Polymer brush bilayers at thermal equilibrium: A theoretical approach†

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Starting from statistical mechanics of polymers and using density functional method, I review theory of polymer brush bilayers at thermal equilibrium thorough a novel point of view. I obtain density profiles, brush heights and interpenetration length in at thermal equilibrium in terms of molecular parameters and distance between brushes. The present work shows witha a transparent analytic approach how polymer brushes balance compression and elasticity when bilayers of brush come into contact. The present results suggest that existing theories about polymer brush bilayers (blob picture) need highly likely to be reviewed.

1 Introduction

Polymers are a class of long molecules that consist of repeated units of atoms or molecules i.e. monomers[1]. The connectivity among monomers in a polymer chain is fulfilled through sharing valance electrons i.e. covalent or molecular bond. Monomers undergoing Brownian motions constantly changes the shape of whole polymer chain so that in long time polymer chain undergoes all possible conformations. Using statistical mechanics and canonical ensemble I review the equilibrium thermodynamic properties of a polymer chain.

Polymer brushes are a class of polymeric structures present in many practical situations[2]. They consist of densely grafted polymer chains to surfaces which swell due to steric repulsion among monomers of nearby chains. Polymer brush bilayers are present in a wast majority of biological systems such as mammalian knee joints as lubricant. Polymer brush bilayers are known to interpenetrate which is source of many interesting effect such as shear thinning and lubrication . Getting to know more about polymer brush bilayers improves our knowledge about how to shape future artificial joint technologies.

2 Polymer in external force

The conformation of a polymer chain changes due to change of monomers position in chain. This situation could be assumed as N vectors of length a that are connected together and are free to rotate in three dimensional space. Theoretically, to obtain elastic properties of the chain, we need to apply a force field to the chain and observe its behavior and at the end remove the force field from the resulting quantities. The leading order terms indicate the elastic properties of the chain in absence of force field.

First of all, I introduce Hamiltonian of the system as inner product of force field and all vectors summed up together. The negative sign ensures that the minimum energy takes place when all vectors purely align toward force field. So, the conformations are determined by θ, the smaller angle between force field and vectors. For simplicity and symmetry considerations, I choose spherical polar coordinates and apply force filed in z direction. So, the angle between force field and vectors is the same as polar angle θ in spherical polar coordinates.

$$H = -fa\sum_{i=1}^{\mathrm{N}}\cos\theta_i \tag{1}$$

Having introduced the Hamiltonian, it will be the next step to calculate partition function which is defined as $Z = \int d\Omega \exp -H/k_BT$ where Ω denotes all possible conformations of chain. The partition function turns out to following integral in spherical polar coordinates,

$$\mathrm{Z}(f,T) = \left(2\pi a^2\int_0^{\pi}\sin(\theta)e^{\frac{af}{k_BT}\cos(\theta)}\,d\theta\right)^{\mathrm{N}} \tag{2}$$

The above integral is simply solvable due to uncorrelated vectors (monomers) and it gives the following result for the partition function,

$$\mathrm{Z}(f,T) = \left(4\pi a^2\frac{\sinh(\frac{af}{k_BT})}{\frac{af}{k_BT}}\right)^{\mathrm{N}} \tag{3}$$

Having obtained the partition function, we can simply calculate canonical free energy as $F(f,T) = -k_BT\log Z(f,T)$ giving following expression,

$$F(f,T) = -\mathrm{N}k_BT\log\left(4\pi a^2\frac{\sinh\left(\frac{af}{k_BT}\right)}{\frac{af}{k_BT}}\right) \tag{4}$$

This is the free energy at constant force and temperature. Since, I fixed the force and temperature, so the length of the polymer chain fluctuates. The mean value of the length can be obtained from the canonical free energy as $-\partial F(f,T)/\partial f$ which gives us the following length,

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$$\langle L\rangle = \mathrm{N}a\left(\coth\left(\frac{af}{k_BT}\right)-\frac{1}{\left(\frac{af}{k_BT}\right)}\right) \tag{5}$$

