

Article

Interpenetration of Solvent-Free Mutually Attracting Brushes

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Abstract

The equilibrium structure and mutual interpenetration of two opposing solvent-free polymer brushes with a negative Flory–Huggins interaction parameter χ are investigated using numerical self-consistent field calculations and an analytical approach. It is numerically demonstrated that strong mutual attraction fundamentally alters the brush structure, transforming the monomer density profiles from a sigmoidal to a linear shape and the overlap function into a broad inverted parabola. An analytical theory is developed that accurately describes these linear density profiles and the overlap integral, seamlessly bridging weak entropy-driven fluctuation interpenetration and strong energy-driven attraction interpenetration. Based on these scaling laws, a comprehensive diagram is constructed, clearly identifying the crossover boundaries between fluctuation-dominated and attraction-dominated regimes, as well as between partial and full brush interpenetration states. It is shown that for a fixed chain length, the overlap integral exhibits a pronounced non-monotonic dependence on the grafting density, passing through a distinct maximum. An exact analytical expression for the optimal grafting density that maximizes inter-brush adhesion is derived, revealing that this optimal value is a universal function of the interaction parameter χ and is practically independent of the chain length.

Keywords: dry polymer brushes; self-consistent field theory; brush interpenetration; adhesive interaction; Flory–Huggins parameter



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1. Introduction

Polymer brushes represent dense layers of macromolecules tethered by one end to a solid surface. In the absence of a free solvent, they form what are known as solvent-free or dry brushes [1–3]. The tethered polymer chains of such brushes are forced to fill the available volume solely through their own conformational degrees of freedom. This leads to strong stretching perpendicular to the grafting surface and a significant entropic penalty compared to polymer brushes immersed in a solvent [1].

The study of solvent-free polymer brushes is of fundamental importance for understanding the extreme regimes of polymer confinement and is critical for numerous practical applications [4]. In the absence of a solvent, intermolecular interactions between the chains entirely dictate the macroscopic properties of the interface. Understanding the physics of

such systems is necessary for the development of polymer nanocomposites [5], surface modification [6], and the tribology of modified surfaces [3,7–9].

To date, the majority of theoretical [3,9,10] and experimental [7,8] studies have focused on brush systems composed of identical polymers with an interaction parameter $\chi = 0$. In such systems, the depth of mutual penetration of the brushes is limited. However, in nature and polymer synthesis, there are widely known pairs of polymers that exhibit complete miscibility due to the presence of specific intermolecular interactions (such as hydrogen bonds or strong dipole-dipole interactions) that compensate for the entropic losses of long chains. For such pairs, the Flory–Huggins parameter takes negative values ($\chi < 0$).

Classic examples of such systems include mixtures of polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) [11], for which $\chi \approx -0.043$, as well as mixtures of polyvinylidene fluoride (PVDF) and polymethyl methacrylate (PMMA) [12], where at a temperature of 160 °C the interaction parameter is $\chi \approx -0.295$. In addition, strong specific attraction is observed in mixtures of polycaprolactone (PCL) and polyvinyl chloride (PVC) [13].

In the studies by Chen and Yu [14,15], molecular dynamics simulations were employed to investigate the interaction between opposing polymer brushes, which model the interstitial space between adjacent polymer-grafted nanoparticles in solvent-free hybrid materials (so-called nanoparticle–organic hybrid materials [16]). These studies examined binary systems where the enthalpic attraction between the monomer units of the distinct brushes was varied to investigate their interpenetration and dynamics. It is important to emphasize that these studies did not employ an atomistic model of specific chemical compounds but rather a generic coarse-grained bead-spring model to describe flexible chains characteristic of organic polymers. The authors did not aim to construct a rigorous, systematic analytical theory; their studies are primarily demonstrative in nature, illustrating the general effect that the presence of favorable enthalpic interactions between dissimilar brushes promotes their mixing and alters relaxation dynamics. However, universal analytical dependencies for the interpenetration profile or tribological characteristics are not derived in these works.

The interaction of two solvent-free brushes formed by mutually attracting polymers with a negative Flory–Huggins parameter will be the focus of the present theoretical study. Understanding this specific regime is crucial because it represents the fundamental opposite of the widely studied case: it features deep, homogeneous interpenetration. Practically, this regime is highly relevant for designing strong polymer adhesives, compatibilized interfaces in nanocomposites, and self-healing materials, where maximizing interfacial strength and chain interdigitation is the primary goal, rather than minimizing it for lubrication.

