1. Introduction

Branched polymers play important roles in many biological and industrial systems, notable among them is the single stranded RNA (ssRNA) that in solution takes on a branched secondary structure [1–10]. Recent experiments on viruses show that some viral RNAs, in particular, assume highly branched structures [11, 12]. The physics of polymer adsorption on different kinds of interfaces has, specifically, attracted a lot of interest for over half a century [13–23, 24]. In particular, it has been shown that polymer topology can affect the thermodynamic behavior of polymers near surfaces [25]. More recently the adsorption of RNA onto spherical gold nano-particles has been the focus of intense research because of its potential application in drug delivery or gene therapy [26–34].

RNA is considered an annealed branched polymer mainly due to the fact that the base-pair binding in RNA is often weak enough that the branching structure can change due to thermal fluctuations [2, 35]. Beyond the adsorption of RNA onto nanoparticles, the behavior of annealed branched polymers next to surfaces of complex geometries is intriguing. Despite the presence of several excellent books and review articles, the impact of branching on adsorption of biopolymers at planar or rough substrates is yet not well-studied.

Several experiments compare the efficiency—directly connected to the free energy—of encapsidation of linear polymers and viral RNAs by virus capsid proteins [36–38]. Field theoretic models have been used extensively to calculate the free energy of linear polymers [39–47]. In a 1972 seminal paper de Gennes noted an equivalence between the statistics of a self-avoiding polymer and the $\mathcal{O}(n)$ limit of an $\mathcal{O}(n)$ model of a magnet [48], see appendix A for a review of an $\mathcal{O}(n)$ model. Using this observation, which relates a mathematically interesting but unphysical limit for the model of a magnet to the statistics of polymers, it became possible to use the tools of statistical field theory to describe the physical properties of a polymer solution. Later, de Gennes field theory was expanded to describe the statistics of annealed branched polymers [49, 50].

In this paper we use a mean field theory to study the adsorption of annealed branched polymers on different types of good solvents, we observe that as branching density increases, surface tension decreases. However, we find a coupling between the branching density and curvature in that a further lowering of surface tension occurs when the wall curves towards the polymer, but the amount of lowering of surface tension decreases when the wall curves away from the polymer. We find that for branched polymers confined into spherical cavities, most of branch-points are located in the vicinity of the interior wall and the surface tension is minimized for a critical cavity radius. For branched polymers next to sinusoidal surfaces, we find that branch-points accumulate at the valleys while end-points accumulate at the peaks.

Keywords: branched polymer, polymer field theory, polymer adsorption

(Some figures may appear in colour only in the online journal)
of surfaces from a semi-dilute polymer solution in a good solvent. We study the effect of curvature by examining the adsorption onto the exterior and interior of a spherical surface, and investigate the impact of roughness by examining the adsorption onto a sinusoidal surface. Instead of considering a random roughness, we employ a grating geometry because of its enormous mathematical simplifications and the fact that it has been shown that qualitatively the essential features of the results are the same [23, 42].

By numerically solving the relevant nonlinear equations we find that compared to the adsorption to a flat wall, branching density, surface tension, and the monomer density all increase if the polymer is adsorbed onto the interior wall of a spherical cavity but decrease if adsorbed on the exterior surface of the sphere. While our results show that surface tension always decreases as branching density increases independent of the geometry of the wall, we find the interplay of curvature and branching density conspires to further lower the surface tension when the wall curves toward the polymers but lessens the amount of decrease in the surface tension when the wall curves away from the polymer. In the limit of large spheres, we solve the nonlinear equations perturbatively, which match the numerical results. Furthermore, in the case of sinusoidal surfaces, we find inhomogeneity in the branching density as it increases in the valleys but decreases in the peaks.

The remainder of this paper is organized as follows. In the first section we present our mean field approach and in the following section we use this method to investigate the impact of branching combined with surface curvature on polymer adsorption. In particular, we will examine what effect the branching structure has on the adsorption of polymers to nano-spheres and sinusoidal surfaces. We will finish with a brief summary and present our main conclusions.

In the appendix, for completeness and pedagogical reasons, we derive a simple field theoretical model for a branched polymer by revisiting the field theory developed by Isaacson and Lubensky [49] for branched polymers and will spell out in detail the equivalence between the polymer statistics and the $n \to 0$ limit of the $O(n)$ model.

2. Mean field approximation

To describe a branched polymer on a lattice, we assume the polymer system consists of branch-points and end-points lying on the lattice sites, and bonds that join neighboring lattice sites. We treat the system as an annealed branched polymer, so the structure of the branched polymer is not fixed. For simplicity, we assume that all branch-points are exactly of order three because all higher order branch-points can be considered as many order three branch-points in close proximity to each other. For example, two order three branch-points close together will behave a very similar way to an order four branch-point. The quantities that describe such a polymer system are: (i) $N_o$, the number of polymers; (ii) $N_b$, the number of bonds; (iii) $N_e$, the number of endpoints; (iv) $N_l$, the number of branch-points; and (v) $N_l$, the number of loops. There is a constraint [49] relating most of these quantities such that

$$2(N_o - N_l) = N_l - N_b.$$  \hspace{1cm} (1)

In this paper, we consider a system of branched polymers with no loops and set $N_l = 0$.

The primary statistical quantity of interest is the multiplicity $\Omega(N_o, N_b, N_e; V)$, defined as the number of ways to arrange a polymer system of $N_b$ bonds, $N_l$ end-points, and $N_e$ branch-points on a lattice that occupies a volume $V$. This quantity is equivalent to the number of microstates for the microcanonical ensemble. From the multiplicity, we can form the grand canonical partition function

$$\Xi(K, f_1, f_2; V) = \sum_{N_o, N_b, N_e} K^{N_o} f_1^{N_b} f_2^{N_e} \Omega(N_o, N_b, N_e; V),$$  \hspace{1cm} (2)

where $K, f_1$, and $f_2$ are the fugacities for the bonds, end-points, and branch-points respectively. Note that we use equation (1) along with the assumption that $N_l = 0$ to eliminate the dependence upon $N_l$. From this definition it is simple to derive expressions for the number of bonds, end-points, and branch-points as derivatives of the logarithm of the grand partition function

$$N_o = K f_1 \frac{\partial}{\partial K} \ln \Xi(K, f_1, f_2),$$  \hspace{1cm} (3)

$$N_b = f_1 \frac{\partial}{\partial f_1} \ln \Xi(K, f_1, f_2),$$  \hspace{1cm} (4)

$$N_e = f_2 \frac{\partial}{\partial f_2} \ln \Xi(K, f_1, f_2).$$  \hspace{1cm} (5)

