delta\left(\mathbf{R}''(N_{\mathrm{g}})-\mathbf{r}_{\mathrm{start}}\right)\delta\left(\mathbf{R}''(N)-\mathbf{r}\right)\exp\left\{-\beta\int\limits_{N}^{N_{\mathrm{g}}}dN'w'\left[\mathbf{R}''(N')\right]\right\}\\ =&\frac{1}{V}\int\mathcal{D}\left[\mathbf{R}(\bullet)\right]\mathcal{P}\left[\mathbf{R}(\bullet)\right]\delta\left(\mathbf{R}(0)-\mathbf{r}_{\mathrm{g}}\right)\delta\left(\mathbf{R}(N)-\mathbf{r}\right)\exp\left\{-\beta\int\limits_{0}^{N_{\mathrm{g}}}dN'w'\left[\mathbf{R}(N')\right]\right\}\end{aligned} \qquad \text{S41}$$

where now the functional integration is performed over all paths $\mathbf{R}(\bullet)$ of an N_{g} segment-long (grafted) chain.

On the other hand, the denominator of the product $G(\mathbf{r}_{\mathrm{g}},\mathbf{r},N)\;q_{\mathrm{m}}(\mathbf{r},N_{\mathrm{g}}-N)$ becomes:

$$denom=\frac{1}{V^{2}}\int\mathcal{D}\left[\mathbf{R}'(\cdot)\right]\mathcal{P}\left[\mathbf{R}'(\cdot)\right]\int\mathcal{D}\left[\mathbf{R}''(\cdot)\right]\mathcal{P}\left[\mathbf{R}''(\cdot)\right]=\frac{1}{V^{2}}\int\mathcal{D}\left[\mathbf{R}(\cdot)\right]\mathcal{P}\left[\mathbf{R}(\cdot)\right] \qquad \text{S42}$$

Dividing eq S41 with S42, we obtain:

$$G(\mathbf{r}_{\mathrm{g}},\mathbf{r},N)\;q_{\mathrm{m}}(\mathbf{r},N_{\mathrm{g}}-N)=\frac{\int\mathcal{D}\left[\mathbf{R}(\bullet)\right]\mathcal{P}\left[\mathbf{R}(\bullet)\right]\delta\left(\mathbf{R}(0)-\mathbf{r}_{\mathrm{g}}\right)\delta\left(\mathbf{R}(N)-\mathbf{r}\right)\exp\left\{-\beta\int\limits_{0}^{N_{\mathrm{g}}}dN'w'\left[\mathbf{R}(N')\right]\right\}}{\frac{1}{V}\int\mathcal{D}\left[\mathbf{R}(\bullet)\right]\mathcal{P}\left[\mathbf{R}(\bullet)\right]} \qquad \text{S43}$$

Combining eqs S36 and S38, we can write the following eq S44 for the partition function of a grafted chain.

$$Q_{\mathrm{g}}\left[\mathbf{r}_{\mathrm{g}};w'(\mathbf{r})\right]=\frac{\int\limits_{V}\mathrm{d}^3r_{\mathrm{end}}\int\mathcal{D}\left[\mathbf{R}(\cdot)\right]\mathcal{P}\left[\mathbf{R}(\cdot)\right]\delta\left(\mathbf{R}(0)-\mathbf{r}_{\mathrm{g}}\right)\delta\left(\mathbf{R}(N_{\mathrm{g}})-\mathbf{r}_{\mathrm{end}}\right)\exp\left\{-\beta\int\limits_{0}^{N_{\mathrm{g}}}\mathrm{d}N'\,w'\left(\mathbf{R}(N')\right)\right\}}{\frac{1}{V}\int\mathcal{D}\left[\mathbf{R}(\cdot)\right]\mathcal{P}\left[\mathbf{R}(\cdot)\right]}$$

$$=\frac{\int\mathcal{D}\left[\mathbf{R}(\cdot)\right]\mathcal{P}\left[\mathbf{R}(\cdot)\right]\delta\left(\mathbf{R}(0)-\mathbf{r}_{\mathrm{g}}\right)\exp\left\{-\beta\int\limits_{0}^{N_{\mathrm{g}}}\mathrm{d}N'w'\left(\mathbf{R}(N')\right)\right\}}{\frac{1}{V}\int\mathcal{D}\left[\mathbf{R}(\cdot)\right]\mathcal{P}\left[\mathbf{R}(\cdot)\right]} \qquad \text{S44}$$

Dividing eq S43 with S44, we obtain the following expression:

$$\frac{1}{Q_{\mathrm{g}}\left[\mathbf{r}_{\mathrm{g}};w'(\mathbf{r})\right]}\int\limits_{0}^{N_{\mathrm{g}}}\mathrm{d}N\;G(\mathbf{r}_{\mathrm{g}},\mathbf{r},N)\;q_{\mathrm{m}}(\mathbf{r},N_{\mathrm{g}}-N)$$

$$=\frac{\int\limits_{0}^{N_{\mathrm{g}}}dN\;\int\mathcal{D}\left[\mathbf{R}(\cdot)\right]\mathcal{P}\left[\mathbf{R}(\cdot)\right]\delta\left(\mathbf{R}(0)-\mathbf{r}_{\mathrm{g}}\right)\delta\left(\mathbf{R}(N)-\mathbf{r}\right)\exp\left\{-\beta\int\limits_{0}^{N_{\mathrm{g}}}\mathrm{d}N'w'\left(\mathbf{R}(N')\right)\right\}}{\int\mathcal{D}\left[\mathbf{R}(\cdot)\right]\mathcal{P}\left[\mathbf{R}(\cdot)\right]\delta\left(\mathbf{R}(0)-\mathbf{r}_{\mathrm{g}}\right)\exp\left\{-\beta\int\limits_{0}^{N_{\mathrm{g}}}\mathrm{d}N'w'\left(\mathbf{R}(N')\right)\right\}}$$

$$=\frac{\int\mathcal{D}\left[\mathbf{R}(\cdot)\right]\mathcal{P}\left[\mathbf{R}(\cdot)\right]\delta\left(\mathbf{R}(0)-\mathbf{r}_{\mathrm{g}}\right)\int\limits_{0}^{N_{\mathrm{g}}}dN'\delta\left(\mathbf{R}(N')-\mathbf{r}\right)\exp\left\{-\beta\int\limits_{0}^{N_{\mathrm{g}}}\mathrm{d}N'w'\left(\mathbf{R}(N')\right)\right\}}{\int\mathcal{D}\left[\mathbf{R}(\cdot)\right]\mathcal{P}\left[\mathbf{R}(\cdot)\right]\delta\left(\mathbf{R}(0)-\mathbf{r}_{\mathrm{g}}\right)\exp\left\{-\beta\int\limits_{0}^{N_{\mathrm{g}}}\mathrm{d}N'w'\left(\mathbf{R}(N')\right)\right\}} \qquad \text{S45}$$

$$=\left\langle\int\limits_{0}^{N_{\mathrm{g}}}\mathrm{d}N'\delta\left(\mathbf{R}(N')-\mathbf{r}\right)\right\rangle_{\substack{\mathbf{R}(0)=\mathbf{r}_{\mathrm{g}}\\ \text{Field }w'}}$$

Using the definition eq S5, we can write:

$$\frac{1}{Q_{\mathrm{g}}\left[\mathbf{r}_{\mathrm{g}};w'(\mathbf{r})\right]}\int\limits_{0}^{N_{\mathrm{g}}}\mathrm{d}N'G(\mathbf{r}_{\mathrm{g}},\mathbf{r},N')\;q_{\mathrm{m}}(\mathbf{r},N_{\mathrm{g}}-N')=\rho_{\mathrm{seg,bulk}}\left\langle\hat{\varphi}_{\mathrm{g}}(\mathbf{r})\right\rangle_{\substack{\mathbf{R}(0)=\mathbf{r}_{\mathrm{g}}\\ \text{Field }w'}}=\rho_{\mathrm{seg,bulk}}\varphi_{\mathrm{g}}(\mathbf{r})=\rho_{g}(\mathbf{r}) \qquad \text{S46}$$

where $\varphi_{\mathrm{g}}(\mathbf{r})$ is the reduced density and $\rho_{\mathrm{g}}(\mathbf{r})$ the segment density contributed by the considered grafted chain, at position $\mathbf{r}$.