Furthermore, since the friction between sliding brushes is determined by the interaction of monomer units in the interpenetration zone, it is fundamentally important to understand how the width and structural organization of this zone depend on the chemical structure of the grafted macromolecules [14]. It is generally accepted that the shear stress in sliding brushes of flexible chains without entanglements exhibits two regimes of dependence on the sliding velocity: linear and sublinear [17]. In the linear friction regime, the width of the interpenetration zone and the distribution of the end segments of the grafted chains practically do not depend on the shear rate and retain their equilibrium values. Therefore, the friction force for dry brushes is proportional to the number of contacts—i.e., the integral of the brush overlap function [3].

For brushes with $\chi < 0$, this overlap integral is significantly enhanced, leading to distinct, high-friction and high-adhesion profiles that require rigorous theoretical quantification. Finally, the interaction of flat brushes serves as the foundational model for describing

the strong interfacial bonding and dispersion behavior of polymer-grafted nanoparticles in colloidal systems and nanocomposites.

2. Materials and Methods

A coarse-grained model of two interacting polymer brushes, composed of linear macromolecules grafted onto opposing flat substrates separated by a distance D is considered (Figure 1). The monomer units of the chains in both brushes are assumed to occupy the same unit volume a^3 . The monomers are connected by perfectly rigid bonds of length a . The entire space between the substrates is filled with two types of polymers, and the system is assumed to be strictly incompressible. The grafted polymers are characterized by the following structural parameters: the degree of polymerization N (identical for both polymer types) and the dimensionless grafting density of the chains $\sigma = a^2/s$ (where s is area of the grafting surface per unit one grafted chain). Due to the incompressibility condition, the grafting density σ is related to the distance D in our model by the following equation:

$$\sigma = \frac{D}{2aN} \quad (1)$$

Hereinafter, the linear size of the monomer unit, a is taken as the unit of length and $k_B T$ as the unit of energy, where k_B is the Boltzmann constant and T is the absolute temperature.

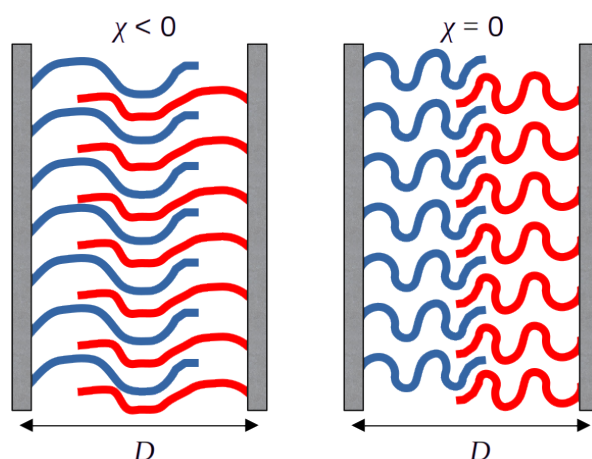


Figure 1. Schematic illustration of two interacting polymer brushes grafted onto opposing impenetrable surfaces at various Flory–Huggins interaction parameters.

To model the mutual interpenetration of the polymer brushes, the Scheutjens–Fleer numerical method [18] was employed. This approach utilizes a discrete lattice representation of the spatial domain. The space is modeled as a cubic lattice with a lattice spacing equal to the linear size of a monomer unit, a . The lattice sites are organized into layers parallel to the grafting surfaces, indexed as $z = 0, \dots, z_{max}$. The layers at $z = 0$ and $z = D + 1$ correspond to the grafting surfaces, whereas the anchor segments of the chains belonging to the opposing brushes are fixed in the layers at $z = 1$ and $z = D$, respectively. The volume fractions $\varphi_{1,2}(z)$ of the monomer units are assumed to be uniform within each individual layer and vary only along the z -direction.

The grafted macromolecules are treated as freely jointed chains subjected to an external effective field $u(z)$, which is induced by inter- and intramolecular interactions. Long-range spatial correlations are neglected. The overlap of multiple segments at a single lattice site is permitted but is heavily penalized by the incompressibility condition:

$$\varphi_1(z) + \varphi_2(z) = 1, \quad \forall z. \quad (2)$$

The free energy per unit area of the grafting surface is defined as the negative logarithm of the partition function of the grafted macromolecules in the effective chemical potential field $-\ln Q[u_{1,2}]$, minus the work done by this field $\sum_z u_{1,2}(z)\varphi_{1,2}(z)$, plus the interaction contribution $\chi \sum_z \varphi_1(z)\varphi_2(z)$:

$$F = -\sigma_1 \ln Q[u_1(z)] - \sigma_2 \ln Q[u_2(z)] - \sum_z u_1(z)\varphi_1(z) - \sum_z u_2(z)\varphi_2(z) + \chi \sum_z \varphi_1(z)\varphi_2(z) \quad (3)$$

Hereinafter, the subscripts 1 and 2 denote the parameters of the “left” and “right” interacting brushes, respectively, while χ represents the interaction parameter between the monomer units of the chains in these opposing brushes (negative values of χ favor mutual attraction between the brushes, whereas positive values of χ induce repulsion).

