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Adsorption of Copolymer Chains at Liquid–Liquid Interfaces: Effect of Sequence Distribution

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ABSTRACT: We use analytic arguments and molecular dynamics simulations to determine how the chemical sequence distribution affects the conformation of a single AB copolymer at a liquid–liquid interface. We define a parameter f which characterizes this sequence distribution along the chain. We determine L^*, the length scale on which the polymer weaves back and forth across the interface. We find that L^* as a function of f has a well-defined minimum, and the two limits are analyzed. Molecular dynamics simulations support the conclusions obtained from our analytical results.

Introduction

The presence of copolymers at an interface between two immiscible fluids is crucial to such processes as emulsion stabilization, wetting, and microemulsion formation.[1] For oil–water interfaces, the copolymers that are utilized in these applications are amphiphilic in nature: one component is soluble in the oil phase, while the other is water-soluble. This difference is solubilities drives the copolymers to adsorb at the boundary between the two liquids. Localized at the boundary, the chains stabilize the interface in the sense that they significantly reduce the surface tension. Recently, Marques and Joanny[2] and Garel et al.[3] studied the behavior of a random hydrophobic–hydrophilic copolymer at a liquid–liquid interface. However, the arrangement or sequence distribution of the monomers in a copolymer can vary widely from random to blocky or purely alternating.

In this paper, we use both analytic arguments and molecular dynamics simulations to determine how the sequence distribution affects the adsorption and conformation of a single macromolecule at the boundary between two immiscible fluids. In particular, we derive an expression for the free energy of a copolymer at the interface and compare the resulting predictions with the outcome of the simulations. Our findings yield design criteria for fabricating polymers that display the desired interfacial properties. The results also reveal how the arrangement of hydrophobic sites affects the interfacial behavior of proteins.

The Model

As in the previous studies,[2,3] we will assume that the liquid–liquid interface remains fixed in space and is perfectly sharp. The polymer is represented by a Gaussian chain composed of two different monomers, A and B. The monomer–solvent interaction energies are taken to be symmetric: $-\Delta$ for a monomer in the favorable solvent and $+\Delta$ in the unfavorable one. We neglect interactions between the monomers along the chain.

Let the variables P_A and P_B be the fraction of A and B sites, respectively, in a single polymer chain. Given a site A in the chain, the parameter $P_{A\to B}$ yields the conditional probability that the next site is a B site. Likewise, given a B site, $P_{B\to A}$ is the conditional probability that the next site corresponds to an A site. For chains that are statistically translational invariant, the variables are related as follows:

$$P_A P_{A\to B} = P_B P_{B\to A} \tag{1}$$

We now introduce the parameter f, which characterizes the sequence distribution in the chain. The value of f is defined through the following equation:

$$P_A P_{A\to B} = (P_A P_B)^{1/2} f \tag{2}$$

where f lies between 0 and 1.

For the sake of simplicity, we will study the symmetric case where $P_A = P_B = 0.5$. In this limit, Garel et al.[3] have shown that as the chain length approaches infinity, a random copolymer will always be localized at the interface. By altering the value of f, we can determine the behavior of other symmetric copolymers at this penetrable surface. For example, for $P_A = P_B = 0.5$, $f = 1$ corresponds to an alternating chain, $f = {}^1/_2$ represents a purely random chain, and $f \to 0$ corresponds to a blocky copolymer.

Having defined a sequence distribution parameter, we can calculate the structural correlation between the ith and the $(i + n)$th monomer, $\langle \sigma_{i+n} \sigma_i \rangle$. Here, $\sigma_i = 1$ if the ith monomer corresponds to state A and -1 if it corresponds to state B. (Note that, in our model, this correlation is independent of i.) The correlation is obtained from the transition matrix

$$\mathbf{M} = \begin{bmatrix} P_{A\to A} & P_{A\to B} \\ P_{B\to A} & P_{B\to B} \end{bmatrix} = \begin{bmatrix} 1 - f & f \\ f & 1 - f \end{bmatrix} \tag{3}$$

The conditional probability of being in state A at site $i + n$ given state B at site i is written as

$$P_n(A|B) = \langle A|\mathbf{M}^n|B \rangle \tag{4}$$

$\mathbf{M}^n$ is obtained by diagonalizing the matrix $\mathbf{M}$ and yields

$$\mathbf{M}^n = \frac{1}{2} \begin{bmatrix} 1 + (1 - 2f)^n & 1 - (1 + 2f)^n \\ 1 - (1 + 2f)^n & 1 + (1 + 2f)^n \end{bmatrix} \tag{5}$$