The average length of polymer chain can alternatively be calculated from integration which is equal to above result. As it is observed, the average length of a polymer chain subject to an external force is non-zero. Certainly, this happens exclusively along external force (here z direction) and in other directions (here x and y directions) the average length vanishes. To obtain fluctuations of polymer chain we need to have mean square length i.e. $\langle L^2\rangle$. Mean square length can be calculated through integration to give following result,

$$\langle L^2\rangle = \mathrm{N}a^2 \tag{6}$$

and fluctuation in polymer length via $\langle L^2\rangle - \langle L\rangle^2$ giving following result,

$$\Delta L^2 = \mathrm{N}a^2 - \mathrm{N}^2a^2\left(\coth\left(\frac{af}{k_BT}\right)-\frac{1}{\left(\frac{af}{k_BT}\right)}\right)^2 \tag{7}$$

The susceptibility $\partial^2F(f,T)/\partial f^2$ at fixed force and temperature reads as follows,

$$\kappa = \frac{\mathrm{N}a^2}{k_BT}\left(\mathrm{csch}^2\left(\frac{af}{k_BT}\right)-\frac{1}{\left(\frac{af}{k_BT}\right)^2}\right) \tag{8}$$

It is interesting to see the behavior of a polymer chain at fixed length and temperature that can be achieved by Helmholtz free energy $A(L,T) = F(f,T) + f\langle L\rangle$ as follows,

$$A(L,T) = \mathrm{N}k_BT\left(\left(\frac{af}{k_BT}\right)\coth\left(\frac{af}{k_BT}\right)-1-\log\left(4\pi a^2\frac{\sinh\left(\frac{af}{k_BT}\right)}{\left(\frac{af}{k_BT}\right)}\right)\right) \tag{9}$$

In this section, I reviewed the thermodynamics of a polymer chain via statistical mechanical point of view. I obtained exact solutions for thermodynamic quantities. They will get more reliable when we consider asymptotic behaviors of the results which I will do in the nest two sections.

3 Polymer in weak external force

In many situations, the magnitude of the external force is much smaller than thermal energy. In this limiting case, I can consider the dimensionless quantity af/k_BT as much smaller than unity and make Taylor expansion in the physical quantities. The Taylor expansions give us following terms,

$$F(f,T) = -\mathrm{N}k_BT\log\left(4\pi a^2\right)-\frac{a^2f^2\mathrm{N}}{(6k_B)T}+O\left(f^4\right) \tag{10}$$

The first term in canonical free energy is the free energy of N freely rotating vectors of fixed length a in three dimensional space. The second term is the leading order term in terms of the external force. This term has most of the information about a polymer chain. Looking at Eqs. 11 and 12, we see that this term can be rewritten as $\frac{1}{2}\kappa^{-1}\langle L\rangle^2$. This is a free energy which introduces us elasticity due to entropy in a polymer chain. This term tries to shrink the chain. The inverse compressiblity or susceptibility plays role of spring constant but with a difference to crystals. The elastic constant in solids decreases by temperature but in a polymer and rubber-like materials the elastic constant increases by temperature. So, by heating up the polymers they contract due to $\langle L\rangle = f/\kappa^{-1}$ in contrast to crystalline materials.

$$\langle L\rangle = \frac{a^2f\mathrm{N}}{3k_BT}+O\left(f^3\right) \tag{11}$$

In Eqs. 11 and 12 average length and compressiblity of the chain is seen in weak external force. The leading order term in average length depends on external force so in absence of external force the average length vanishes as it is expected. Naturally, when a polymer chain is subject to an external force, it tends to align to the force direction. This causes non-zero average length which occures in absence of external force.

$$\kappa = \frac{a^2\mathrm{N}}{3k_BT}-\frac{f^2\left(a^4\mathrm{N}\right)}{15\left(k_B^3T^3\right)}+O\left(f^4\right) \tag{12}$$

The leading order term of compressibility is independent of external force. It gives an intrinsic property of polymer chain $\kappa^{-1} = \frac{3k_BT}{a^2\mathrm{N}}$ which indicates the elasticity originated from entropy.