Following the idea of de Gennes [48], and using the methods of Lubensky and Isaacson [49], we equate the grand partition function for the branched polymers system with the $n \to 0$ limit of the partition function of an $O(n)$ model of a magnet

$$\Xi(K, f_1, f_2; V) \approx Z(K, f_1, f_2; V).$$  \hspace{1cm} (6)

The partition for the $O(n)$ model of a magnet can be written as a function integral over a continuous field $\psi(x)$

$$Z(K, f_1, f_2; V) = \int D\psi \exp(-\beta \mathcal{H}(\psi, K, f_1, f_2; V)).$$  \hspace{1cm} (7)

where $\mathcal{H}$ is the effective Hamiltonian

$$\mathcal{H}(\psi, K, f_1, f_2; V) = \sum_x \left( \frac{1}{2} \psi(x) \delta_{\psi(x), \psi(x')} - K \frac{1}{2} |\psi(x')|^2 ight) + \frac{K^2}{8} |\psi(x)|^4 - f_1 \sqrt{K} \psi(x) - \frac{f_2 K^3}{6} \psi^3(x).$$  \hspace{1cm} (8)

We emphasize here that the parameters $K, f_1$ and $f_2$ take on different meanings for the $O(n)$ model of the magnet (see appendix A). For example, the $K$ parameter represents the coupling constant between the nearest neighbors spins in the $O(n)$ model of a magnet and the $\psi$ field is the average magnetization in a small region for the magnet. However, the $\psi$ field in equation (8) is proportional to the monomer density for the branched polymer. The first term in equation (8) is an
entropic term that smoothes out the $\psi(x)$ field. The $\delta(x-x')$ in the first term is the inverse of the nearest neighbor number $\kappa_{x,x'}$, defined as 1 if $x$ and $x'$ are neighboring sites on a lattice and 0 otherwise. The second term in equation (8) proportional to $|\psi|^2$ is due to the nearest neighbor attraction, which tends to increase the $\psi(x)$ field. The third term proportional to $|\psi|^4$ is repulsive representing the self-avoiding nature of the polymer, and leads to a decrease in the $\psi(x)$ field. The fourth and fifth terms proportional to $\psi(x)$ and $\psi(x')$ are both attractive, and show that both branch-points and endpoints serve to increase the $\psi(x)$ field. It is the balance of these attractive and repulsive terms that creates a well-defined finite $\psi(x)$ field in equilibrium. For completeness, as well as pedagogical reasons, we show the derivation of the equivalence between the grand canonical partition function, equation (2), for the polymer system and the partition function for the $n \to 0$ limit of the $\mathcal{O}(n)$ model and all relevant approximations for finding the effective Hamiltonian, equation (8), in appendix A.

We now make a mean field approximation and assume that the value of the field $\psi(x)$ is uniform and is well approximated by its average value $\psi_0$. Thus the sum over the nearest neighbors simply becomes

$$\sum_x \delta(x-x') \psi(x') = z \psi_0,$$

with $z$ the number of nearest neighbors or coordination number. The inverse of the nearest neighbor delta function is then simply the reciprocal of the coordination number $\sum_x \delta(x-x') = 1/z \psi_0$. So in the mean field theory, the grand canonical partition function is the exponential of the effective Hamiltonian evaluated at its minimum

$$\Xi(K,f_1,f_2;V) \approx e^{-\beta H(K,f_1,f_2;V)},$$

with $\psi_0$ found by minimizing equation (8), $\delta H \delta \psi |_{\psi_0} = 0$,

$$\left(\frac{1}{z} - K\right) \psi_0 - f_1 \sqrt{K} - \frac{f_3 K^2 z}{2} \psi_0 + \frac{K^2 z^2}{2} \psi_0 = 0.$$  (11)

From statistical mechanics we can identify the grand potential, $\beta \Phi_\Xi(K,f_1,f_2;V) = -\ln[\Xi(K,f_1,f_2;V)]$ using equations (8)–(10),

$$\beta \Phi_\Xi(K,f_1,f_2;V) = \frac{V}{a^3} \left[ \frac{1}{2} \left( \frac{1}{z} - K \right) \psi_0^2 - f_1 \sqrt{K} \psi_0 - \frac{f_3 K^2 z}{2} \psi_0^2 + \frac{K^2 z^2}{2} \psi_0^2 \right].$$

with $a$ the lattice spacing. Inserting equation (12) in equation (3) and using equation (11) we find the average monomer density

$$c_b = N_b/V = \frac{\psi_0^2}{2z a^3}.$$  (13)

At this point it is convenient to define a new field $\phi(x)$ such that in the mean field approximation the average value $\phi_0^2 = \psi_0^2 / 2 z a^3$ is the monomer density. The grand potential written in terms of the new field is

$$\frac{\beta \Phi_\Xi(K,f_1,f_2;V)}{V} = \left(1 - \frac{z K}{2} \right) \phi_0^2 - f_1 \sqrt{\frac{2 z K}{a^3}} \phi_0^2 - \frac{1}{6} f_3 (2 z a K)^{3/2} \phi_0^4 + \frac{1}{2} K^2 z^2 a^3 \phi_0^4.$$  (14)

By comparing equation (14) with the expression for the grand potential for a linear polymer in good solvent [42], we can identify $r = (1 - z K)$ as the chemical potential of monomers (such that $\partial \beta \Phi_\Xi / \partial r = c_b$) and $v = K^2 z^2 a^3$ as the excluded volume. It is also convenient to absorb $\sqrt{2 z K}$ and $(2 z K)^{3/2}$ constants in the end and branch point fugacities, respectively such that the grand potential can be written in a much simpler form

$$\frac{\beta \Phi_\Xi(K,f_1,f_2;V)}{V} = r \phi_0^2 - f_1 \sqrt{a^3} \phi_0^2 - \frac{f_3}{6} \sqrt{a^3} \phi_0^4 + \frac{v}{2} \phi_0^4.$$  (15)

The parameters $f_1$ and $f_3$ are to physical quantities. Using equations (4) and (5), we find the end-point and branch-point densities

$$c_1 = \frac{f_1}{\sqrt{a^3}} \phi_0^2,$$

$$c_3 = \frac{1}{6} f_3 \sqrt{a^3} \phi_0^4.$$  (17)

3. Results and discussion: branched polymers adsorption onto different surfaces

We now apply the field theory presented in the previous section to a semi-dilute system of annealed branched polymers and investigate their adsorption to different surfaces. More specifically, we consider a solution of branched polymers with a monomer density $c_b$, where the polymers all have a fixed length $L$, and a tunable average branching number $N_b$.