Taking into account eq S37, which relates the partition function of a grafted chain to the restricted partition function of a matrix chain, we rewrite eq S46 for a specific grafted chain, i_{g}, as

$$\varphi_{i_{\mathrm{g}}}(\mathbf{r}) = \frac{1}{\rho_{\mathrm{seg,bulk}} q_{\mathrm{m}}\left(\mathbf{r}_{i_{\mathrm{g}}}, N_{\mathrm{g}}\right)} \int_{0}^{N_{\mathrm{g}}} \mathrm{d}N' G(\mathbf{r}_{i_{\mathrm{g}}}, \mathbf{r}, N')\, q_{\mathrm{m}}(\mathbf{r}, N_{\mathrm{g}} - N') \qquad \text{S47}$$

The total reduced density due to all grafted chains will be:

$$\begin{aligned} \varphi_{\mathrm{g}}(\mathbf{r}) &= \sum_{i_{\mathrm{g}}=1}^{n_{\mathrm{g}}} \varphi_{i_{\mathrm{g}}}(\mathbf{r}) = \frac{1}{\rho_{\mathrm{seg,bulk}}} \sum_{i_{\mathrm{g}}=1}^{n_{\mathrm{g}}} \frac{1}{q_{\mathrm{m}}\left(\mathbf{r}_{i_{\mathrm{g}}}, N_{\mathrm{g}}\right)} \int_{0}^{N_{\mathrm{g}}} \mathrm{d}N'\, G(\mathbf{r}_{i_{\mathrm{g}}}, \mathbf{r}, N')\, q_{\mathrm{m}}(\mathbf{r}, N_{\mathrm{g}} - N') = \\ &= \int_{0}^{N_{\mathrm{g}}} \mathrm{d}N' \left\{ \sum_{i_{\mathrm{g}}=1}^{n_{\mathrm{g}}} \frac{1}{\rho_{\mathrm{seg,bulk}} q_{\mathrm{m}}\left(\mathbf{r}_{i_{\mathrm{g}}}, N_{\mathrm{g}}\right)} G(\mathbf{r}_{i_{\mathrm{g}}}, \mathbf{r}, N') \right\} q_{\mathrm{m}}(\mathbf{r}, N_{\mathrm{g}} - N') \end{aligned} \qquad \text{S48}$$

Let us set

$$q_{\mathrm{g}}(\mathbf{r}, N) = \sum_{i_{\mathrm{g}}=1}^{n_{\mathrm{g}}} \frac{N_{\mathrm{g}}}{\rho_{\mathrm{seg,bulk}} q_{\mathrm{m}}\left(\mathbf{r}_{i_{\mathrm{g}}}, N_{\mathrm{g}}\right)} G(\mathbf{r}_{i_{\mathrm{g}}}, \mathbf{r}, N) \qquad \text{S49}$$

With this definition,

$$\varphi_{\mathrm{g}}(\mathbf{r}) = \frac{1}{N_{\mathrm{g}}} \int_{0}^{N_{\mathrm{g}}} \mathrm{d}N\, q_{\mathrm{g}}(\mathbf{r}, N)\, q_{\mathrm{m}}(\mathbf{r}, N_{\mathrm{g}} - N) \qquad \text{S50}$$

S2. Solving the diffusion equation in 1D spherical coordinates

In spherical polar coordinates the Laplacian is written as follows:

$$\nabla^2 u = \frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} = \frac{1}{r}\frac{\partial^2 (ru)}{\partial r^2} + \frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial u}{\partial\theta}\right) + \frac{1}{r^2 \sin^2\theta}\frac{\partial^2 u}{\partial\phi^2} \qquad \text{S51}$$

In the planar surface case, $u = u(z,t)$, $\frac{\partial^2 u}{\partial x^2} = 0$ and $\frac{\partial^2 u}{\partial y^2} = 0$ with *z* being the direction normal to the surface. Therefore, the Edwards diffusion equation in Cartesian coordinates assumes the one-dimensional form:

$$\frac{\partial u(z,t)}{\partial t} - D\frac{\partial^2 u(z,t)}{\partial z^2} + au(z,t) = 0 \qquad \text{S52}$$

with *t* corresponding to the contour length along a chain, *u* being a restricted partition function (propagator), *D* determined by the conformational stiffness, and *a* by the self-consistent field (compare eq 1 in main text).

In the case of a spherical nanoparticle with uniformly smeared grafting points on its surface, there is spherical symmetry. There is no dependence on the polar and azimuthal angles, $u = u(r,t)$ and the Edwards diffusion equation in spherical polar coordinates simplifies to:

$$\begin{gathered} \frac{\partial u}{\partial t} - D\left[\frac{1}{r}\frac{\partial^2 (ru)}{\partial r^2}\right] + au = 0 \quad \text{or} \\ \frac{\partial (ru)}{\partial t} - D\frac{\partial^2 (ru)}{\partial r^2} + a(ru) = 0 \end{gathered} \qquad \text{S53}$$

If we set

$$\psi(r,t) = ru(r,t) \qquad \text{S54}$$

eq S53 becomes

$$\frac{\partial \psi(r,t)}{\partial t} - D\frac{\partial^2 \psi(r,t)}{\partial r^2} + a\psi(r,t) = 0 \qquad \text{S55}$$

We see that the function $\psi(r,t)=ru(r,t)$ follows a unidimensional diffusion equation, eq S55, that is entirely analogous to eq S52.