$$\Delta L^2 = a^2\mathrm{N}-\frac{f^2\left(a^4\mathrm{N}^2\right)}{9\left(k_B^2T^2\right)}+O\left(f^4\right) \tag{13}$$

The fluctuation of chain length in weak external force is extremely interesting quantity. To understand which term dominates in the perturbation expansion, we need to compare their magnitude. Since the second term is $\sim \mathrm{N}^2$ it appears to dominate the first term but it is multiplied by the perturbation coefficient squared $\left(\frac{af}{k_BT}\right)^2$. So to see which term dominates we need to make numerical comparison. Typical polymer chains consist $\mathrm{N} = 10^5$ monomers and usually force is in order of pN and a monomer has size of 0.1 Nano-meters. Considering order of magnitude of the Boltzmann constant as 10^{-23} and room temperature $T = 300\mathrm{K}$, the perturbation coefficient gets $\left(\frac{af}{k_BT}\right)\sim 10^{-2}$. Consequently, the first and the second terms have almost same order of magnitude and both are leading order terms. As it is expected when temperature increases the fluctuations of the chain length increases as well and in extreme limit of $T\to\infty$ then $\Delta L^2 \to a^2\mathrm{N}$. It means than at very large temperatures, the length fluctuations equals the mean square length. Interestingly, in presence of external force, fluctuations are small compared to mean squared length but in absence of external force, fluctuations equal mean squared length. It means that under the influence of external force, the chain is elongated along the force direction and shows minor fluctuations in length.

$$A(L,T) = -\mathrm{N}k_BT\log\left(4\pi a^2\right)+\frac{a^2f^2\mathrm{N}}{6k_BT}+O\left(f^4\right) \tag{14}$$

The Helmholtz free energy at fixed length and temperature shows that at small external forces, elasticity of a polymer chain

is $\kappa^{-1}\langle L\rangle^2/2$. This is an important result that will be used in the next section as the free energy of a polymer chain.

4 Polymer in strong external force

Another interesting case is a very strong external force applied to a polymer chain. In this limit, the chain stretches extremely and at sufficiently large forces the chain becomes a line. The behavior of physical quantities under this extreme condition can be seen by making limit of them when external force approaches infinity.

$$\begin{aligned}
\lim_{f\to\infty} F(f,T) &\to -\infty \\
\lim_{f\to\infty} \langle L\rangle &\to \mathrm{N}a \\
\lim_{f\to\infty} \langle L^2\rangle &\to \mathrm{N}a^2 \\
\lim_{f\to\infty} \Delta L^2 &\to \mathrm{N}a^2 - \mathrm{N}^2a^2 \\
\lim_{f\to\infty} \kappa &\to 0 \\
\lim_{f\to\infty} A(L,T) &\to \infty
\end{aligned} \tag{15}$$

Interestingly, average length goes to $\mathrm{N}a$ as it is expected from rod limit. The squared length fluctuations goes to $\mathrm{N}a^2 - \mathrm{N}^2a^2$ as rod limit achieved but this this a negative value and it is an imaginary quantity. Therefore, I would say at rod limit length fluctuations has no real quantity. The susceptibility goes to zero i.e. the elasticity goes to infinity that means a very stiff spring resembling rod limit. Both free energies go to infinity at rod limit.

5 Polymer brushes

Polymer brushes are composed of linear polymer chains densely grafted to a surface[2]. The steric repulsion between monomers of nearby chains swells any chain to collectively form brush-like structure. Here, I review theoretical analysis of polymer brushes through density functional theory. I start from grand potential functional as follows,

$$\Phi[\mathrm{n}(z)] = \int_0^h \left(\frac{3k_BTz^2}{a^2N^2}\mathrm{n}(z) + \frac{b}{2}k_BT\mathrm{n}(z)^2 - \mu\mathrm{n}(z) \right) dz \tag{16}$$