The adsorption mean field energy of the branched polymer, $F - F_0$ can then be written as

$$F - F_0 = -\gamma a^3 \int dS \phi^2 + \int dV \left( \frac{\phi^2}{6 \beta} \left( \nabla \phi^2 \right)^2 + \frac{1}{2} \frac{v}{\beta} (\phi^4 - c_b^2) \right)$$

$$- \frac{1}{\beta a^3} \left( f_1 (\phi - c_b^{1/2}) + f_3 a^3 (\phi^3 - c_b^{3/2}) \right).$$  (18)

The first term in equation (18) is a surface integral that gives the contact energy between the surface and the polymer. The first term in the volume integral is associated with the entropic cost of a non-uniform polymer distribution [51]. The rest of the terms in equation (18) are related to the free energy of a branched polymer in mean field approximation, see equation (15).

Considering the constraint that the total number of monomers is fixed

$$\int dV \, \phi^2 = \text{constant} = N,$$  (19)
Equation (18) can be rewritten as

\[ F - F_0 = -\gamma a^3 \int dS \phi^2 + \int dV \left( \frac{a^2}{6\beta} \nabla^2 \phi^2 + \frac{1}{2} \nu (\phi^2 - c_b^2) \right) - \frac{1}{2\sqrt{a^3}} \left( f_1(\phi - c_b^2) + f_2 \frac{a^3}{6} (\phi^3 - c_b^3/2) \right) - \lambda(\phi^2 - c_0) \]

(20)

where \( \lambda \) is the Lagrange multiplier.

Minimizing equation (20) with respect to the field \( \phi(x) \) gives the following Euler–Lagrange equation

\[ \frac{a^2}{6} \nabla^2 \phi = -\lambda \phi + \nu \phi^3 - \frac{1}{2\sqrt{a^3}} \left( f_1 + \frac{a^3}{2} f_2 \phi^2 \right) \]

(21)

subject to the boundary condition

\[ [\hat{n} \nabla \phi + (6/\kappa) \phi]_v = 0 \]

(22)

For simplicity, we rescale the Lagrange multiplier \( \tilde{E} = \frac{6\lambda}{a^2} \) and introduce a length that characterizes the strength of the attraction between the surface and monomers as \( \kappa^{-1} = \frac{1}{6\nu} \). The other boundary condition is natural, far from the surface the field should be uniform, \( \nabla^2 \phi \to 0 \), and on take on the bulk value \( \phi(x) \to \sqrt{c_b} \). Using equation (21), the Lagrange multiplier can be written as

\[ E = \frac{6}{\alpha} \left( \nu c_b - \frac{1}{2} c_1 - \frac{3}{2} c_3 \right) \]

(23)

where \( c_1 = f_1^{1/2} \sqrt{a^3} \) and \( c_3 = f_3^{1/2} \sqrt{a^3} c_b^{3/2} / 6 \) are respectively the end-point and branch-point concentrations far from the surface. For long polymers with no loops in which \( N_b = N_l + 2 \), the second and third terms in equation (23) correspond to the ratio of the end-points and branch-points to monomers. To make all the quantities dimensionless, we rescale the field with respect to the bulk value \( \theta(x) = \phi(x) / \sqrt{c_b} \) and the spatial coordinate with respect to the Edwards correlation length [52]

\[ x = \xi_E \]

where \( \xi_E = \frac{a}{\sqrt{\kappa \nu}} \), the equation of motion simply becomes

\[ \nabla^2 \theta = 2(\theta^3 - \theta) + A_1(\theta - 1) + 3A_3(\theta - \theta^2) \]

(24)

with \( A_1 = (c_1/c_b)(\nu c_b) \), \( A_3 = (c_3/c_b)(\nu c_b) \). The \( A_1 \) and \( A_3 \) quantities measure the relative importance of the branching structure of the polymer to the steric effect or excluded volume interaction between monomers in solution. The numerators \( c_1/c_b \) and \( c_3/c_b \) are the ratios of the concentrations of endpoints and branch-points to the total number of monomers, respectively. For large polymers, these ratios can approach 1/2 for a maximally branched polymer. The denominator \( \nu c_b \) is a filling fraction of the polymer; dilute solutions will have small values of \( \nu c_b \), and a dense polymer system with no solvent will have a value of one. With the new scaled coordinates, the boundary conditions become

\[ \left[ \frac{\partial \theta}{\partial n} + \tilde{\kappa} \theta \right]_v = 0 \]

(25)

\[ \lim_{x \to \infty} \theta = 1 \]

(26)

with \( \tilde{\kappa} = \kappa \xi_E \). In terms of the new mean-field order parameter, \( \tilde{\theta} \), we can rewrite equation (20), the adsorption energy, as

\[ \tilde{F} - \tilde{F}_0 = \frac{a^2}{6\beta} \xi_E c_b \left( -\tilde{\kappa} \int dS \theta^2 + \int dV (\nabla^2 \theta^2) + (\theta^2 - 1) \right) - A_1(\theta - 1) - A_3(2\theta^3 - 3\theta + 1) \]

(27)

In the following sections we employ equation (27) to calculate the free energy of a polymer next to a flat, curved, spherical and sinusoidal surfaces. We note that while the Lagrange multiplier \( \lambda \) acts like a chemical potential in open surfaces for fixing the density of bulk polymers, in the closed systems, like inside a sphere, it’s used to fix the number of monomers inside the shell.