S3. Evaluations of the free energy densities and field from Sanchez-Lacombe and Helfand models

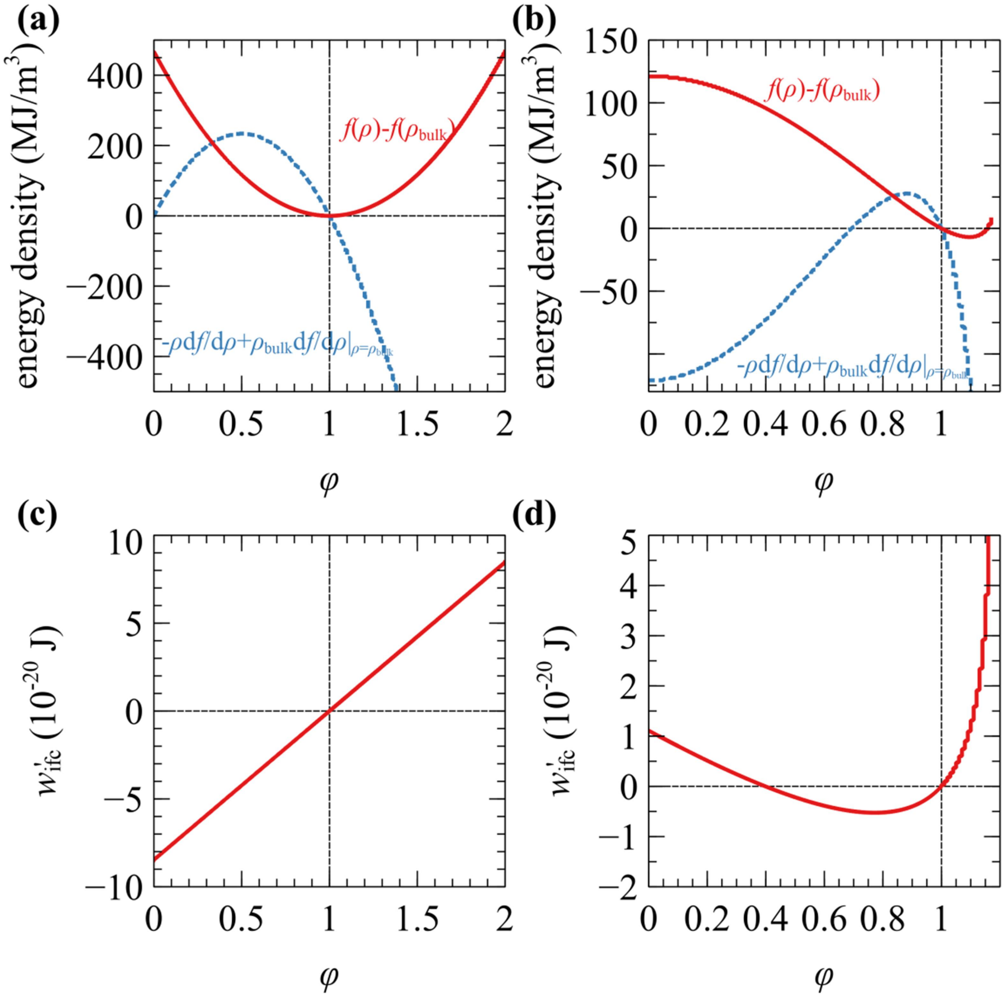

Figure S2. Top panels depict $f(\rho)$-$f(\rho_{\mathrm{seg,bulk}})$ (red line) and $-\rho\,\mathrm{d}f/\mathrm{d}\rho\big|+\big[\rho\mathrm{d}f/\mathrm{d}\rho\big]\big|_{\rho=\rho_{\mathrm{seg,bulk}}}$ (dotted line) from **(a)** Helfand and **(b)** Sanchez-Lacombe free energy densities. Bottom panels depict $w'_{\mathrm{ifc}}=w'-w'_{\mathrm{bulk}}$ from **(c)** Helfand and **(d)** Sanchez-Lacombe free energy densities, in absence of solid-polymer interactions and gradient correction.

S4. Derivation of the density gradient term from the square gradient and the Laplacian

The general expression of the gradient term of the free energy in three dimensions is the following:

$$\Omega_{\mathrm{SGT}} = \kappa \int_{\mathcal{R}^3} \left[\nabla \rho(\mathbf{r})\right]^2 \ \mathrm{d}\mathbf{r} \qquad \text{S56a}$$

with $\rho(\mathbf{r})$ being the local segment density and κ the influence parameter. The corresponding free energy function used in our calculations is

$$f\left[\rho(\mathbf{r}), \nabla\rho(\mathbf{r})\right] = f\left[\rho(\mathbf{r}), \mathbf{0}\right] + f_{\mathrm{SGT}}(\nabla\rho(\mathbf{r})) = f\left[\rho(\mathbf{r}), \mathbf{0}\right] + \kappa\left[\nabla\rho(\mathbf{r})\right]^2 \qquad \text{S56b}$$

with $f\left[\rho(\mathbf{r}), \mathbf{0}\right]$ being the Helmholtz energy density of a homogeneous polymer fluid of segment density $\rho(\mathbf{r})$ at the considered temperature, calculated from an equation of state. In many cases, the gradient term E_{SGT} can be calculated instead from the Laplacian of the density, as will be shown below.

S4.1. Planar geometries

In planar geometries one can take advantage of the homogeneity along the planar (x, y) directions (i.e., cylindrical symmetry). Since $\partial\rho / \partial x = \partial\rho / \partial y = 0$, the gradient term can be written as follows:

$$\Omega_{\mathrm{SGT}} / \mathcal{S} = \kappa \int_{\mathcal{R}^1} \left(\frac{\mathrm{d}\rho}{\mathrm{d}h}\right)^2 \ \mathrm{d}h \qquad \text{S57}$$

with h being the segment-surface distance and $\mathcal{S}$ the considered surface area. Alternatively, the gradient term can be written in terms of the Laplacian as follows:

$$\Omega_{\mathrm{SGT}} / \mathcal{S} = \kappa \int_0^L \frac{\mathrm{d}\rho}{\mathrm{d}h}\frac{\mathrm{d}\rho}{\mathrm{d}h} \ \mathrm{d}h = \kappa \left[\frac{\mathrm{d}\rho}{\mathrm{d}h}\rho\right]_0^L - \kappa \int_0^L \frac{\mathrm{d}^2\rho}{\mathrm{d}h^2}\rho \ \mathrm{d}h \qquad \text{S58}$$

Either $\rho = 0$ at the Dirichlet boundaries ($q = 0$) or dρ/dz=0 at the Neumann boundaries (dq/dz=0); thus, eq S58 becomes:

$$\Omega_{\text{SGT}} / S = -\kappa \int_0^L \frac{\mathrm{d}^2\rho}{\mathrm{d}h^2} \rho \ \mathrm{d}h \tag{S59}$$

S4.2. Spherical geometries

In systems with spherical homogeneity with respect to the center of the nanoparticle one can express eq S56 as follows:

$$\Omega_{\text{SGT}} = \kappa \int_0^R \left(\frac{\mathrm{d}\rho}{\mathrm{d}r} \right)^2 4\pi r^2 \mathrm{d}r \tag{S60}$$

with *r* being the distance between the center of the spherical nanoparticle and the polymer segment. The gradient term can be written in terms of the Laplacian as follows:

$$\begin{aligned} \Omega_{\text{SGT}} &= \kappa \int_0^R \frac{\mathrm{d}\rho}{\mathrm{d}r} \frac{\mathrm{d}\rho}{\mathrm{d}r} \ 4\pi r^2 \mathrm{d}r = \kappa \left[\frac{\mathrm{d}\rho}{\mathrm{d}r} \int_0^r \left(\frac{\mathrm{d}\rho}{\mathrm{d}r'} \ 4\pi r'^2 \right) \mathrm{d}r' \right]_0^R - \kappa \int_0^R \frac{\mathrm{d}^2\rho}{\mathrm{d}r^2} \int_0^r \left(\frac{\mathrm{d}\rho}{\mathrm{d}r'} \ 4\pi r'^2 \mathrm{d}r' \right) \mathrm{d}r \\ &= -\kappa \int_0^R \frac{\mathrm{d}^2\rho}{\mathrm{d}r^2} \int_0^r \left(\frac{\mathrm{d}\rho}{\mathrm{d}r'} \ 4\pi r'^2 \mathrm{d}r' \right) \mathrm{d}r \end{aligned} \tag{S61}$$