The volume fraction profile $\varphi(z)$, corresponding to the minimum of the free energy under the incompressibility constraint, is obtained by optimizing the following functional:

$$\mathcal{F} = F\{\varphi_{1,2}(z), u_{1,2}(z)\} + \sum_{z=1}^{z=D} \alpha(z)[\varphi_1(z) + \varphi_2(z) - 1], \quad (4)$$

where $\alpha(z)$ is the Lagrange multiplier field (a set of Lagrange multipliers).

The numerical minimization of this functional via gradient descent with respect to $u_{1,2}$, $\varphi_{1,2}$, and α enables the determination of the equilibrium volume fraction profiles of the monomer units in the brushes. All other properties of the systems under consideration are subsequently derived from these profiles. A detailed description of the computational algorithm can be found in Refs. [19,20]. The simulations presented in this work were performed using custom-developed software.

3. Results and Discussion

Numerical simulations demonstrate that under moderate compression, as the mutual attraction between the polymer brushes increases (i.e., as the Flory–Huggins parameter χ decreases from zero to negative values), the density profile undergoes a transition from a sigmoidal to a linear shape. Upon reaching a critical negative value of χ , the grafted chains extend all the way to the opposing grafting surfaces and overgrow them (see Figure 2A,B). Concurrently, the overlap functions, defined as the product of the density profiles of the two opposing brushes, also evolve as χ decreases, transforming from a narrow bell-shaped curve into a broader parabolic profile. Furthermore, under conditions of strong compression (at low grafting densities), the density profiles become nearly uniform, approaching a mean volume fraction of 0.5 for each individual brush (see Figure 2C,D).

The primary characteristic of brush overlap that governs their lubrication properties is the overlap integral, which represents the mean number of inter-brush contacts per unit area

$$\Gamma = \int_0^D \varphi_1(z)\varphi_2(z)dz \quad (5)$$

Another crucial characteristic is the width of the brush overlap zone, δ , which can be defined as

$$\delta \sim \frac{\Gamma}{\phi_m}, \quad (6)$$

where ϕ_m is the total volume fraction of the polymer material confined between the grafting surfaces. Since the total polymer volume fraction in solvent-free brushes is unity ($\phi_m = 1$) across all layers, the overlap width is proportional to the overlap integral, $\delta \sim \Gamma$. The overlap integral exhibits non-monotonic behavior as the chain grafting density σ increases, passing through a distinct maximum (see Figure 3). Under conditions of strong brush compression (i.e., at low grafting densities σ), the width of the overlap zone is strictly governed by the distance D between the grafting planes. Because D is directly proportional

to σ in the incompressible limit, the overlap integral Γ increases linearly with σ up to its maximum value. This linear regime persists until the chain stretching becomes sufficiently pronounced, at which point the effective width of the overlap zone becomes smaller than the inter-surface distance D .