3.1. Analytical calculations

3.1.1. Flat wall. Next to a flat wall, the Euler–Lagrange equation, equation (24), subject to the boundary conditions given in equations (25) and (26) can be solved perturbatively. We assume the attractive interaction between monomers and wall is smaller than the monomer–monomer repulsion \( (\kappa \ll 1) \). The solution to equation (24) to the second order in \( \tilde{\kappa} \) can then be written as

\[ \tilde{\theta} \approx 1 + \tilde{\kappa} \left( 1 + \frac{\tilde{\kappa}}{A} \right) e^{-A \xi E} \]

(28)

where \( A = \sqrt{4 + A_1 - 3A_3} \) with \( A_1 \) and \( A_3 \) proportional to the number of end (\( N_1 \)) and branch (\( N_b \)) points as given below equation (24). For a single long polymer with no loops equation (1) yields \( N_b = N_l + 2 \). So we can simply write \( A_1 - 3A_3 = 2(1 - N_b/\nu N_l^2) \), implying that \( A_1 - 3A_3 < 0 \) and \( |A_1 - 3A_3| < 4 \) should be satisfied for real solutions. For \( A_1 = 3A_3 = 0 \), equation (28) converges to the profile of a linear polymer next to the flat wall [42]. As clearly shown in equation (28), the density of branched polymers are larger than the linear ones next to a flat wall.

Inserting equation (28) into equation (27), we find the change in surface tension, energy per unit area, to the second order in \( \tilde{\kappa} \)

\[ \gamma - \gamma_0 \approx \frac{a^2 c_b}{6\beta \xi_E} \left( -\tilde{\kappa} - \frac{\tilde{\kappa}^2}{2} - \Gamma_b(\tilde{\kappa}, A_1, A_3) \right) \]

(29)

where \( \Gamma_b(\tilde{\kappa}, A_1, A_3) \) is the difference in tension from a linear chain due to branching and is given by

\[ \Gamma_b(\tilde{\kappa}, A_1, A_3) = \left( (A_1 + 3A_3) / A^2 \right) \tilde{\kappa} \]

\[ + \left( 3A_1^2 - A_3^2 - 4 + 2A_1 + 12A_3 \right) / 2A^4 \]

(30)

Since the quantity \( \Gamma_b(\tilde{\kappa}, A_1, A_3) \) is always positive, according to equation (29) the surface tension due to adsorption of a linear polymer to a flat wall is always higher than that of a branched one. In the next section, we calculate the impact of curvature on the polymer density profile and the free energy of the system.
3.12. **Curved wall.** To investigate the effect of curvature analytically, we assume that the flat wall is slightly bent to form a large sphere. The curvature could be either toward or away from the polymer. The radius of curvature \( b \) is considered to be large compared to the correlation length \( \theta = \rho \xi \gg 1 \). We can obtain the perturbative solutions in spherical coordinates through equation (24) assuming that \( \theta = 1 + \delta \theta \) at the weak adsorption limit \( \theta = \xi \ll 1 \). According to the direction of wall curvature, polymer solution is considered either to be in the interior (in) or the exterior (out) of a sphere of radius \( b \). The perturbative solutions are then

\[
\theta_{\text{out}}(\rho) \approx 1 + \frac{\rho b}{1 + Ab - \rho b} \left( \frac{b}{\rho} \right)^{-\kappa(1 - \rho)}
\]

for \( \rho < \rho < \infty \) and

\[
\theta_{\text{in}}(\rho) \approx 1 + \frac{\rho b}{1 + Ab - \rho b} \sinh A\rho
\]

for \( 0 < \rho < \rho \). Assuming \( \rho \gg 1 \), we can write the monomer concentration on the surface to the second order in \( \kappa \)

\[
\theta_{\text{out}} \approx 1 + \frac{\rho b}{1 + Ab + \rho b} \left( \frac{b}{\rho} \right)^{-\kappa(1 - \rho)}
\]

(33)

\[
\theta_{\text{in}} \approx 1 + \frac{\rho b}{1 + Ab + \rho b} \left( \frac{b}{\rho} \right)^{-\kappa(1 - \rho)}
\]

(34)

Comparison of equations (33) and (34) with equation (28) reveals that branched polymer concentration in the vicinity of a flat wall increases if the wall bends toward the polymer and decreases if the wall bends away from the polymer, consistent with the results obtained for linear polymers [42]. In order to obtain the change in surface tension due to the wall curvature, we insert the concentration profiles givem in equations (31) and (32) into equation (27) and keep terms up to the first order in \( 1/b \). Then we have

\[
(\gamma - \gamma_0)_{\text{out}} \approx \gamma - \gamma_0 + \frac{a_s^2 c_b}{6\beta \xi^2 E_b} \left( \frac{\rho^2}{4b} + \Gamma_\delta(\rho, \rho, A_1, A_3) \right)
\]

(35)

and

\[
(\gamma - \gamma_0)_{\text{in}} \approx \gamma - \gamma_0 - \frac{a_s^2 c_b}{6\beta \xi^2 E_b} \left( \frac{\rho^2}{4b} + \Gamma_\delta(\rho, \rho, A_1, A_3) \right)
\]

(36)

where \( \gamma - \gamma_0 \) is the surface tension for the polymer next to a flat wall based on equation (29) and \( \rho^2/4b \) is the difference in surface tension due solely to the geometry of the wall. The quantity

\[
\Gamma_\delta(\rho, \rho, A_1, A_3) = \frac{8\theta^2 - A^2 - 16 + 4A_1 + 36A_2}{4\beta A_1}\rho^2
\]

(37)

is due to the the coupling between the geometry and branched structure of the polymers. If we set \( A_1 = 0 \) and \( A_3 = 0 \) then \( A = 2 \) and equations (35) and (36) reveal the impact of wall curvature on the surface tension for the case of linear polymers. As expected, the surface tension decreases if the wall bends toward the polymer and it increases if the wall bends away from the polymer.

Quite interestingly, the \( \Gamma_\delta \) expression shows the importance of coupling between wall curvature and polymer branching on the surface tension. A glance through table 1 shows that the sum or difference \( \Gamma_\delta \pm \Gamma_\delta \) corresponds to the change in the surface tension due to the coupling between branching and wall curvature. Since this term is positive for both the convex and concave surfaces, we see that branching always decreases the surface tension. However, the coupling between branching and curvature further lowers the surface tension when the wall curves toward the polymers compared to when the wall curves away from the polymer.