However,

$$4\pi \int_0^r \frac{\mathrm{d}\rho}{\mathrm{d}r'} \ r'^2 \mathrm{d}r' = 4\pi \left[\rho(r') r'^2 \right]_0^r - 8\pi \int_0^r \rho(r') \ r' \mathrm{d}r' = -8\pi \int_0^r \rho(r') \ r' \mathrm{d}r'$$

Thus, eq S61 becomes:

$$\Omega_{\text{SGT}} = 8\pi\kappa \int_0^R \frac{\mathrm{d}^2\rho}{\mathrm{d}r^2} \int_0^r \rho(r') \ r' \mathrm{d}r' \ \mathrm{d}r \tag{S62}$$

S5. Hamaker potential

In this work, the solid-polymer interactions are described via the Hamaker potential.[4] The essence of Hamaker theory is to treat the interacting bodies as collections of homogeneously distributed infinitesimal domains interacting via a nonbonded interaction potential (usually Lennard-Jones, 12-6). Then an integration along the volumes of the bodies takes place to account for interactions amongst all possible pairs of domains, resulting in the total potential energy. The Hamaker constant of the effective solid-polymer interaction can be estimated by the following geometric mean $A_{\mathrm{PS\text{-}SiO_2}} = \sqrt{A_{\mathrm{PS}} A_{\mathrm{SiO_2}}}$. Vogiatzis and Theodorou[5] employed an effective solid-polymer interaction, $A^{\mathrm{eff}}_{\mathrm{PS\text{-}SiO_2}} = \sqrt{A_{\mathrm{PS}} A_{\mathrm{SiO_2}}} - A_{\mathrm{PS}}$ instead of $A_{\mathrm{PS\text{-}SiO_2}}$, in order to restore the proper effective cohesive interactions at the polymer/solid interface. In this study we opted to work with $A_{\mathrm{PS\text{-}SiO_2}}$, since the energy of cohesion of the polymer is taken into account as part of $f\left[\rho(\mathbf{r}), \nabla\rho(\mathbf{r})\right]$. Furthermore, the effective collision diameter can be calculated as $\sigma_{\mathrm{eff}} = (\sigma_{\mathrm{PS}} + \sigma_{\mathrm{SiO_2}})/2$ with σ_{PS} and $\sigma_{\mathrm{SiO_2}}$ being the effective diameters of solid and polymeric segment interaction sites, respectively. In each of the following cases of interacting geometries a wall distance was used, so that the maximum value of the repulsive term felt by the polymer segments does not exceed 5 $k_{\mathrm{B}}T$ (e.g., see Figure **S3**).

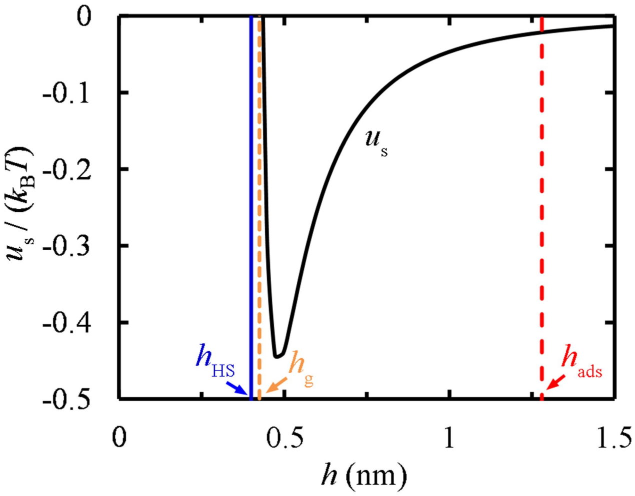

Figure S3. Interaction energy $u_s(h)$ between a PS monomer unit and a planar SiO$_2$ substrate as calculated from the Hamaker potential at $T = 500$ K. The blue line, $h_{HS} = 0.4$ nm, intersects the $u_s(h)$ curve at $u_s = 5\ k_BT$ and depicts the distance of the hard-sphere wall from the surface employed in the calculations. The orange dashed line depicts the distance of the grafting points from the surface (h_g), and the red dashed line delimits the critical distance (h_{ads}), below which a matrix chain is considered adsorbed.

S5.1. Sphere-sphere

For the purpose of calculating the potential energy of dispersive interactions between the polystyrene, either matrix or grafted, and a nanoparticle immersed in it, we consider the atactic polystyrene monomers as small spheres with an effective radius $a_1 = \sqrt[3]{\frac{3}{4\pi\rho_{seg}}}$, interacting with the spherical silica nanoparticle of radius $a_2 = R_{NP}$. The solid-polymer interaction potential per monomer, u_s, can be split into an attractive[4] and a repulsive term.[6] The two terms, u_A and u_R respectively, are functions of the center-to-center distance, r_{12}, between two interacting spherical bodies:

$$u_A = -\frac{A_{12}}{6}\left[\frac{2a_1a_2}{r_{12}^2-(a_1+a_2)^2}+\frac{2a_1a_2}{r_{12}^2-(a_1-a_2)^2}+\ln\left(\frac{r_{12}^2-(a_1+a_2)^2}{r_{12}^2-(a_1-a_2)^2}\right)\right] \quad \text{S63a}$$

$u_{\mathrm{R}} =$

$$\frac{A_{12}}{37800}\frac{\sigma_{\mathrm{eff}}^{6}}{r_{12}}\left[\begin{array}{l}\dfrac{r_{12}^{2}-7r_{12}\left(a_1+a_2\right)+6\left(a_1^2+7a_1a_2+a_2^{2}\right)}{\left(r_{12}-a_1-a_2\right)^7}+\dfrac{r_{12}^{2}+7r_{12}\left(a_1+a_2\right)+6\left(a_1^{2}+7a_1a_2+a_2^{2}\right)}{\left(r_{12}+a_1+a_2\right)^7}\\ -\dfrac{r_{12}^{2}+7r_{12}\left(a_1-a_2\right)+6\left(a_1^2-7a_1a_2+a_2^{2}\right)}{\left(r_{12}+a_1-a_2\right)^7}-\dfrac{r_{12}^{2}-7r_{12}\left(a_1-a_2\right)+6\left(a_1^{2}-7a_1a_2+a_2^{2}\right)}{\left(r_{12}-a_1+a_2\right)^7}\end{array}\right] \quad \text{S63b}$$

where $A_{12} = A_{\mathrm{PS\text{-}SiO_2}}$ is the Hamaker constant and σ_{eff} is the effective collision diameter.

S5.2. Sphere-flat surface

The attractive and the repulsive components from the interaction of a sphere with a semi-infinite solid terminating at a flat surface can be obtained in the context of Hamaker theory as follows:

$$u_{\mathrm{A}} = -\frac{A_{12}}{6}\left(\frac{1}{r'}+\frac{1}{2+r'}+\ln\left(\frac{r'}{2+r'}\right)\right) \quad \text{S64a}$$

$$u_{\mathrm{R}} = \frac{A_{12}}{7560}\frac{\sigma_{\mathrm{eff}}^{6}}{a_1^{6}}\left(\frac{8+r'}{\left(2+r'\right)^7}+\frac{6-r'}{r'^7}\right) \quad \text{S64b}$$

with $r' = d_{12}/a_1$ and d_{12} being the distance between the surface of the sphere and the solid surface. We have $u_{\mathrm{s}}=u_{\mathrm{A}}+u_{\mathrm{R}}$ for this case which is shown in Figure **S3** as a function of $h=d_{12}+a_1$.