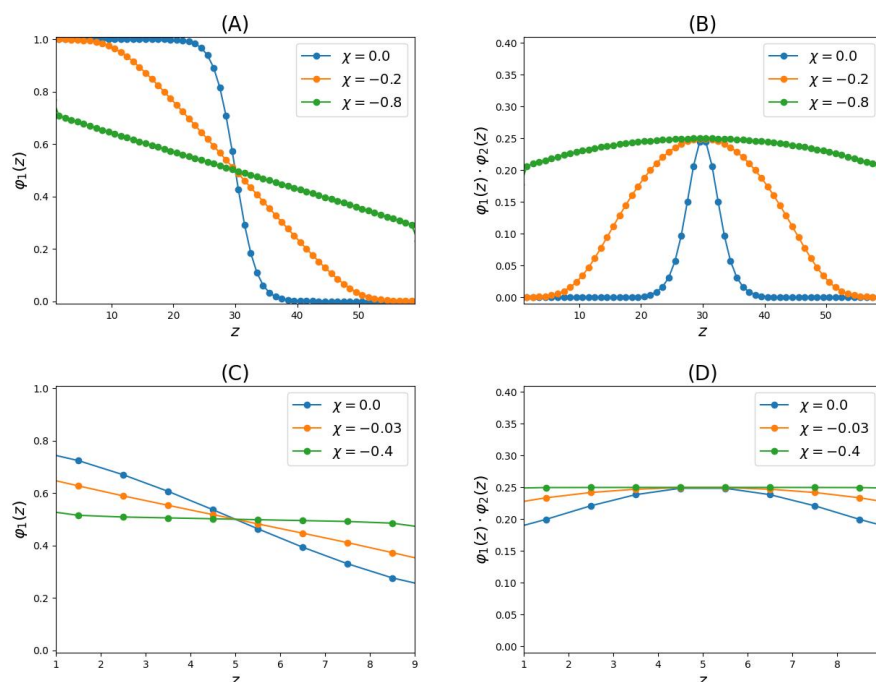


Figure 2. Volume fraction profiles of monomer units of one of the interacting brushes ((A) for $D = 60$ and (C) for $D = 10$) and the corresponding overlap functions (B,D). In all cases, the degree of polymerization of the grafted chains is $N = 200$.

The dashed line in Figure 3, representing the linear dependence at low grafting densities, is given by $\Gamma = 0.25D = 0.5\sigma N$. As the mutual attraction between the brushes increases (i.e., as χ becomes more negative), the position of the maximum naturally shifts toward larger values of the overlap integral. Thus, maximum inter-brush adhesion can be achieved by tailoring the grafting density during the synthesis process. Alternatively, for a predetermined grafting density, the adhesion can be optimized by tuning the Flory–Huggins interaction parameter, for instance, through temperature variations.

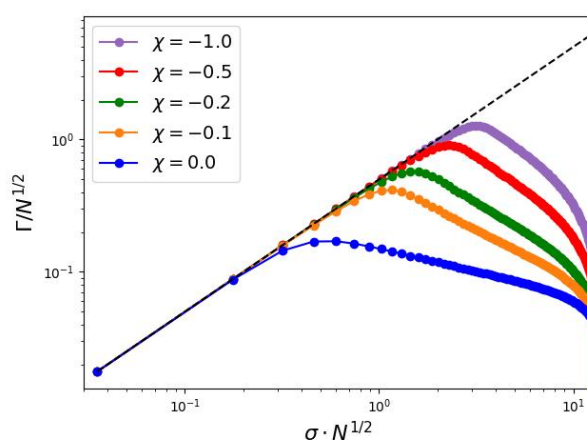


Figure 3. Overlap integral as a function of polymer grafting density in reduced double-logarithmic coordinates. The dashed line indicates a linear scaling. In all cases $N = 200$.

To provide a more detailed physical interpretation, how the properties of solvent-free mutually attracting brushes depend on their composition, we have developed an analytical theory within the mean-field approximation, assuming Gaussian stretching of the grafted chains. We assume that both brushes penetrate each other by distance Δ beyond the midplane located at $z = D/2$. The free energy functional (per unit area) for the pair of dry monodisperse brushes has the following form [10]:

$$F = 2\sigma \int_0^{D/2+\Delta} dz' \rho(z') \int_0^{z'} dz E(z', z) + \int_0^D dz f(\varphi_1(z), \varphi_2(z)). \quad (7)$$

Here, the first integral represents the elastic free energy, $E(z', z) = \frac{dz}{dn}$ is the local strain provided dz' is the end monomer position, $dz' = z(N)$, $\rho(z')$ is the probability density for the end monomer positions, and the factor of 2 reflects the symmetry of the two brushes.

In order to avoid dealing with an additional constraint imposing dense packing, we start with a system of small but finite compressibility κ , and then we take the limit $\kappa \rightarrow 0$. The second integral gives the density-dependent part of the free energy, and the free energy per unit volume, f , has two contributions:

$$f(\varphi_1(z), \varphi_2(z)) = f_{dense}(\varphi_{tot}) + \chi \varphi_1(z) \varphi_2(z), \quad (8)$$

where $\varphi_{tot} = \varphi_1 + \varphi_2$. The first term describes inert brushes and ensures the (approximate) dense packing condition, while the second term introduces mutual interaction (attraction for $\chi < 0$).

The connection between the chain end probability density and the partial density profile has the form

$$\varphi_1(z) = \sigma \int dz' \rho(z') \int_0^{z'} \frac{dz}{E(z', z)}, \quad (9)$$

with a natural modification for $\varphi_2(z)$.

Instead of solving the variational problem from scratch, we exploit the central result valid for any situation involving monodisperse brushes: the local chemical potential $\mu = \frac{\partial f}{\partial \varphi}$ must be a quadratic function of the coordinate counted from the grafting surface,

$$\mu = \lambda - \frac{3\pi^2}{8N^2} z^2, \quad (10)$$

where λ is a Lagrange multiplier originating from the normalization condition for $\rho(z')$.