| Flat surface | Convex surface | Concave surface |
|--------------|---------------|----------------|
| \( \theta_{\text{flat}} = 1 + \frac{\rho b}{1 + Ab + \rho b} \left( \frac{b}{\rho} \right)^{-\kappa(1 - \rho)} \) | \( \theta_{\text{flat}} = \theta_{\text{flat}} - \frac{\rho b}{1 + Ab - \rho b} \left( \frac{b}{\rho} \right)^{-\kappa(1 - \rho)} \) | \( \theta_{\text{flat}} = \theta_{\text{flat}} + \frac{\rho b}{1 + Ab - \rho b} \left( \frac{b}{\rho} \right)^{-\kappa(1 - \rho)} \) |

| Flat surface | Convex surface | Concave surface |
|--------------|---------------|----------------|
| \( \Delta \gamma_{\text{flat}} \approx \frac{a_s^2 c_b}{6\beta \xi^2 E_b} \left( \frac{\rho^2}{4b} + \Gamma_\delta \right) \) | \( \Delta \gamma_{\text{flat}} \approx \Delta \gamma_{\text{flat}} + \frac{a_s^2 c_b}{6\beta \xi^2 E_b} \left( \frac{\rho^2}{4b} + \Gamma_\delta \right) \) | \( \Delta \gamma_{\text{flat}} \approx \Delta \gamma_{\text{flat}} - \frac{a_s^2 c_b}{6\beta \xi^2 E_b} \left( \frac{\rho^2}{4b} + \Gamma_\delta \right) \) |

**Table 1. Summary of the analytic results.**

Note: The table shows the impact of the wall geometry and the topology of the polymer (embedded in \( \Gamma_\delta \) and \( \Gamma_\delta \) see the text) for two physical quantities of \( \theta \) and \( \Delta \gamma \). The quantity \( \theta \) is related to the concentration of the polymer at the surface by \( \theta \theta^2 \) with \( c_b \) monomer density. \( \Delta \gamma \) is the change in the surface tension due to the presence of the wall.

3.2. **Numerical calculations.**

The above analytical calculations were related to the surfaces with large radius of curvature. To study polymer adsorption on the surfaces with higher curvature, we need to numerically solve equation (24) for both the interior and exterior of smaller spheres. Since this is mainly a phenomenological model, we follow similar parameters to previous numerical works [12, 36, 42, 43, 53–55].

3.2.1. **Outside the sphere.** In this section, we consider smaller spheres and obtain the polymer concentration profile outside the sphere versus the scaled distance from the surface of the sphere, \( \tilde{\rho} = \rho / \hat{b} \). We obtain numerical results by solving the nonlinear differential equation (24) subject to the boundary conditions given in equations (25) and (26). The results are presented in figure 1, which illustrates that both the monomer concentration at the wall and the thickness of the adsorption layer increases as the branching density increases. The surface excess adsorbed onto the sphere can also be calculated using the concentration profile \( \theta \),

\[
n_{\text{ex}} = \xi \theta_{0} c_b \int_{\hat{b}}^{\infty} d\tilde{\rho}(\tilde{\rho}^2 - 1) \left( \frac{\tilde{\rho}}{\hat{b}} \right)^2
\]

(38)
Figure 1. Profiles of the scaled polymer density amplitude $\theta$ versus scaled distance from the surface of the sphere $\tilde{r} - \tilde{b}$ for several relative branching density $A_3$. The solid line gives the profile for a linear polymer with no branching, and dashed lines give the profiles for branched polymers with branching density $A_3 = 0.2$, 0.4, 0.8, 1.0. Other parameters used are $\tilde{r} = 1, \tilde{b} = 5.0$ and $\nu = 0.5$. The inset of figure 1 is the concentration profile for several values of the radius of the sphere ($\tilde{b} = 0.1, 1.5, 100$) for the branching density $A_3 = 0.8$ with $\tilde{r} = 1$ and $\nu = 0.5$. As the radius of the sphere increases, monomer concentration on the surface increases.

Figure 2. Surface excess (in units of $\xi_0 c_b$) versus branching density for $\tilde{r} = 1.0, \tilde{b} = 5.0$ and $\nu = 0.5$. Inset shows the excess on different sizes of spheres for $\tilde{r} = 1.0$ and $\nu = 0.5$. The solid line represents the linear chain with $A_3 = 0$, and the dashed lines give the surface excess for branched polymers with branching density $A_3 = 0.2$, 0.4, 0.6, 0.8, 1.0 as dashing gets smaller.

Figure 3. Surface tension (in units of $a^2 c_b$) versus branching density for $\tilde{r} = 1.0, \tilde{b} = 5.0$ and $\nu = 0.5$. Inset is a plot of surface tension as a function of radius of the sphere for $\tilde{r} = 1.0$ and $\nu = 0.5$. The solid line represents the linear chain with $A_3 = 0$, and the dashed lines give the surface tension for branched polymers with branching density $A_3 = 0.2$, 0.4, 0.6, 0.8, 1.0 as dashing gets smaller. Using the numerical solution for $\theta$ and equation (27), the surface tension can be written as

$$\gamma_{\text{out}} - \gamma_0 = \frac{a^2 c_b}{6 \beta \xi_E} \left( -\tilde{r} \theta^2 (\tilde{b}) + \int_0^\infty (\theta^2 - 1)^2 - A_3 (\theta - 1) - A_3 (2\theta^3 - 3\theta + 1) + (\nabla \theta)^2 \left( \frac{\tilde{r}}{\tilde{b}} \right)^2 \right).$$ (39)

Figure 3 is a plot of the surface tension as a function of the branching density, which shows that as the branching density increases, the surface tension decreases. The inset shows the tension versus the sphere radius for different branching densities $A_3 = 0.2$, 0.4, 0.6, 0.8, 1.0. As the radius of sphere increases, the tension decreases consistent with the perturbative results.

3.2.2. Inside a sphere. In this section, we obtain the polymer concentration profile inside a sphere ($r < b$) by solving the nonlinear differential equation (24) subject to the boundary conditions given in equation (25). In addition, because the polymer is now confined inside an impermeable sphere, the total number of monomers, $N$ is fixed. In terms of normalized length scale and the order parameter $\theta$, we have

$$N = c_b \xi_E^3 \int_0^b 4\pi \tilde{r}^2 \theta^2 d\tilde{r}.$$. (40)

The surface tension in this case can be written as

$$\gamma_{\text{in}} - \gamma_0 = \frac{a^2 c_b}{6 \beta \xi_E} \left( -\tilde{r} \theta^2 (\tilde{b}) + \int_0^\infty (\theta^2 - 1)^2 - A_3 (\theta - 1) - A_3 (2\theta^3 - 3\theta + 1) + (\nabla \theta)^2 \left( \frac{\tilde{r}}{\tilde{b}} \right)^2 \right).$$ (41)
that in figure 7 is 10 times smaller than that in figure 6. The figure also illustrates that the concentration inside the sphere, is chosen to be relatively small towards the bottom of the valley. The optimal radius becomes smaller. This is mainly due to lower density increases.