Now $\langle \sigma_{n+i} \sigma_i \rangle$ can be expressed as

$$\langle \sigma_{n+i} \sigma_i \rangle = P_A(\langle A|\mathbf{M}^n|A \rangle - \langle B|\mathbf{M}^n|A \rangle) + P_B(\langle B|\mathbf{M}^n|B \rangle - \langle A|\mathbf{M}^n|B \rangle) = (1 - 2f)^n \tag{6}$$

In the limit of small f (the blocky limit), expression 6 can be approximated as $\exp(-2nf)$. This implies that, for small f, the average run or block length of A (or B) is $1/(2f)$. On the other hand, as f approaches unity (the alternating chain

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limit), this correlation length is $1/(2(1 - f))$.

We make an Imry–Ma type[4] argument to estimate the free energy of the chain at the interface. We assume that the chain weaves back and forth across the boundary, forming loops L monomers in length on either side of the interface. Since the chain structure is correlated, we need to consider two contiguous segments. There are two possible ways to have one loop in one solvent and the second loop in the other solvent. The two configurations will have different energies, and, on average, the energy of the favored state is lower by an amount given by

$$\Delta E = -2\Delta\langle|\sum_{i=1}^{L}\sigma_i - \sum_{i=L+1}^{2L}\sigma_i|\rangle \tag{7}$$

which we approximate as

$$(\Delta E)^2 \approx \langle(\delta E)^2\rangle = 4\Delta^2\left[\sum_{i=1}^{L}\sum_{j=1}^{L}\langle\sigma_i\sigma_j\rangle + \sum_{i=L+1}^{2L}\sum_{j=L+1}^{2L}\langle\sigma_i\sigma_j\rangle - 2\sum_{i=1}^{L}\sum_{j=L+1}^{2L}\langle\sigma_i\sigma_j\rangle\right] = 4\Delta^2\left[\frac{2L(1-f)}{f} - \frac{2(1-2f)}{f^2}(1-(1-2f)^L) - \frac{1}{2f^2}(1-(1-2f)^L)^2\right] \tag{8}$$

We also must consider the entropy loss associated with having L monomers restricted to one side of the interface. The Green function for a continuum random walk of L steps restricted to $z > 0$ and starting and ending at Z' is[5]

$$G(Z',Z',L) = \left[\frac{3}{2\pi La^2}\right]^{1/2}\left[1 - \exp\left(-\frac{6Z'^2}{La^2}\right)\right] \tag{9}$$

where a is the mean length of an individual step in the random walk. For Z' in the vicinity of the interface, the entropy loss associated with requiring the chain to return to the interfacial region for the first time after L steps is

$$\Delta S = \ln\ G(Z',Z',L) \sim -\frac{3}{2}\ln L \quad \text{as } L \rightarrow \infty \tag{10}$$

Collecting terms, we can estimate the change in the free energy per monomer associated with placing the two segments of length L on opposite sides of the interface as

$$\frac{\delta F}{L} \sim -\frac{[(\delta E)^2]^{1/2}}{L} + \frac{T}{L}\ln L \tag{11}$$

Here, T is the temperature and we have ignored coefficients of order unity. (We have absorbed k_B in the definition of temperature.) For the purposes of the discussion, we will replace $\ln L$ in the entropy by a constant since this produces only logarithmic corrections to the asymptotic power laws. To find the observed loop length L^*, we numerically minimize expression 11 with respect to L. Figure 1 shows L^* as a function of f for several values of Δ/T. In Figure 2, we have plotted L^* vs $f/(1 - f)$ on a log–log scale.

A surprising result is that, for fixed Δ/T, L^* has a minimum at a finite value of f. Hence, this analysis indicates that there is a specific sequence distribution for which the chain is maximally localized at the interface. By forming small loops and frequently intersecting the boundary, this architecture will be the most efficient at reducing the interfacial tension. Consequently, the result has important implications in tailoring chains to optimize the desired interfacial properties.

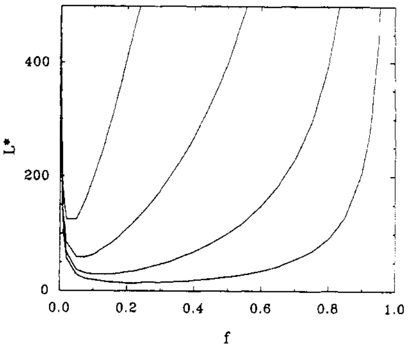

Figure 1. L^* vs f. Going from top to bottom, Δ/T = 0.05, 0.1, 0.2, and 0.4.