S6. Numerical solution of the Edwards diffusion equation

In order to solve the time/contour-dependent Edwards diffusion equation, we discretize the domain of interest into u_h intervals and the chain contour length variable into u_c intervals, where $u_h = \frac{L}{\Delta h}$ and $u_c = \frac{N_c}{\Delta N}$, respectively. The spatial and chain contour length step intervals, Δh and ΔN respectively, are chosen so that maximum accuracy and stability are obtained with minimum computational cost.

The first derivative of the chain propagator, q, with respect to the chain-contour variable, N, is approximated with the finite-differences eq S65.

$$\frac{\partial q}{\partial N} = \frac{q_h^{N+1} - q_h^{N}}{\Delta N} \tag{S65}$$

The second derivative of q with respect to h is approximated via the centered differences in eq S66. It is essential to emphasize that an implicit time-stepping scheme is adopted, since the chain propagator at all space-nodal points is evaluated at contour length N+1 (the code also supports the solution of one-dimensional partial differential equations with a semi-implicit finite-differences scheme, also known as the Crank-Nicholson method).[7,8]

$$\frac{\partial^2 q}{\partial h^2} = \frac{q_{h+1}^{N+1} - 2q_h^{N+1} + q_{h-1}^{N+1}}{\Delta h^2} \tag{S66}$$

Combining eqs S65 and S66, we obtain the space and chain-contour discretized form of the Edwards diffusion equation, as presented in eq S67.

$$-2Dq_{h-1}^{N+1} + \left(1 + 4D + \Delta c \beta w_{\mathrm{ifc},h}\right) q_h^{N+1} - 2Dq_{h+1}^{N+1} = q_h^{N} \tag{S67}$$

where $D = \dfrac{R_{\mathrm{G},c}{}^{2} \Delta N}{2N_c \Delta h^2}$.

S7. Optimization of the simulation parameters

S7.1. Spatial and chain-contour discretization

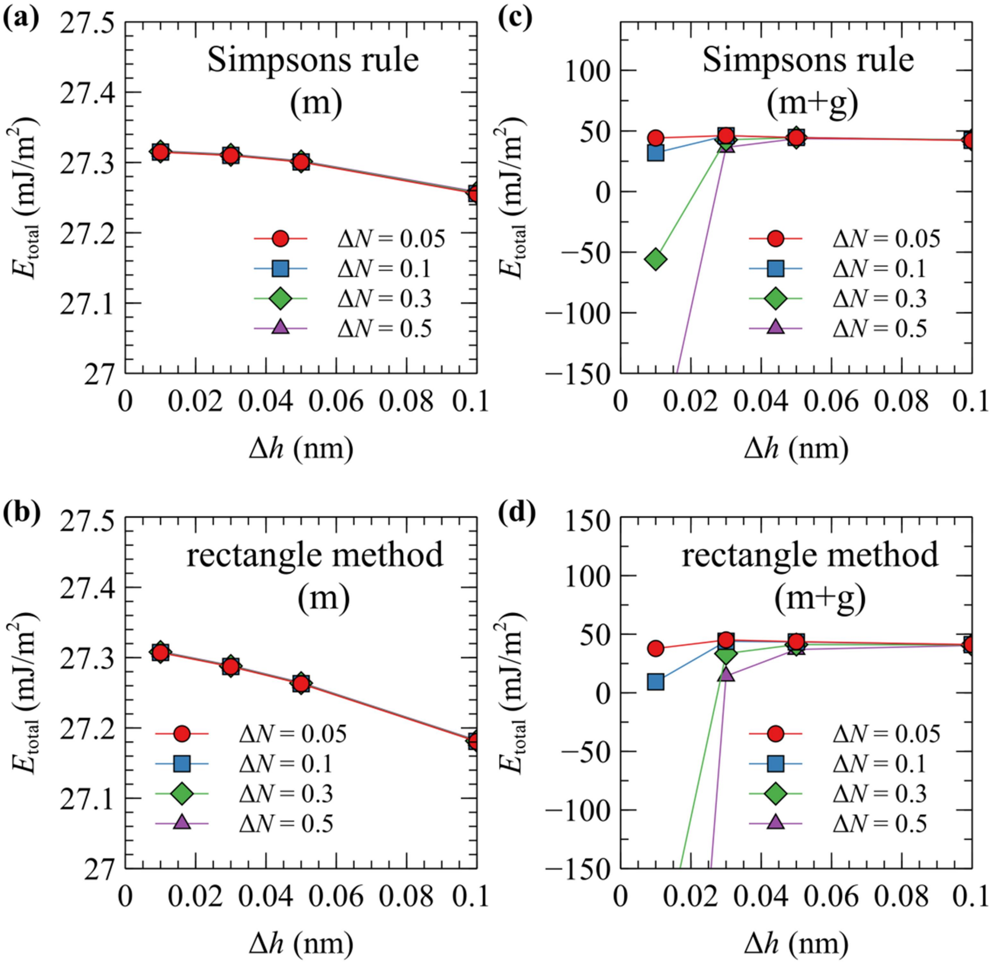

Figure S4. Evaluations of the grand potential from systems with matrix (m) **(a, b)** and with matrix and grafted (m+g) chains **(c, d)**, for various degrees of spatial (Δh) and chain-contour (ΔN) discretization and integration methods. **(ac)** and **(bd)** panels correspond to evaluations of the convolution integrals with the Simpson and rectangle integration methods, respectively. These evaluations were performed in planar geometries, for $M_{\mathrm{g}} = M_{\mathrm{m}} = 5.2$ kg/mol, $\sigma_{\mathrm{g}} = 0.5$ nm^{-2} (when grafted chains are present), in the absence of polymer-solid interactions.

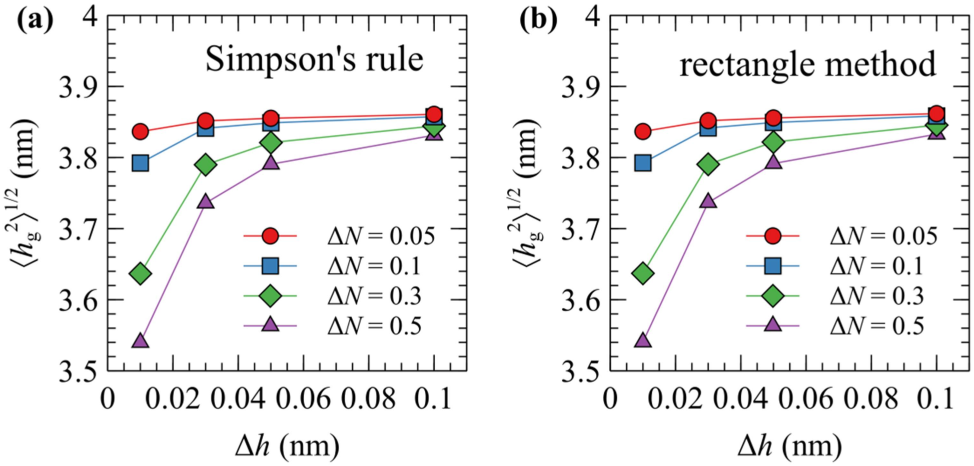

Figure S5. Evaluations of the mean brush thickness from systems for various degrees of spatial (Δh) and chain-contour (ΔN) discretizations. **(a)** and **(b)** panels correspond to evaluations of the convolution integrals with the Simpson and rectangle integration methods, respectively. These evaluations were performed in planar geometries, for $M_g = M_m = 5.2$ kg/mol, $\sigma_g = 0.5$ nm^{-2} (when grafted chains are present), in the absence of polymer-solid interactions.