The first term in Eq. 16 refers to leading order term of Helmholtz free energy which describes elastic energy coming from entropy in chain. Since energy is distributed throughout the chain according to probability distribution function, I multiply Helmholtz free energy by $\mathrm{P}(z) = \mathrm{n}(z)/\mathrm{N}$. The second term comes from the fact that I assume chain as a monomer gas. This term refers to the first correction to free energy of a gas based on consideration of binary interactions among monomers. Here, $b = (1/2)\int d^3r\,(1-\exp(-\mathrm{U}(r)/k_BT))$ is second virial coefficient that represents strength of binary correlations among monomers. For hard spheres of diameter a, $b = (2\pi/3)a^3$ independent of temperature. For Lennard-Jones particles $b = (2\pi/3)a^3\left(\frac{1.73}{\bar{T}^{1/4}} - \frac{2.56}{\bar{T}^{3/4}} + \dots\right)$ with $\bar{T} = k_BT/\varepsilon$[3].

The equilibrium density profile, brush height and chemical potential are to be obtained through simultaneous solution of following three equations. The first equation performs a functional derivative of grand potential with respect to density profile. It leads to a Euler-Lagrange differential equation. The solution of corresponding Euler-Lagrange differential equation results in equilibrium density profile of polymer brush.

The second equation refers to derivative of grand potential with respect to brush height having inserted equilibrium density profile in it. The third equation indicates that total number of monomers in polymer brush is obtained through integration over equilibrium density profile.

$$\begin{aligned}
\frac{\delta\Phi[\mathrm{n}(z)]}{\delta\mathrm{n}(z)} &= 0 \\
\frac{\partial\Phi[\mathrm{n}(z)]}{\partial h} &= 0 \\
\int_0^h \mathrm{n}(z) &= \mathrm{N}\sigma
\end{aligned} \tag{17}$$

Solving Eqs. 17, gives following results,

$$\begin{aligned}
\mathrm{n}(z) &= \frac{3\sigma^{2/3}}{2^{2/3}a^{2/3}b^{1/3}} - \frac{3z^2}{a^2\mathrm{N}^2b} \\
h &= \frac{a^{2/3}b^{1/3}N\sigma^{1/3}}{2^{3/2}} \\
\mu &= \frac{3b^{2/3}\sigma^{2/3}k_BT}{2^{2/3}a^{2/3}}
\end{aligned} \tag{18}$$

Eq. 18 shows a parabolic density profile for brush together with universal power laws of brush height and chemical potential in terms of molecular parameters. Here, brush height and chemical potential follow universal power laws in terms of molecular parameters.

6 Polymer brush bilayer

Polymer brush bilayer is a system that is observed in many a wide range of physical systems from biology to industry. The most designated application for polymer brush bilayers is devoted to lubrication inside mammalian joints. To understand theoretically the equilibrium properties of a polymer brush bilayer system, I consider two polymer brushes grafted to two surfaces at $z = 0$ and $z = \mathrm{D}$. I can start from following grand potential where the first integral represents the bottom brush, the second integral represents the top brush and the third integral represents the steric repulsion among monomers of two brushes through interpenetration length. The two brushes are totally same in context of the molecular parameters.

$$
\begin{aligned}
\Phi[\mathrm{n}(z),\mathrm{m}(z)] &= \int_0^h \left(\frac{3k_BTz^2}{a^2N^2}\mathrm{n}(z)+\frac{b}{2}k_BT\mathrm{n}(z)^2-\mu\mathrm{n}(z)\right)dz \\
&+ \int_{D-h}^D \left(\frac{3k_BT(z-D)^2}{a^2N^2}\mathrm{m}(z)+\frac{b}{2}k_BT\mathrm{m}(z)^2-\mu\mathrm{m}(z)\right)dz \\
&+ \frac{b}{2}k_BT\int_{D-h}^h \mathrm{n}(z)\mathrm{m}(z)\,dz \qquad (19)
\end{aligned}
$$

The equations bellow lead to achieve density profiles of each brush, the height of each brush and chemical potentials. I note here that it suffices to take derivative of grand potential with respect to h as well as to calculate total monomers of bottom brush for calculations. This becomes possible due to similarity of two brushes.