In our case we have two different (although symmetric) chemical potential profiles, and we focus on that for the left brush:

$$\mu_1 = \frac{\partial f}{\partial \varphi_1} = \frac{\partial f_{dense}}{\partial \varphi_{tot}} + \chi \varphi_2. \quad (11)$$

The exact form of the free energy density ensuring the approximate dense packing condition is not important, so we expand the chemical potential about the point $\varphi_{tot} = 1$ up to the first order:

$$\mu_{dense}(\varphi_{tot}) \simeq \mu_{dense}(1) + \frac{\partial \mu_{dense}}{\partial \varphi_{tot}} (\varphi_{tot} - 1). \quad (12)$$

Using the relation for the osmotic pressure

$$\Pi = \varphi_{tot} \mu_{dense} - f_{dense}(\varphi_{tot}), \quad (13)$$

one finds the connection between the compressibility $\kappa = -\frac{1}{\varphi_{tot}} \frac{\partial \varphi_{tot}}{\partial \Pi}$ and the partial derivative $\frac{\partial \mu_{dense}}{\partial \varphi_{tot}}$ as

$$\frac{\partial \mu_{dense}}{\partial \varphi_{tot}} = \varphi_{tot}^{-2} \kappa^{-1} \simeq \kappa^{-1}, \quad (14)$$

leading to

$$\mu_{dense}(z) \simeq \mu_0 + \kappa^{-1}(\varphi_1(z) + \varphi_2(z) - 1), \quad (15)$$

where

$$\mu_0 = \mu_{dense}(\varphi_{tot} = 1). \quad (16)$$

Finally, the chemical potential profile for the monomers of the left brush satisfies the equation

$$\mu_1(z) = \mu_0 + \kappa^{-1}(\varphi_1(z) + \varphi_2(z) - 1) + \chi \varphi_2(z) = \lambda - \alpha z^2, \quad (17)$$

where $\alpha = \frac{3\pi^2}{8N^2}$.

We introduce the coordinate $y = z - \frac{D}{2}$ counted from the midplane, and we write the partial brush density profiles as a series in powers of y :

$$\varphi_1(y) = \sum_{k=0}^{\infty} b_k y^k. \quad (18)$$

Due to mirror symmetry,

$$\varphi_2(y) = \varphi_1(-y) = \sum_{k=0}^{\infty} (-1)^k b_k y^k. \quad (19)$$

At the midplane,

$$\varphi_1(0) = \varphi_2(0) = b_0 = \frac{1}{2}. \quad (20)$$

Equation (17) now has the form

$$\mu_0 + 2\kappa^{-1} \sum_{k=1}^{\infty} b_{2k} y^{2k} + \chi \sum_{k=0}^{\infty} (-1)^k b_k y^k = \lambda - \alpha(y + D/2)^2. \quad (21)$$

Finally, equating separate terms with different powers of y we obtain

$$\begin{aligned} \mu_0 + \frac{\chi}{2} &= \lambda - \frac{\alpha}{4} D^2, \\ b_1 &= \frac{\alpha D}{\chi}, \\ b_2 &= \frac{\alpha \kappa}{-2 - \kappa \chi}, \\ b_k &= 0, \quad k \geq 3. \end{aligned} \quad (22)$$

The first equation connects the Lagrange multiplier λ to a particular chemical potential value μ_0 but is of no practical consequence. Note that all the higher-order terms drop out. Moreover, in the limit of vanishing compressibility, the coefficient $b_2 \rightarrow 0$, and the partial density profile φ_1 simplifies to a linear function in the interpenetration zone:

$$\varphi_{1,2}(y) = \frac{1}{2} \pm \frac{\alpha D}{\chi} y = \frac{1}{2} \pm \frac{3\pi^2 D}{8\chi N^2} \left(z - \frac{D}{2} \right). \quad (23)$$

Importantly, the attraction-driven interpenetration is a strong effect that scales linearly with N at fixed grafting density σ and attraction parameter χ , so the interpenetration zone constitutes a finite fraction of the total brush thickness even in the asymptotic limit $N \rightarrow \infty$.

For inert brushes ($\chi = 0$), Equation (25) suggests that the interpenetration length vanishes, which is a known artifact of the strong stretching approximation. Actually, fluctuations lead to non-zero interpenetration even for inert brushes, but the interpenetration length scales as $\delta \sim \left(\frac{N}{\sigma}\right)^{1/3}$, which is weaker than the attraction-driven interpenetration in Equation (25) [10].