Figure 5 shows that the profile of a branched polymer next to a sinusoidal adsorbing surface. In all cases we keep the strength of the attractive interaction between the surface and monomers the same.

Figure 6 shows that the profile of a branched polymer next to a sinusoidal surface is similar to that of a flat wall if the wavelength of surface fluctuations is large, for example $\bar{\lambda} = 20 > 1.25$ that increases to $\theta = 3.6$ towards the bottom of the valley. The $\tilde{x}$ and $\tilde{z}$ coordinates are distances along and perpendicular to the corrugations respectively.

3.2.3 Sinusoidal grating. In this section, we consider a polymer solution next to a sinusoidal surface, $z = z_0 \cos((2\pi/\lambda_0) x)$. Here $z_0$ is the amplitude and $\lambda$ is the wavelength of the surface. As mentioned in the introduction, this should give some insight into the behavior of branched polymer next to a rough random surface because the qualitative features of the results are the same. To obtain the concentration profile, $\theta$ we solve equation (24) subject to the boundary condition given in equation (25) using a finite element method in 2D. The numerical results are shown in figures 6–8 as contour plots of the polymer density next to the sinusoidal adsorbing surface. In all cases the strength of the attractive interaction between the surface and monomers remains the same.

Figure 6 shows that the profile of a branched polymer next to a sinusoidal surface is similar to that of a flat wall if the wavelength of surface fluctuations is large, for example $\tilde{\lambda} = \lambda \xi_E = 20$. The figure also illustrates that the concentration of genome is higher in the valley compared to the peaks. This is consistent with the perturbative results presented in previous section, in that if the wall curves away from the genome, the monomer concentration decreases, otherwise, it increases. The non-uniformity in the concentration profile at the wall becomes more apparent as we decrease $\tilde{\lambda}$; i.e. the genome concentration becomes much higher at the valley compared to the peaks, see figure 7. In the figure, the amplitude of surface fluctuations, $z_0 = z/\xi_E = 0.5$, is chosen to be relatively small to emphasize on the difference between the genome profile next to the flat and sinusoidal walls. Note that the amplitude $z_0 = 0.5$ in figure 7 is 10 times smaller than that in figure 6. Nevertheless, since $\tilde{\lambda} = 2$ is 10 times smaller in figure 7, the impact of surface fluctuations are more pronounced.

In addition, we find that not only the concentration profile at the wall is not uniform, the distribution of branch-points is not homogeneous either. Figure 8 illustrates the ratio of branch density to the monomer density at a sinusoidal surface. The figure shows that the branching concentration is higher at
the valley with respect to peaks consistent with our perturba-
tive results in section 2, where we found that the branching
density increases if the surface is curved toward the polymer
and decreases if the surface is curved away.

4. Conclusion

In this paper, we use the field theory methods based on the
\( n \to 0 \) limit of an \( \mathcal{O}(n) \) model to describe the statistics of
an annealed branched polymer. We, in particular, carefully
examine the behavior of branched polymers next to various
adsorbing walls both analytically and numerically.

We show that for the annealed branched polymers,
increasing the branching density will increase the concen-
tration of polymer but decrease the surface tension next to
flat, inward curving, and outward curving walls. In com-
parison to a flat adsorbing wall, we find that when the wall
curves toward the polymer solution, the tension decreases
but when it curves away from it, the tension increases.

While these results are consistent with those found for linear
polymers next to different types of walls, we interestingly
found a correlation between the branching and curvature
that causes a further lowering of surface tension when the
wall curves towards the polymer, but decreases the amount
of lowering surface tension when the wall curves away from
the polymer.

Our numerical solutions for the adsorption of polymer
to the exterior of small spheres show that increasing the
branching leads to an increase in the surface excess. For the
polymers adsorbed in the interior of small spheres, we find
a minimum in the surface tension as a function of radius of
the sphere. This clearly demonstrates the interplay between
monomer-wall attraction and monomer–monomer excluded
volume interaction. Our findings also indicate that branching
decreases the optimal radius of the sphere, as more poly-
mers can sit in the vicinity of the wall without a huge cost
for monomer–monomer repulsion. This result has a consid-
erable consequence for the encapsulation of RNA by virus
shell proteins, and could suggest a non-specific mechanism
for the preferential packaging of viral RNA to cellular RNA
\textit{in vivo} \cite{56}.

Furthermore, we find a similar effect for the adsorption of
polymers onto sinusoidal surfaces. The concentration of poly-
mers increases in the valleys compared to the peaks and also
the branching density goes up in the valley section compared
to the peaks. This effect becomes more pronounced as the
wave-length decreases.

Understanding the mechanisms involved with the adsorp-
tion of annealed branched polymers onto different surfaces
will play a critical role in biomedical technologies. In par-
ticular, the paper was inspired by the idea of using functional-
ized gold nano-particles to bind RNA for gene delivery \cite{27},
which has industrial applications for biosensors and microflu-
iddic devices, and even possible medical applications for gold
nano-particles encapsulated by virus coats as potential tools
for gene therapy \cite{26–31}.

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Appendix A. O(n) model of a magnet

In this appendix, we derive the equivalence between the grand canonical partition function, equation (2), for the polymer system and the partition function for the \( n \to 0 \) limit of an O(n) model. Note that the O(n) model corresponds to a magnet whose magnetic dipole of its atoms has n components. The Ising model commonly studied in most statical mechanics courses is the O(n) model for \( n = 1 \). The \( n = 0 \) limit is an interesting case as it reproduces the statistics of a self-avoiding linear polymer.

The Hamiltonian of the O(n) model of a magnet is

\[
H((S), K, f_1, f_2; V) = -K \sum_{\langle x,y \rangle} S_x \cdot S_y - f_1 \sum_{x} J_1[S_x] - f_2 \sum_{x} J_2[S_x],
\]

where \( S_x \) is an \( n \) dimensional vector of fixed length at each lattice point \( x \) and \( K, f_1, \) and \( f_2 \) are coupling constants. The first sum in equation (A.1) is over all pairs of nearest neighbors and \( J_1[S_x] \) and \( J_2[S_x] \) are the source terms for end-points and branch-points respectively. We have used some prescience in giving the coupling constants \( K, f_1, \) and \( f_2 \) the same symbol as the fugacities in equation (2).