$$
\begin{aligned}
\frac{\delta\Phi[\mathrm{n}(z),\mathrm{m}(z)]}{\delta\mathrm{n}(z)} &= 0 \\
\frac{\delta\Phi[\mathrm{n}(z),\mathrm{m}(z)]}{\delta\mathrm{m}(z)} &= 0 \\
\frac{\partial\Phi[\mathrm{n}(z),\mathrm{m}(z)]}{\partial h} &= 0 \\
\int_0^h \mathrm{n}(z) &= \mathrm{N}\sigma \qquad (20)
\end{aligned}
$$

Eqs. 20 lead to following results for density profiles, heights and chemical potentials. Noting that height of top brush is obtained via $\mathrm{D}-h$ and chemical potentials are same.

$$
\begin{aligned}
\mathrm{n}(z) &= \frac{\eta^2+\frac{2\mathrm{D}^3}{\eta}+2\mathrm{D}(\eta-4z)+\frac{\mathrm{D}^4}{\eta^2}-\mathrm{D}^2-4z^2}{2a^2b\mathrm{N}^2} \\
\mathrm{m}(z) &= \frac{\eta^2+\frac{2\mathrm{D}^3}{\eta}+2\mathrm{D}(\eta+8z)+\frac{\mathrm{D}^4}{\eta^2}-13\mathrm{D}^2-4z^2}{2a^2b\mathrm{N}^2} \\
h &= \frac{1}{2}\left(\eta+\mathrm{D}\left(\frac{\mathrm{D}}{\eta}-1\right)\right) \\
\mu &= \frac{3k_BT\left(2\mathrm{D}\eta+\eta^2+\frac{2\mathrm{D}^3}{\eta}+\frac{\mathrm{D}^4}{\eta^2}-5\mathrm{D}^2\right)}{4a^2\mathrm{N}^2} \qquad (21)
\end{aligned}
$$

where η is a length that is defined as follows,

$$
\eta = \left(\sqrt{3a^2b\mathrm{N}^3\sigma\left(3a^2b\mathrm{N}^3\sigma-2\mathrm{D}^3\right)}+3a^2b\mathrm{N}^3\sigma-\mathrm{D}^3\right)^{1/3}
$$

Having brush heights an important quantity here is interpenetration length which is obtained as $2h-\mathrm{D}$ giving following result,

$$
l = \frac{(\mathrm{D}-\eta)^2}{\eta} \qquad (22)
$$

In Fig. 1, I present density profiles of polymer brush bilayer, their overlap density profiles and density profile of an isolated brush to see visually how it changes in contact to top brush. I choose $a=1$, $b=2.09$, $\sigma=0.1$, $\mathrm{N}=30$ and $\mathrm{D}=15$. It is seen that brushes compressed due to contact with each other. This is an important point since here we see a balance between elasticity of brushes and compressive force from other brush. Moreover, density profiles in bilayer has less smaller curvature than isolated brush.

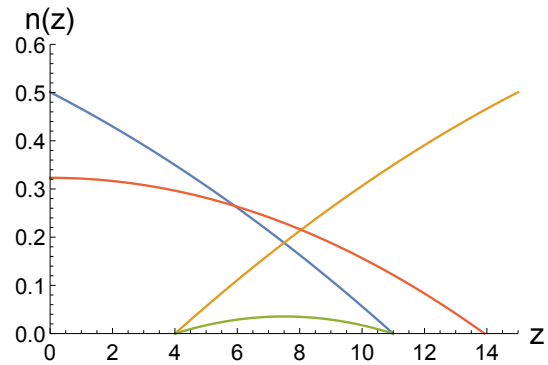

Fig. 1 Density profiles of bottom brush (blue), top brush (orange), the overlap density profile of bottom and top brushes (green) and density profile of bottom brush in absence of top brush (red).