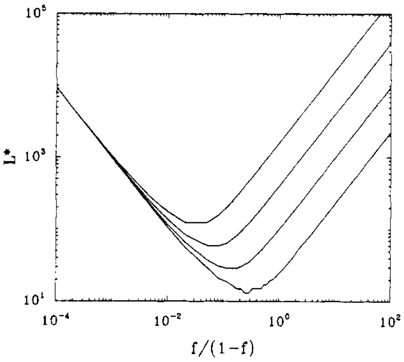

Figure 2. L^* vs $f/(1 - f)$ on a log–log scale for the same values of Δ/T as in Figure 1. As $f \rightarrow 0$, $L^* \rightarrow 1/f$ while in the weak interaction limit, $L^* \sim f/(1 - f)$ as $f \rightarrow 1$.

An additional interesting feature is the fact that as $f \rightarrow 0$, L^* does not depend on the amplitude of Δ/T. In this limit, the chain contains long blocks of A and B. For $\Delta > 0$ and sufficiently small f, segregation of entire blocks minimizes the free energy. In other words, loops of average size $1/f$ (the structural correlation length) will form. Since we have assumed a Gaussian chain, the polymer will be localized at the interface with an average width $W \sim L^{1/2} \sim f^{-1/2}$. We will refer to this regime as the strong interaction limit.[6]

In the opposite limit, which we refer to as the weak interaction limit, the entropic contribution in eq 11 is important. The L^* that minimizes the free energy will be much larger than the length over which the chain structure is correlated. Therefore, we choose L such that $L \gg 1/f$ and $L \gg 1/(1 - f)$. (The latter condition is necessary since as $f \rightarrow 1$, the correlation length along the chain $\sim 1/(1 - f)$.) In other words, the segment length L will contain many uncorrelated blocks of A and B monomers. In this case, we can ignore all but the first term in $(\delta E)^2$ (eq 8), and the free energy per monomer associated with restricting the loops to the interface can be written as

$$\frac{\delta F}{L} \sim -\frac{\Delta}{L^{1/2}}\left(\frac{1-f}{f}\right)^{1/2} + \frac{T}{L} \tag{12}$$

where, as discussed earlier, we have replaced the $\ln L$ term in the entropy by a constant. Minimizing this expression with respect to L yields

$$L^* \sim \left(\frac{T}{\Delta}\right)^2\frac{f}{1-f} \tag{13}$$

On length scale L^*, the chain will resemble a random copolymer. We recover the result of Garel et al. if we replace the interaction energy Δ with an effective energy:

$$\Delta_{\mathrm{eff}} = \Delta\left(\frac{1-f}{f}\right)^{1/2} \qquad (14)$$

From eq 13, we see that L^* increases as $f/(1-f)$ with increasing f, giving the behavior to the right of the minima in Figures 1 and 2. Furthermore, L^* decreases with an increase in Δ. In the weak interaction limit, the Gaussian chain is localized with width $W \sim (L^*)^{1/2} \sim (T/\Delta)(f/(1-f))^{1/2}$.

From eq 13 and the requirement that L^* is much greater than the length on which the chain structure is correlated, we see that for $f < {}^1/_2$ the self-consistency condition for the weak interaction limit is

$$\frac{T}{\Delta} \gg \frac{(1-f)^{1/2}}{f} \qquad (15)$$

while for $f > {}^1/_2$, the condition is

$$\frac{T}{\Delta} \gg \frac{1}{f^{1/2}} \qquad (16)$$

In both cases, the conditions will be satisfied at high temperatures or small values of Δ.