The partition function for the O(n) model is then

\[
Z_{\alpha}(K, f_1, f_2; V) = \prod_x \text{tr}_S e^{-H(S), K, f_1, f_2; V)},
\]

where \( \text{tr}_S \) defined as

\[
\text{tr}_S e^{kS} = \frac{\prod \left( \int_{-\infty}^{\infty} dS_x e^{\sum_x S_x^2 - n} \right)}{\prod \left( \int_{-\infty}^{\infty} dS_x \right)} \left( \sum_x S_x^2 - n \right)^{k/2}.
\]

and the size of the spin is subject to the condition \( |S| = \sqrt{n} \) or \( \sum_x S_x^2 = n \).

Using the power series definition of the exponential, equation (A.2) can be written as

\[
Z_{\alpha}(K, f_1, f_2; V) = \sum_{N_0 = 0}^{\infty} N_2 \sum_{N_0 = 0}^{N_2} \sum_{N_1 = 0}^{N_2} L_0(N_0, N_2; V),
\]

with \( L_0 \) defined as

\[
L_0(N_0, N_2; V) = \prod_x \text{tr}_S \left( \sum_{\langle x, y \rangle} S_x \cdot S_y \right)^{N_0} \left( \sum_x J_1[S_x] \right)^{N_1} \left( \sum_x J_2[S_x] \right)^{N_2}.
\]

The comparison of the grand canonical partition functions defined in equation (2) with the partition function for the O(n) model in equation (A.4) reveals the similarity between the two models. It is now obvious why the coupling constants in the O(n) model were chosen to be labeled the same as the fugacities in the polymer system on a lattice with the excluded volume interaction. To show full equivalence between the grand canonical ensemble of self-avoiding branched polymers

**Figure A1.** Two possible configurations of 4 bonds, 3 end-points, and 1 branch-point on a 3 x 3 two-dimensional square lattice. The left diagram is not a valid configuration while the right diagram is a valid configuration and is counted.

\( \Xi \) in equation (2) and the \( n \to 0 \) limit of partition function for the O(n) model of a magnet (equation (A.2)), we only need to show that in the \( n \to 0 \) limit the \( I_0 \) expression gives the multiplicity \( \Omega \), or counts the number of ways of arranging a self-avoiding branched polymer on the lattice.

Each \( C_{\alpha}([S]) \) in equation (A.5) can be represented graphically. For the lattice, a product of neighboring \( S \)-vectors that lie on points \( x \) and \( x' \) can be represented by a line drawn between the points. The \( J_1[S_x] \) and \( J_2[S_x] \) source terms at point \( x \) and \( x' \) can be represented by circles and triangles placed on their respective points.

As an example we present two possible configurations, one that represents a valid branched polymer configuration and one that does not, with \( N_0 = 4, N_1 = 3 \), and \( N_2 = 1 \) on a 3 x 3 square lattice in figure A1. The corresponding \( C_{\alpha}([S]) \) terms for both graphs in figure A1 contain 4 dot products of neighboring \( S \)-vectors (one for each bond), 3 \( J_1[S] \) terms (3 circles), and 1 \( J_2[S] \) term (1 triangle). The \( C_{\alpha}([S]) \) term for the right diagram in figure A1 is

\[
C_{\alpha}([S]) = (S_2 \cdot S_3)(S_2 \cdot S_5)(S_5 \cdot S_8)
\]

where the indices indicate which lattice site is associated with each term.

We will show below that in the \( n \to 0 \) limit the trace of a single configuration gives one if the graph corresponds to a physically valid branched polymer configuration and zero otherwise, i.e.

\[
\lim_{n \to 0} \left( \prod_x \text{tr}_S C_{\alpha}([S]) \right) = \begin{cases} 1 & \text{for } \alpha \text{ valid}, \\ 0 & \text{for } \alpha \text{ invalid}. \end{cases}
\]

This indicates, in the \( n \to 0 \) limit, the \( I_0 \) term given in equation (A.4) counts the number of valid physical configurations, which is how multiplicity \( \Omega \) is defined in equation (2). The condition in equation (A.7) establishes the equivalence between the partition function for the O(n) model in equation (A.4) with the grand canonical partition function for a flexible branched polymer in equation (2), i.e.

\[
\lim_{n \to 0} Z_{\alpha}(K, f_1, f_2; V) = \Xi(K, f_1, f_2; V).
\]

A.1. Evaluation of the trace

The trace of the configurations \( C_{\alpha}([S]) \) in equation (A.7) takes the form of products of \( S \)-vectors on each lattice site \( x \). These
products can be evaluated by using the following generating function

$$\text{tr} S_h \cdots S_0 = \left. \frac{\partial}{\partial k_1} \cdots \frac{\partial}{\partial k_p} \text{tr} e^{k S} \right|_{k \to 0}. \quad (A.9)$$

The trace of the generating function $\text{tr} e^{k S}$ can be evaluated in closed form

$$\text{tr} e^{k S} = \sum_{p=0}^{\infty} \frac{\Gamma\left(\frac{n}{2} + p\right)}{\Gamma\left(\frac{n}{2}\right)} \left(\frac{\vert k \vert^2}{4}\right)^p. \quad (A.10)$$

In the limit of $n \to 0$ it simplifies to the form

$$\lim_{n \to 0} \text{tr} e^{k S} = 1 + \frac{1}{2} \vert k \vert^2. \quad (A.11)$$

A detailed step by step derivation of equation (A.10) is presented in appendix A of [57]. Inserting equation (A.11) into equation (A.9), we find the product of the components of the $S$-vectors in the absence of source terms is

$$\lim_{n \to 0} \text{tr} S_h \cdots S_0 = \begin{cases} 1 & \text{if } p = 0, \\ \delta_{ij} & \text{if } p = 2, \\ 0 & \text{otherwise.} \end{cases} \quad (A.12)$$

The expression in equation (A.12) evaluates to a non-zero value only in the lattice sites with exactly 0 or 2 bonds terminating on them.