Figure **S4** and Figure **S5** illustrate a sensitivity analysis of the grand potential and the mean brush thickness on the degree of spatial (Δh) and chain-contour (ΔN) discretization using either the Simpson or the rectangle integration method for the evaluation of the convolution integrals. Overall, Simpson's rule has slightly better performance in terms of accuracy than the rectangle method. It is noteworthy that in the presence of grafted chains, the solution becomes more sensitive to ΔN with decreasing Δh. This can be attributed to the fact that decreasing Δh leads to sharper delta functions ($\Delta(h) \sim \Delta h^{-1}$); hence, much smaller ΔN are required.

An advantage of rectangle method is that it results in slightly more accurate prediction of the desired grafting density via the segment balance equation; in detail, the error with the Simpson and the rectangle integration methods is on the order of $\sim 10^{-4}$ and $\sim 10^{-5}$, respectively. In addition, it offers the possibility to compute the gradient energy term via both the square gradient and the Laplacian of the segment density (see section **S3** above). This probably has to do with that Simpson's rule does not weigh all the points evenly; e.g., in Simpson 3/4 rule the weights on the first and last points is 3/4, whilst the weight of the remaining points alternates between 4/3 and 2/3.

S7.2. Field mix fraction

Figure **S6a and c** presents the number of steps to convergence as a function of the field mix fraction (a_{mix}) in eq 5. As can be seen, the number of steps for convergence is inversely proportional to a_{mix}. Figure **S6b and d** depicts the optimum values for a_{mix} as a function of the molar mass of the grafted chains. Slightly larger a_{mix} values than those depicted in Figure S6 (right) affect the stability of the iterative scheme. According to our tests, three different situations may arise for large a_{mix} values: i) the field diverges, ii), $\Delta w'^{\max}_{\mathrm{ifc}}$ oscillates indefinitely around a value that is larger than the tolerance value, $\Delta w'^{\mathrm{tol}}_{\mathrm{ifc}}$, (see Figure **S7b**) or iii) the field converges to an unphysical solution (e.g., the matrix chains or part of them becomes extinct, as shown in Figure **S7c**.

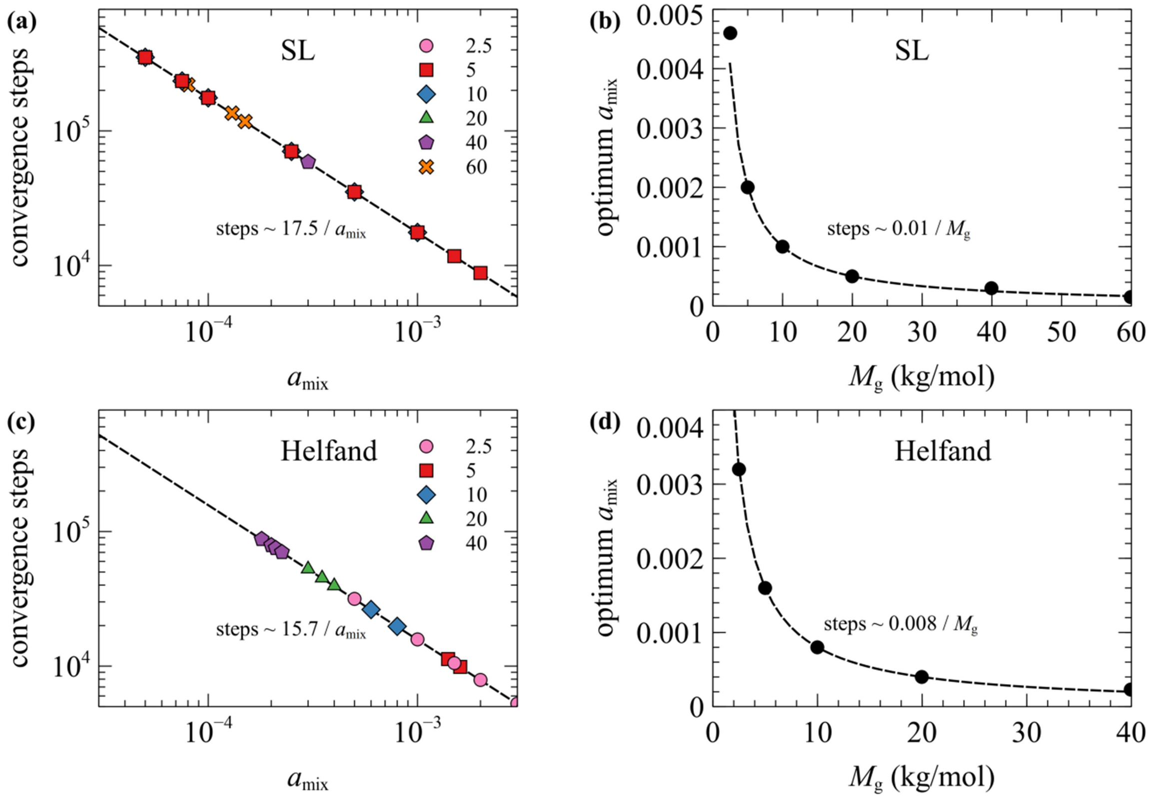

Figure S6. (a, c) Number of steps for convergence ($\Delta w'^{\max}_{\mathrm{ifc}} \leq 10^{-5}\, k_B T$) for various molecular weights. **(b, d)** Optimal mix fraction versus chain molar mass. In (a, b) the Sanchez-Lacombe EoS was used in conjunction with the square gradient theory, while in (c, d) the Helfand free energy density was used. In all cases, $M_g = M_m$, $R_{\mathrm{NP}} = 80$ nm and $\sigma_g = 0.8$ nm^{-2}.