Simulations

To test these predictions, we have performed a series of molecular dynamics simulations. In these simulations, we consider a one-dimensional Gaussian chain near an interface. We need only consider a one-dimensional chain since the other dimensions will not be affected by the interface. The configuration of the N-monomer chain is given by $\{Z_i\}_{i=1,N}$. The interface is located at $Z = 0$ and the A type monomers favor the $Z > 0$ region, while the B's prefer the $Z < 0$ domain. We assume Rouse dynamics[7] and solve the following Langevin equation:

$$\frac{\partial Z_n(t)}{\partial t} = -\frac{1}{\gamma}\frac{\partial H}{\partial Z_n} + A_n(t) \qquad (17)$$

The frictional constant per monomer, γ, is assumed to be the same in both solvents. H is the "Hamiltonian" of the chain:

$$H\{Z\} = \frac{1}{\beta}\left[\sum_{n=2}^{N}\frac{1}{2b^2}(Z_n - Z_{n-1})^2 - \beta\Delta\sum_{n=1}^{N}\sigma_n \operatorname{sign}(Z_n)\right] \qquad (18)$$

where b is the bond length and $\beta = 1/T$. $A_n(t)$ is a Gaussian noise term, which represents the random force of the heat bath that acts on the polymer. This term is specified by

$$\langle A_n(t)\rangle = 0$$

$$\langle A_n(t)A_m(t')\rangle = \frac{2}{\gamma}T\delta_{nm}\delta(t-t') \qquad (19)$$

Substituting eq 18 into eq 17, we obtain

$$\frac{\partial Z_n(t)}{\partial t} = (Z_{n+1} - 2Z_n + Z_{n-1}) + 2\tilde{\Delta}\sigma_n\delta(Z_n) + A_n(t) \qquad (20)$$

where we have rescaled length and time variables,[8] so that $\tilde{\Delta} = \Delta/T$ and

$$\langle A_n(t)A_m(t')\rangle = 2\delta_{nm}\delta(t-t')$$

The δ function, $\delta(Z_n(t))$, can be rewritten as

$$\delta(Z_n(t)) = \sum_{i=1}\left|\frac{\mathrm{d}Z_n}{\mathrm{d}t}\right|^{-1}\delta(t - t^0_{n,i}) \qquad (21)$$

where $t^0_{n,i}$ is the time when the nth monomer crosses the interface ($Z = 0$) for the ith time. Equation 20 is solved using a standard Euler discretization scheme with the updating procedure given by the following prescription:

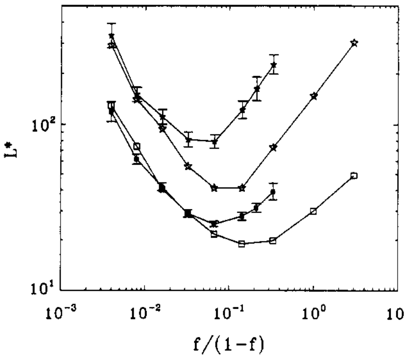

Figure 3. L^* (boxes) and $\bar{Z}^2$ (stars) vs $f/(1-f)$ on a log–log scale obtained from the molecular dynamics simulations. Two interaction strengths $\tilde{\Delta} = 0.05$ (filled symbols) and $\tilde{\Delta} = 0.1$ (open symbols) are shown. Only the uncertainties for $\tilde{\Delta} = 0.1$ are shown. The uncertainties for $\tilde{\Delta} = 0.05$ are of the same order.

$$Z_n(t + \delta t) = \begin{cases} Z_n'(t) & \text{if sign } (Z_n'(t)) = \text{sign } (Z_n(t)) \\ Z_n'(t) + 2\tilde{\Delta}\sigma_n \dfrac{\delta t}{Z_n'(t) - Z_n(t)} & \text{otherwise} \end{cases} \qquad (22)$$

where

$$Z_n'(t) = Z_n(t) + \delta t(Z_{n+1}(t) - 2Z_n(t) + Z_{n-1}(t)) + \tilde{A}_n(t) \qquad (23)$$

and

$$\langle \tilde{A}_n(t)\tilde{A}_m(t')\rangle = 2\delta t\delta_{n,m}\delta_{t,t'} \qquad (24)$$

At the start of the simulation, the polymer configuration is chosen to be a random walk chain with the time step, δt, set to 0.1. Chains of length 1024 bonds were examined. The chains were equilibrated over times much longer than the longest relaxation time of the Rouse model. To test the program, we set the polymer–solvent interaction energy equal to 0 (thus removing the presence of the interface and reducing the problem to a Gaussian chain in a single solvent) and determined the radius of gyration, R_g, for the chain. The results reproduced the expected $R_g^2 = N/6$.