To describe the generating function for end- and branch-points, we construct $J_1$ and $J_3$ functions, respectively, such that they satisfy the following equations

$$\lim_{n \to 0} \text{tr} S_h J_1[S] = \lim_{n \to 0} \frac{1}{\sqrt{n}} \sum_i \delta_{ij}, \quad (A.13a)$$

$$\lim_{n \to 0} \text{tr} S_h S_0 J_3[S] = \lim_{n \to 0} \frac{1}{\sqrt{n}} \sum_i \delta_{ij} \delta_{ij}, \quad (A.13b)$$

while all other traces involving the sources such as $\text{tr} S_h S_0 J_3[S]$, $\text{tr} S_h J_0[S]$ and $\text{tr} S_0 J_0[S]$ are equal to zero in the $n \to 0$ limit. Using equation (A.10) it is straightforward to derive the following expressions for $J_1$ and $J_3$,

$$J_1[S] = \frac{1}{\sqrt{n}} \sum_i S_i, \quad (A.14a)$$

$$J_3[S] = \frac{4}{3n^2} \sum_i \left( S_i^3 - \frac{3}{n} S_i^2 S_i + 3S_i \right). \quad (A.14b)$$

The sum in equation (A.13a) evaluates to a non-zero value only if for every lattice site containing the source term $J_1$ there exists exactly one bond terminating on that site. Similarly the sum in equation (A.13b) evaluates to a non-zero value only if for the sites with branch-point $J_3$ there are exactly three bonds terminating on that site. The factors of $1/\sqrt{n}$ in equation (A.13a) and $1/\sqrt{n}$ in equation (A.13b) enforce the no-loops condition necessary to obtain the statistics of a self-avoiding polymer.

In general, for every valid configuration with $N_p$ connected graphs, $N_1$ end-points, and $N_3$ branch-points the product of all the lattice site integrals gives

$$\lim_{n \to 0} \text{tr} C_n[S] = \lim_{n \to 0} n^{N_p + \frac{1}{2} (N_1 - N_3)}. \quad (A.15)$$

Using equation (1), the exponent in equation (A.15) is equal to the number of loops, so in the $n \to 0$ limit only those valid configurations with no loops evaluate to 1, while all others evaluate to 0.

It is important to note that the conditions given in equations (A.13a) and (A.13b) do not forbid the multiple source terms sharing the same lattice site. This oversight can be remedied by redefining the partition function (see equations (A.1) and (A.2)) such that the exponential of the source terms is replaced by the constant and linear terms in the power series expansion

$$Z_d(K, f_1, f_3; V) = \prod_x \text{tr} S_x e^{K \sum_x s_x s_x} \times \prod_x (1 + f_1 J_1[S_x] + f_3 J_3[S_x]). \quad (A.16)$$

The structure in equation (A.16) ensures that there will be at most one single source term per lattice site and otherwise does not have any impact on the derivation presented above. From here on, we will only consider the partition function presented in equation (A.16) for the branched polymers system.

### A.2. Mean Field Hamiltonian

We can now convert the lattice model over a discrete set of $S$-vectors into a continuous field theory $\psi(x)$ using a Hubbard–Stratonovich transformation and connect the lattice fugacities $K, f_1, f_3$ to physical quantities of chemical potential and concentration in the mean field approximation.

It is necessary to carefully treat the sum over nearest neighbors on the lattice given in equation (A.16) in order to change the lattice model into a continuous field theory. The sum can be written as a double sum over lattice sites multiplied by a nearest neighbor delta function

$$\sum_{\langle x, x' \rangle} = \frac{1}{2} \sum_{x} \sum_{x'} \delta_{\langle x, x' \rangle}. \quad (A.17)$$

The function $\delta_{\langle x, x' \rangle}$ is similar to a Kronecker delta function, and is explicitly defined as an operator that evaluates to 1 when $x$ and $x'$ are neighbors and 0 otherwise. The additional factor of half prevents double counting. Using equation (A.17), we now perform a Hubbard–Stratonovich transformation to introduce the auxiliary field $\psi(x)$

$$\frac{8}{7} \sum_{\langle x, x' \rangle} \delta_{\langle x, x' \rangle} S_x S_x' = \int_{-\infty}^{\infty} D\psi \ e^{-\frac{1}{2} \sum_x \delta_{\langle x, x' \rangle} \psi(x) \psi(x')} \times \sum \sqrt{K} \psi(x) \ S_x. \quad (A.18)$$

where $\delta_{\langle x, x' \rangle}$ is the inverse of the $\delta_{\langle x, x' \rangle}$ operator. Using equation (A.18), the partition function equation (A.16) can be written as

$$Z_d(K, f_1, f_3; V) = \int_{-\infty}^{\infty} D\psi \ e^{-\frac{1}{2} \sum_x \psi(x) \psi(x')} \times \prod_x \text{tr} S_x e^{K \sum_x \psi(x) S_x} (1 + f_1 J_1[S_x] + f_3 J_3[S_x]). \quad (A.19)$$
The first term in the second line of equation (A.19) is simply the generating function performed in equation (A.9). We now use equations (A.13a) and (A.13b) to evaluate the integrals associated with the sources $J_1$ and $J_3$ in equation (A.19) in the $n \to 0$ limit. Without loss of generality, the source terms can pick a special direction. To simplify the integrations, we choose the $(1, 0, \ldots, 0)$ direction and thus equations (A.13a) and (A.13b) can be written

$$\lim_{n \to 0} \text{tr}_S S[J[S] = \delta_{11}, \quad (A.20)$$

$$\lim_{n \to 0} \text{tr}_S S_n S[J[S] = \delta_{11} S_{11}. \quad (A.21)$$

Inserting equations (A.20) and (A.21) into equation (A.19) and performing the integral over $S$-vector, the partition function in the $n \to 0$ limit becomes

$$Z_d(K, f_1, f_2, V) = \int D\psi \exp \left\{ \frac{1}{2} \sum_{i=1}^N (\bar{\psi}_{i1})^2 (\bar{\psi}_{i1})^2 + f_1 \bar{\psi}_{i1} \bar{\psi}_{i1} + f_2 \bar{\psi}_{i2} \bar{\psi}_{i2} \right\} \prod_{i=1}^N \left( 1 + \frac{K}{2} (\bar{\psi}_{i1}^2 + f_1 \bar{\psi}_{i1} + f_2 \bar{\psi}_{i2}^2) \right).$$

(A.22)

The $f_1 \bar{\psi}_{i1}^2$ and $f_2 \bar{\psi}_{i2}^2$ terms are proportional to the end and branch-point densities, while $\psi^2$ is proportional to the monomer density. Since for most physically relevant systems the ratio of branch or end-points to monomers is low, the $f_1 \bar{\psi}_{i1}^2$ and $f_2 \bar{\psi}_{i2}^2$ terms will be much smaller than the $\psi^2$ term. Raising the second line of equation (A.22) into the exponent, we define a new effective Hamiltonian as given in equation (8).

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