A theoretical description of the density profiles in the case of inert brushes ($\chi = 0$) with fluctuation-driven interpenetration was proposed in Ref. [3] and has the following form:

$$\varphi_{1,2}(z) = \frac{1}{1 + \exp[\pm 5.3 D^{1/3} N^{-2/3} (z - D/2)]} \quad (24)$$

Here, the numerical prefactor in the exponent is a best fit parameter. The validity of the obtained analytical Equations (23) and (24) is confirmed by excellent agreement with the results of numerical simulations (see Figure 4).

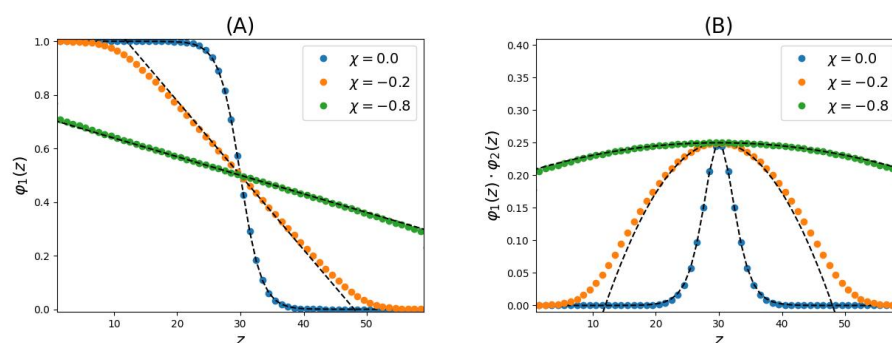


Figure 4. Volume fraction profiles of monomer units of one of the interacting brushes (A) and the corresponding overlap functions (B). In all cases, the degree of polymerization of the grafted chains is $N = 200$ and distance between grafting surfaces is $D = 60$. The dashed lines represent the corresponding analytical curves.

In the case of mutually attractive brushes with negative χ , the attraction-driven penetrating tail density decreases linearly with distance from the midplane. The density vanishes at $y = \Delta$, which gives

$$\Delta = -\frac{\chi}{2\alpha D} = \frac{2}{3\pi^2} \left(-\frac{\chi N}{\sigma} \right). \quad (25)$$

Clearly, the last result applies if interpenetration is partial (the penetrating tail does not reach the opposing wall). Otherwise, both $\varphi_1(y)$ and $\varphi_2(y)$ are positive everywhere, the situation we refer to as full interpenetration.

The overlap function has the form of an inverted parabola:

$$\varphi_1(y)\varphi_2(y) = \frac{1}{4} \left(1 - \left(\frac{y}{\Delta} \right)^2 \right). \quad (26)$$

Integrating over the interpenetration zone $-\Delta \leq y \leq \Delta$ gives the overlap integral

$$\Gamma = \frac{\Delta}{3} = \frac{2}{9\pi^2} \left(-\frac{\chi N}{\sigma} \right). \quad (27)$$

In fact, the strong stretching approximation is able to capture only the effects that scale linearly with N . In the following, we show that capturing both interpenetration mechanisms

simultaneously is very difficult. For the purpose of a semi-quantitative description, we assume that the two mechanisms driving the interpenetration are simply additive, and we propose an empirical formula which describes the overlap integral in the case of partial interpenetration rather accurately:

$$\Gamma = 0.148 \left(\frac{N}{\sigma} \right)^{1/3} + \frac{2}{9\pi^2} \left(-\frac{\chi N}{\sigma} \right). \quad (28)$$

The additivity assumption overestimates the overlap integral if the two interpenetration mechanisms are comparable in strength. Apart from that, extra deviations are due to two factors:

1. At small grafting densities (large N/σ), interpenetration is decreased by the opposing wall effect.
2. At large grafting densities (small N/σ), interpenetration is decreased by a non-linear elastic response (finite chain extensibility effect).

For a fixed value of the interaction parameter χ , the overlap integral Γ is predicted to be a function of a single variable N/σ as illustrated in Figure 5.

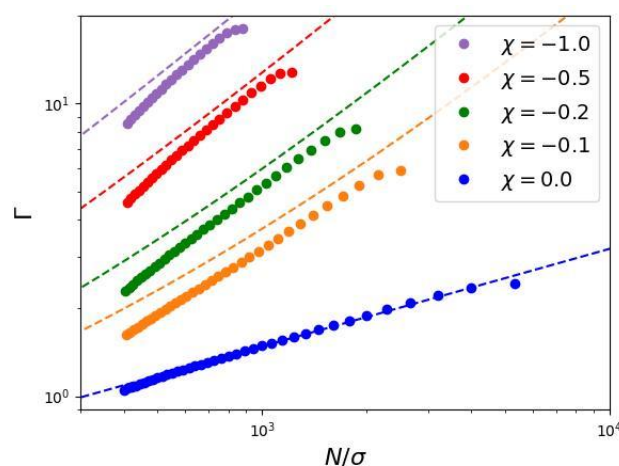


Figure 5. Values of Γ obtained from numerical simulations (at $N = 200$) compared with the analytical theory (Equation (28)) within the range of applicability of the theoretical model.