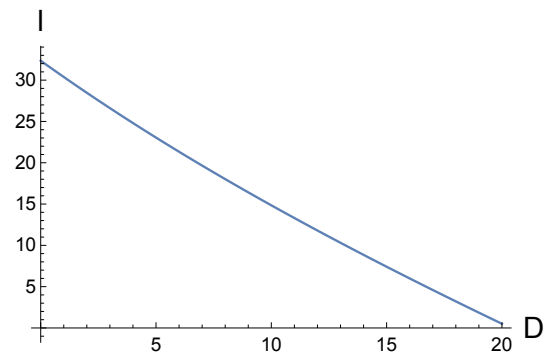

Fig. 2 Interpenetration length in terms of wall distance.

In Fig. 2, I present interpenetration length in terms of wall distance. This plot, surprisingly, does not fit to any universal power law. However, interpenetration length decrease as wall distance increases as it is expected. In Ref.[4], it is mentioned that interpenetration length in polymer brush bilayers at melt concentration scales as $\sim \mathrm{D}^{-1/3}$ and at semidilute concentration as $\sim \mathrm{D}^{-(1-\nu)/3(3\nu-1)}$. Having Flory exponent $\nu \approx 0.588$ it indicates universal power law $\sim \mathrm{D}^{-0.17}$.

In Fig. 4, I present Interpenetration length in terms of index of polymerization. I plot Eq. 22 and a power law fit as $\sim \mathrm{N}^{0.976}$. This power law almost fits to Eq. 22. In Ref.[4], universal power law $\sim \mathrm{N}^{2/3}$ and $\sim \mathrm{N}^{0.51}$ respectively for melt and semidilute regimes are proposed. Naturally, as index of polymerization increases, longer polymer chains tend to increase interpenetration length.

In Fig. 3, I present interpenetration length in terms of second virial coefficient. Eq. 22 fits to power law $\sim b^{0.38}$. It is natural that brush bilayers respond to binary correlations among monomers. For instance, the quality of solvent is determined by b to be poor, theta or good solvent. In poor solvent conditions, monomers attract each other, in theta solvent monomers do not possess binary correlations and in good solvent conditions monomers repel each

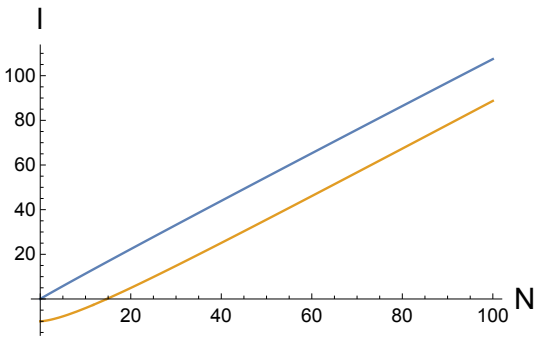

Fig. 3 Interpenetration length in terms of index of polymerization. Eq. 22 (orange) and universal scaling law $\sim \mathrm{N}^{0.976}$ (blue).

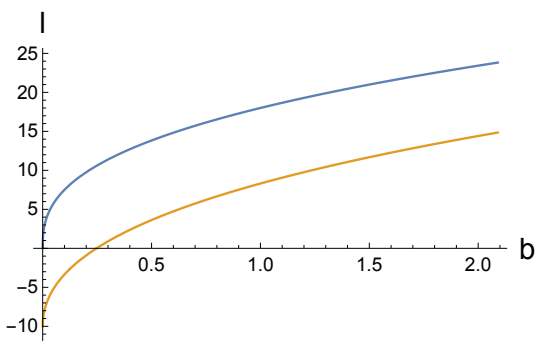

Fig. 4 Interpenetration length in terms of second virial coefficient. Eq. 22 (orange) and universal scaling law $\sim b^{0.38}$ (blue).

other[5].

In Fig. 5, I present interpenetration length in terms of grafting density. This plot fits to power law $\sim \sigma^{0.39}$. In Ref.[4], interpenetration length is independent of grafting density for melts and it scales as $\sim \sigma^{-0.51}$ for semidilutes. However, one may criticize this prediction since interpenetration length naturally may increases as grafting density increases.