We performed simulations for two different values of the interaction strength, $\tilde{\Delta} = 0.05$ and $\tilde{\Delta} = 0.1$. Eleven to twenty-one different initial configurations and arrangement of monomers were examined for each value of f. The statistics for each trial were obtained from an average over the last 1.8×10^6 updates. To quantify the localization of the chain, we measure the average $\bar{Z}^2$ of the polymer:

$$\bar{Z}^2 = \frac{1}{N}\langle\sum_{i=1}^{N} Z_i^2\rangle \qquad (25)$$

where the angular brackets indicate an average over time and initial conditions. We have also calculated the average radius of gyration and obtained an average value of L^* by dividing the length of the chain by the number of times it crosses the interface. Figure 3 shows $\bar{Z}^2$ and L^* vs f. (The radius of gyration and $\bar{Z}^2$ behave in a very similar manner.)

As predicted, the curves have a well-defined minimum. The beginning of the strong interaction regime can be seen at the smaller values of f. In this limit, the L^*'s (and $\bar{Z}^2$'s) for the two different $\tilde{\Delta}$ are seen to converge and L^* behaves as approximately $1/f$. Consistent with Figures 1

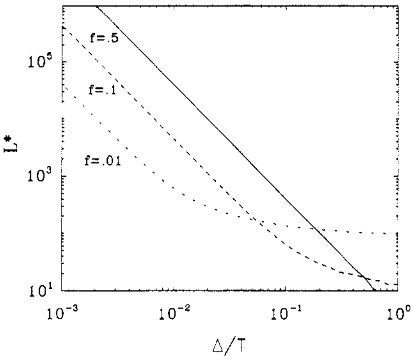

Figure 4. L^* vs Δ/T for fixed f. $f = 0.01$, $f = 0.1$, and $f = 0.5$ are shown. In the weak interaction regime, L^* increases with increasing f, while L^* decreases with increasing f in the strong interaction regime.

and 2, we find that the minimum in L^* is shifted to higher f for the larger $\tilde{\Delta}$. The weak interaction regime is seen at larger values of f. We find that L^* for $\tilde{\Delta} = 0.1$ is much smaller than that for $\tilde{\Delta} = 0.05$ as is predicted by eq 13. However, due to finite chain limitations, we have not reached the regime where $L^* \sim f/(1 - f)$.

To further clarify the effect of the polymer–solvent interaction energy and temperature on L^*, we have solved eq 11 for L^* as a function of Δ/T at a fixed value of f. The resulting plot is shown in Figure 4. As anticipated, increasing the polymer–solvent attraction drives the chain to lie closer to the interface. Furthermore, increasing Δ also broadens the range of f's for which the chain is localized at the boundary (see also Figure 1). Increasing temperature causes the opposite effect: at high temperature, entropy dominates and enhances the length of the excursion away from the boundary. Note that as Δ/T is increased, L^* approaches an asymptotic value of $1/f$.

Summary

In a previous paper,[9] Monte Carlo simulations were used to examine the behavior of two-dimensional multiblock copolymers at the penetrable fluid–fluid interface. In particular, AB polymers with sequence distributions characterized by $0 < f < 1/2$ were examined. The chains were assumed to be self-avoiding random walks, while in the present analysis the chains are Gaussian. However, both results show similar trends. Namely, the Monte Carlo studies also reveal that the chains weave across the interface. For long block lengths, the different segments are segregated in their respective good solvents. Furthermore, the width at the interface, W, is proportional to N_b^{ν}, where N_b is the block length and ν is the Flory exponent (or $3/4$ for a self-avoiding chain in two dimensions). Finally, a stronger polymer–solvent interaction is necessary to localize chains with smaller block lengths at the interface. These observations coincide with our current results for chains with $f \rightarrow 0$.

The results for $f \approx 1$ may be related to the localization characteristics of the chain at $f = 1$. To analyze this latter case requires different techniques from those presented here. Work in this direction is in progress.[10]

In summary, we have used both analytical arguments and molecular dynamics simulations to establish how the behavior of an AB copolymer at a liquid–liquid interface depends on the chain's sequence distribution. Given a set of solvent–polymer interaction energies and a fixed temperature, we can specify a range of f's for which the chain will be highly localized at the surface. (Note that the equations can be readily modified to account for cases where the monomer–solvent energies are not symmetric.) Furthermore, given a chain with a specific sequence distribution, we can determine a range of temperatures or solvents that will cause the chain to be maximally localized at the interface. These predictions can be used in tailoring macromolecular surfactants, for example, that will provide the optimal reduction in surface tension. Furthermore, the results indicate that the conformation of proteins at a membrane–fluid interface will be strongly affected by the arrangement of hydrophobic sites within a protein.

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