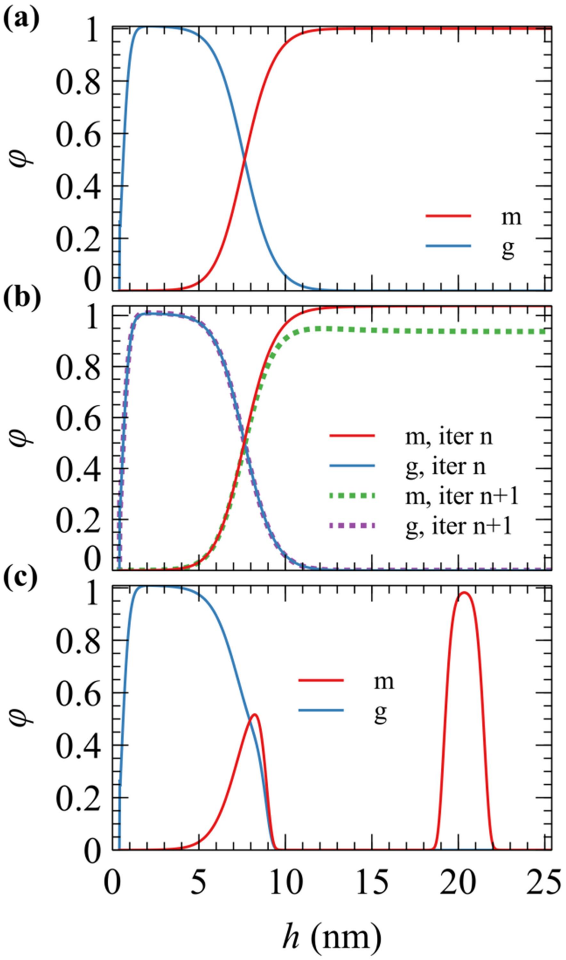

Figure S7. Reduced radial density profiles for a system with M_g = M_m=5 kg/mol, σ_g = 0.8 nm^{-2} and R_NP = 8 nm. The field mixing fraction, a_mix, for each case was set to **(a)** 0.002, **(b)** 0.0025 and **(c)** 0.005; the corresponding maximum field errors are $\Delta w'^{\,\mathrm{max}}_{\mathrm{ifc}} = 10^{-6}$, 0.42 and 0.6 $k_\mathrm{B}T$.

S8. Total reduced density profiles across the (R_{NP}, σ_g, M_g) parameter space

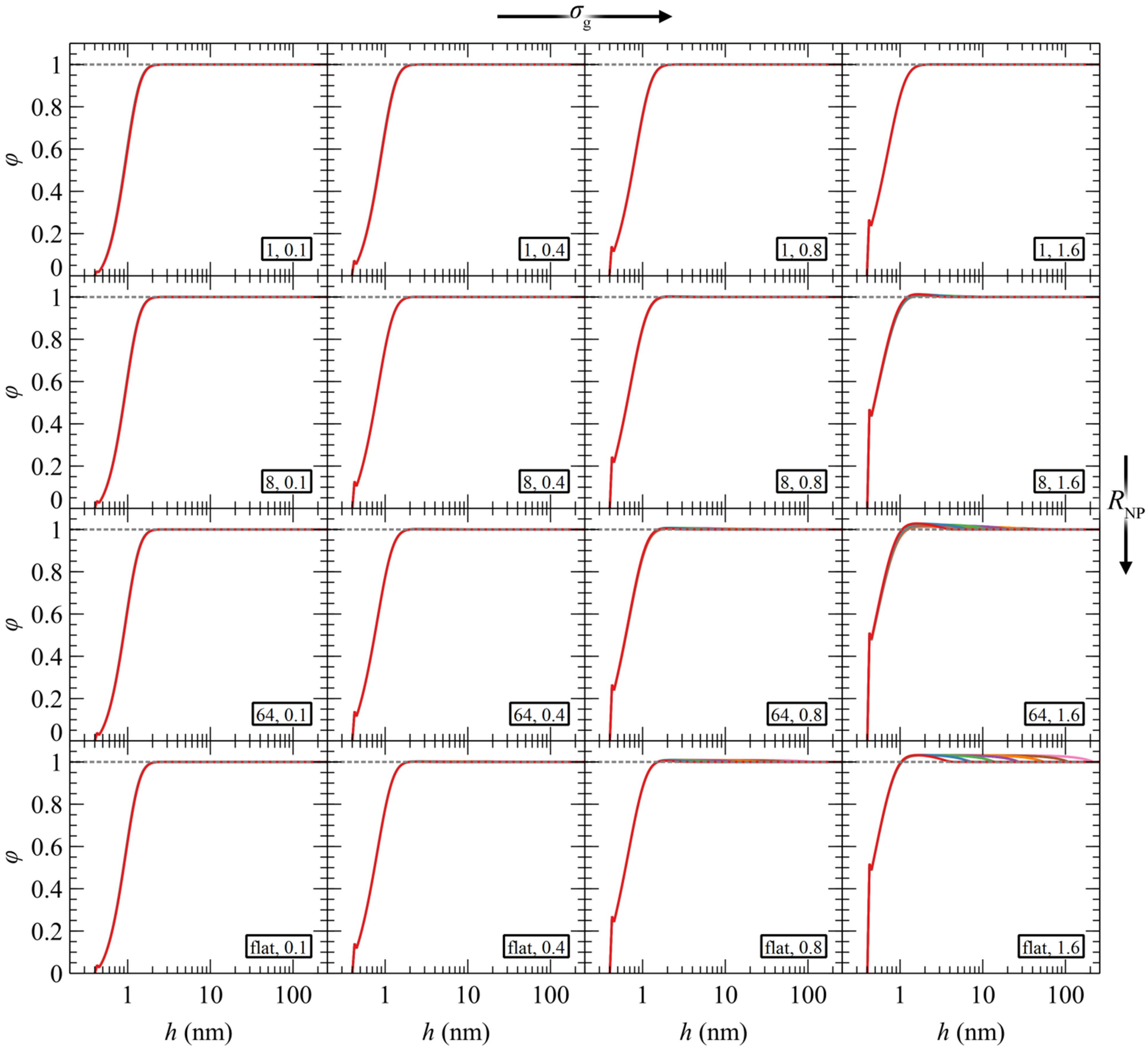

Figure S8. Total φ profiles of chains for grafted chain molar mass equal to 1.25 (red), 2.5 (blue), 5 (green), 10 (violet), 20 (orange), 40 (brown) and 80 (pink) kg/mol. In all cases, M_m=M_g. Legend in rectangles: R_{NP}(nm), σ_g(nm^{-2}). The dashed line, φ = 1, is a guide to the eye. The little blip at h = 0.4 nm is caused by the grafting points.