In Fig. 6, I present interpenetration length in terms of segment length. This plot fits to power law $\sim a^{0.69}$. While Ref.[4] proposes a power law $\sim a^{4/3}$ for melts and $\sim a^{0.15}$ for semidilutes. The prediction of Ref.[4] about interpenetration at melts is quit close to my calculations.

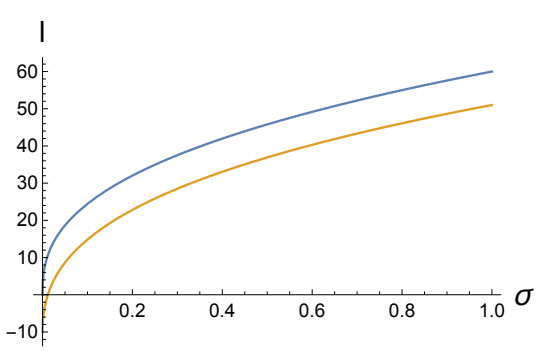

Fig. 5 Interpenetration length in terms of grafting density. Eq. 22 (orange) and universal scaling law $\sim \sigma^{0.39}$ (blue).

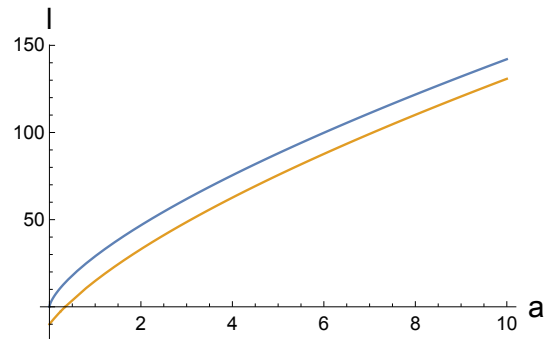

Fig. 6 Interpenetration length in terms of segment length. Eq. 22 (orange) and universal scaling law $\sim a^{0.69}$ (blue).

7 Conclusion and discussion

In this report, I reviewed theoretically equilibrium properties of polymer chains with aiming at theoretical description of polymer brush bilayers. I theoretically showed that how polymer brushes interpenetrate in each other through giving exact density profiles of two brushes. I showed theoretically how interpenetration length in polymer brush bilayers depend upon molecular parameters. Interpenetration length decreases by wall distance through a non power law behavior. This suggests that interpenetration length does not obey similarity rules. This is in complete contrast to dependence of interpenetration length upon molecular parameters. All molecular parameters follow similarity rules among them index of polymerization has a major impact and grafting density as well as second virial coefficient have minor impact on interpenetration length. Calculations show that all molecular parameters increase interpenetration length but with different power law. This is interesting, for instance, about second virial coefficient which describes binary correlations among monomers. I have considered all binary interactions the same. One might say that increase in interpenetration length is due to repulsion among monomers inside brushes and not due to repulsion among monomers of different brushes. Consideration of this point can help better understanding this system. I guess if one takes different biary correlations among monomers of different brushes, it will be presented that the correlations among different brushes decreases interpenetration length.

The blob picture which have been utilized in Ref.[4] is seems to be extremely simple and it does not capture important details. For instance, as I showed, the interpenetration length is not independent of binary correlations among monomers and it increases by grafting density, two facts that contradicts results of blob picture. It is worth noting that since in complex systems there are different length and time scales, therefore approaches like blob picture considering only one length scale are not able to deliver sufficient information.

References

1 M. Rubinstein and R. Colby, *Polymer Physics*, OUP Oxford, 2003.

2 R. Advincula, W. Brittain, K. Caster and J. Rühe, *Polymer Brushes*, Wiley-VCH, Weinheim, 2004.

3 F. Schwabl and W. Brewer, *Statistical Mechanics*, Springer Berlin Heidelberg, 2006.
4 T. Kreer, *Soft Matter*, 2016, **12**, 3479.
5 P. G. Gennes, *Scaling Concepts in Polymer Physics*, Cornell University Press, 1979.