The additive structure allows one to define two regimes depending on whether interpenetration is entropy- or energy-dominated. Fluctuation-dominated interpenetration scales as $\sim N^{1/3}$ at fixed grafting density σ , while attraction-dominated interpenetration asymptotically scales as $\sim N$ and constitutes a finite fraction of the isolated brush thickness.

The crossover between the fluctuation- and attraction-dominated regimes is defined by equating the two terms. The result can be expressed as

$$-\chi N \approx 0.666\pi^2 \xi^{2/3}, \quad (29)$$

where

$$\xi = \sigma N^{1/2} \quad (30)$$

is the chain stretching parameter, which has the meaning of a typical brush chain extension in comparison to its Gaussian coil size.

We identify two other distinctive regimes as partial interpenetration (the individual brush density profile not reaching the opposing wall) and full interpenetration (the density profile significantly affected by the opposing wall). The crossover condition is given by

$$\Gamma \sim \sigma N. \quad (31)$$

or

$$\varphi_1(z=0) = 1 \quad (32)$$

In the attraction-dominated interpenetration, this has the form

$$-\chi N = \frac{3\pi^2}{2} \xi^2, \quad (33)$$

while in the entropy-dominated scenario, it reduces simply to

$$\xi \sim 1. \quad (34)$$

Finally, the crossover between the entropy- and energy-dominated interpenetration in the case of full interpenetration is naturally given by

$$-\chi N \sim 1. \quad (35)$$

The regimes and crossover boundaries are summarized in the $(-\chi N, \xi)$ diagram shown in Figure 6.

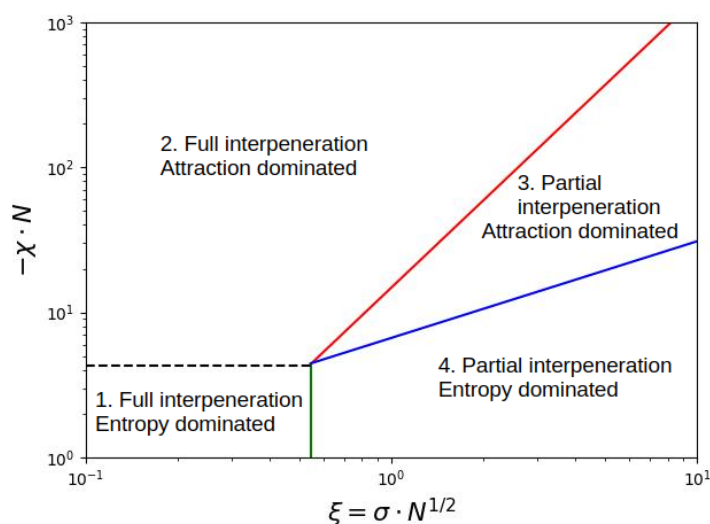


Figure 6. Diagram illustrating various overlap regimes of solvent-free polymer brushes. Zones 1 and 2 correspond to $\Gamma \sim N\sigma$, Zone 3 corresponds to $\Gamma \sim -\chi N/\sigma$ and Zone 4 to $\Gamma \sim (N/\sigma)^{1/3}$. The contour lines are color-coded as follows: red line represents $|\chi|N \sim \xi^2$, blue line represents $|\chi|N \sim \xi^{2/3}$.

To connect the regimes identified in the phase diagram (Figure 6) with the numerical SCF results, we note that the density profiles shown in Figures 2 and 4 correspond to representative points in different zones. Specifically, for the case $N = 200$ and $D = 60$, the profile obtained at $\chi = -0.2$ (i.e., $-\chi N = 40$) is representative of Zone 3 (partial, attraction-dominated interpenetration): the density profile is linear in the overlap region but does not reach the opposing grafting surface. In contrast, the profile at $\chi = -0.8$ (i.e., $-\chi N = 160$) falls into Zone 2 (full, attraction-dominated interpenetration): the chain ends reach the opposing wall and the density profile is essentially linear across the entire gap. These two representative cases are marked in Figure 6 and illustrate the crossover from partial to full brush interpenetration as $|\chi|N$.

Choosing a particular pair of mutually attracting polymers fixes the value of χ . At fixed grafting density, the overlap integral Γ is a monotonically increasing function of N (asymptotically

totically linear). Since both D and Γ grow linearly with N , full/partial penetration regimes remain asymptotically invariant under changes in the chain length at fixed χ and σ .