S9. Predictions from a simple model with homogeneous density

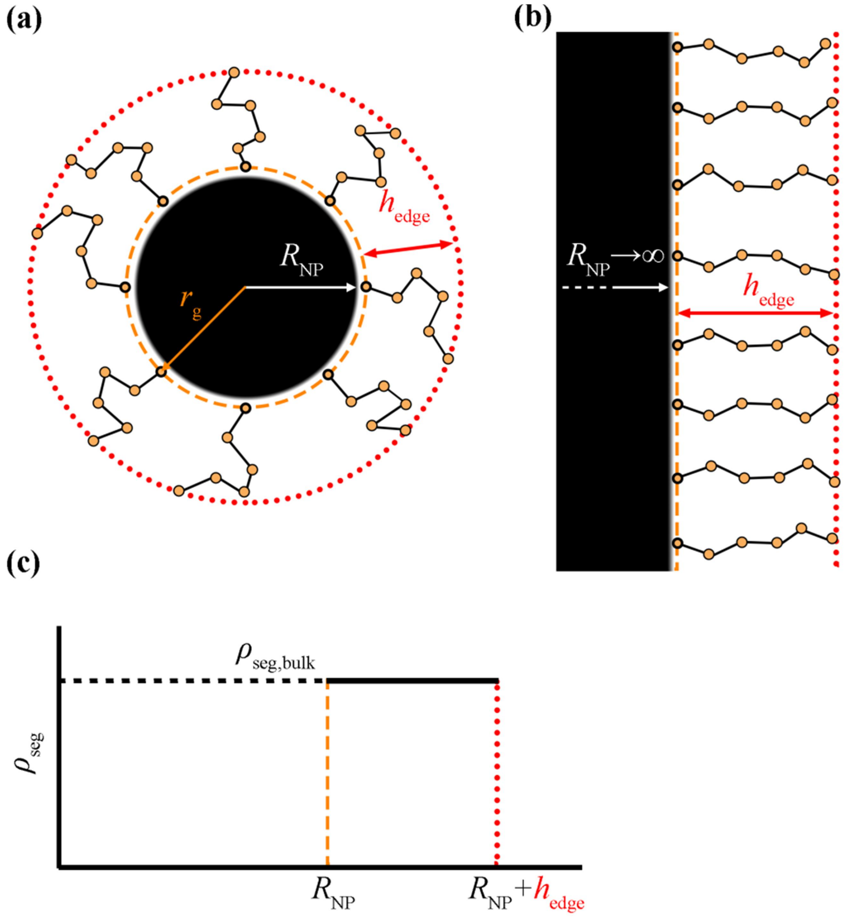

Figure S9. (a) A nanoparticle with grafted chains that form a brush which ends at h_{edge}. **(b)** In the limit $R_{\mathrm{NP}}\rightarrow\infty$, the surface of the nanoparticle becomes flat. **(c)** The segment density profile of a brush with constant segmental density, $\rho_{\mathrm{seg,bulk}}$.

It is instructive to compare the predictions of SCFT with the predictions of a simpler brush model such as that of incompressible Alexander brushes.[9,10] Let h_{edge} be the edge of a brush comprising n_{g} grafted chains of length N_{g}, emanating from a nanoparticle with radius, R_{NP}, such as the one shown in Figure **S9a**. For simplicity, let us assume that the segment density is constant and equal to $\rho_{\mathrm{seg,bulk}}$ across the region occupied by the brush of grafted chains, $\left[R_{\mathrm{NP}}, R_{\mathrm{NP}}+h_{\mathrm{edge}}\right]$ which are terminated at h_{edge}; Figure **S9c** presents the corresponding density profile for this model. Consequently, the volume occupied by the brush can be calculated as the number of the brush segments in this region divided by its segment density.

$$V = \frac{n_{\mathrm{g}} N_{\mathrm{g}}}{\rho_{\mathrm{seg,bulk}}} = \frac{\sigma_{\mathrm{g}} 4\pi R_{\mathrm{NP}}{}^{2} N_{\mathrm{g}}}{\rho_{\mathrm{seg,bulk}}} \qquad \text{S68}$$

where $\sigma_{\mathrm{g}} = N_{\mathrm{g}} / \left(4\pi R_{\mathrm{NP}}{}^{2}\right)$ is the grafting density. Alternatively, the volume of a brush of constant density that terminates at h_{edge} can be calculated as follows:

$$V = \frac{4}{3}\pi \left[\left(R_{\mathrm{NP}} + h_{\mathrm{edge}} \right)^{3} - R_{\mathrm{NP}}{}^{3} \right] \qquad \text{S69}$$

By combining eqs S68 and S69, and solving for h_{edge}, we get for h_{edge}:

$$h_{\mathrm{edge}} = \left(\frac{3\sigma_{\mathrm{g}} N_{\mathrm{g}}}{\rho_{\mathrm{seg,bulk}}} R_{\mathrm{NP}}{}^{2} + R_{\mathrm{NP}}{}^{3} \right)^{\frac{1}{3}} - R_{\mathrm{NP}} \qquad \text{S70}$$

With h_{edge} known and given that the density profiles are uniform, $h_{\mathrm{g,99\%}}$, can be calculated as follows:

$$h_{\mathrm{g,99\%}} = 0.99 \cdot h_{\mathrm{edge}} + R_{\mathrm{NP}} \qquad \text{S71}$$

Similarly, $\left\langle h_{\mathrm{g}}{}^{2} \right\rangle^{1/2}$ can be obtained by eq S72.

$$\begin{aligned} \left\langle h_{\mathrm{g}}{}^{2} \right\rangle^{1/2} &= \left(\frac{\int_{0}^{h_{\mathrm{edge}}} h^{2} \rho(h) \mathrm{d}h}{\int_{0}^{h_{\mathrm{edge}}} \rho(h) \mathrm{d}h} \right)^{1/2} = \left(\frac{1}{h_{\mathrm{edge}}} \int_{0}^{h_{\mathrm{edge}}} h^{2} \mathrm{d}h \right)^{1/2} = \frac{1}{\sqrt{3}} h_{\mathrm{edge}} \\ &= \frac{1}{\sqrt{3}} \left(\frac{3\sigma_{\mathrm{g}} N_{\mathrm{g}}}{\rho_{\mathrm{seg,bulk}}} R_{\mathrm{NP}}{}^{2} + R_{\mathrm{NP}}{}^{3} \right)^{\frac{1}{3}} - \frac{1}{\sqrt{3}} R_{\mathrm{NP}} \end{aligned} \qquad \text{S72}$$

In the limit of very large nanoparticles (flat surfaces), $\left\langle h_{\mathrm{g}}{}^{2} \right\rangle^{1/2}$ becomes,

$$\lim_{R_{\mathrm{NP}} \to \infty} \left\langle h_{\mathrm{g}}{}^{2} \right\rangle^{1/2} = \frac{\sigma_{\mathrm{g}} N_{\mathrm{g}}}{\sqrt{3} \rho_{\mathrm{seg,bulk}}} = \frac{1}{\sqrt{3}} \lim_{R_{\mathrm{NP}} \to \infty} h_{\mathrm{edge}} \qquad \text{S73}$$

Thus, for this model $\left\langle h_{\mathrm{g}}{}^{2} \right\rangle^{1/2}$ appears to be proportional to σ_{g} and N_{g} in the limit of large nanoparticles/flat surfaces (i.e., see Figure **S9b**).

The thermodynamics of these brushes can be described by a total free energy which has as follows:

$$A_{\text{total}} = A_{\text{coh}} + A_{\text{stretch}} \qquad \text{S74}$$

where A_{coh} is the contribution from the cohesive interactions described by the free energy density (i.e., $A_{\text{coh}} \equiv \Omega_{\text{coh}}$ from eq 9 in the main text), and A_{stretch} is the entropic contribution from the stretched grafted chains. Given that the grafted chains are terminated at the edge of the brush, and assuming they can be described by Gaussian strings, the contribution of the brushes to the free energy due to stretching could be approximated as follows:

$$A_{\text{stretch}} = S_{\text{solid}} \sigma_{\text{g}} \frac{3k_{\text{B}}T}{2\left\langle R_{\text{end,g}}{}^{2} \right\rangle} h_{\text{edge}}{}^{2} \qquad \text{S75}$$

with $\left\langle R_{\text{end,g}}{}^{2} \right\rangle = N_{\text{g}} C_{\infty} l_{\text{c-c}}{}^{2}$ being the end-to-end distance of the grafted chain.

Combining eqs S75 and S70, the stretching free energy per unit area as a function of R_{NP} is the following:

$$\frac{A_{\text{stretch}}}{S_{\text{solid}}} = \sigma_{\text{g}} \frac{3k_{\text{B}}T}{2\left\langle R_{\text{end,g}}{}^{2} \right\rangle} \left(\left[\frac{3\sigma_{\text{g}} N_{\text{g}}}{\rho_{\text{seg,bulk}}} R_{\text{NP}}{}^{2} + R_{\text{NP}}{}^{3} \right]^{\frac{1}{3}} - R_{\text{NP}} \right)^{2} \qquad \text{S76}$$

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