However, if instead N is fixed and the grafting density is varied, the overlap integral is non-monotonic, reaching a maximum $\Gamma_{max} \sim N\chi^{1/2}$ at the crossover condition of Equation (33), $\sigma \sim \chi^{1/2}$.

Numerical simulations demonstrate that the grafting density corresponding to the maximum brush overlap is a universal function of χ , which is practically independent of the degree of polymerization of the grafted chains (see Figure 7). Furthermore, the simulation results are in good agreement with the predictions of the proposed analytical theory:

$$\sigma(\Gamma_{max}) = \sqrt{-2\chi/(3\pi^2)}, \quad -\chi N \gg 1. \quad (36)$$

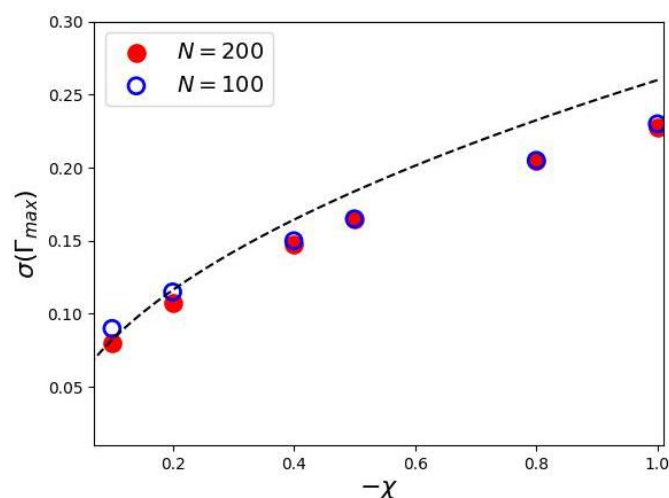


Figure 7. Grafting density corresponding to the maximum overlap of the brushes as a function of the Flory–Huggins interaction parameter between their monomer units. The dashed line corresponds to the prediction of the analytical theory.

4. Conclusions

In this work, we have theoretically investigated the equilibrium structure and mutual interpenetration of two opposing solvent-free polymer brushes with a negative Flory–Huggins interaction parameter ($\chi < 0$). By combining numerical Scheutjens–Fleer self-consistent field calculations with a newly developed analytical mean-field theory, we have provided a comprehensive description of how strong mutual attraction alters the structural organization of the interpenetration zone.

Our numerical simulations demonstrate that strong enthalpic attraction fundamentally transforms the monomer density profiles from a sigmoidal to a linear shape, while the overlap function evolves into a broad inverted parabola. To capture these effects analytically, we derived explicit expressions for the partial density profiles in the limit of vanishing compressibility, confirming their linear dependence on the distance from the midplane for strongly attracting brushes.

We formulated an empirical additive model for the overlap integral that seamlessly bridges the weak entropy-driven fluctuation interpenetration (scaling as $N^{1/3}$) and the strong energy-driven attraction interpenetration (scaling as N). Based on these scaling laws, we constructed a comprehensive phase diagram in the $(-\chi N, \xi)$ plane, clearly identifying the crossover boundaries between fluctuation- and attraction-dominated regimes, as well as between partial and full interpenetration states.

Furthermore, we revealed that, at a fixed chain length, the overlap integral exhibits a pronounced non-monotonic dependence on the grafting density, passing through a distinct

maximum. We derived an exact analytical expression for the optimal grafting density that maximizes inter-brush adhesion. Crucially, this optimal value is shown to be a universal function of the interaction parameter χ and is practically independent of the grafted chains length N .

Finally, we note that while the strict incompressibility condition couples the system size, grafting density, and chain length, the main qualitative results of this study remain valid for weakly compressible systems. In such cases, the fundamental balance between elastic chain stretching and enthalpic attraction still governs the interpenetration, preserving the linear density profiles and the same core scaling laws, albeit with a slight smearing of the density interfaces.

These findings provide a theoretical framework for controlling the tribological and adhesive properties of dry polymer interfaces. The ability to predict and maximize the overlap integral by tuning either the grafting density during synthesis opens new avenues for the design of strong polymer adhesives, compatibilized interfaces in nanocomposites, and self-healing materials.

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Abbreviations

The following abbreviations are used in this manuscript:

MD	molecular dynamics
PCL	polycaprolactone
PMMA	polymethyl methacrylate
PPO	poly(2,6-dimethyl-1,4-phenylene oxide)
PS	polystyrene
PVC	polyvinyl chloride
PVDF	polyvinylidene fluoride
SCF	self-consistent field

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