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Copolymers at Interfaces: Scaling and Monte Carlo Studies

Jens-Uwe Sommer (*), Gongwen Peng (**) and Alexander Blumen

Universität Freiburg, Theoretische Polymerphysik, Rheinstrasse 12, 79104 Freiburg, Germany

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Abstract. — We investigate using scaling arguments and Monte Carlo simulations the adsorption properties of AB-copolymers at the interface between two selective solvents. For random copolymers adsorption is determined by a single scaling variable, which is the same both for ideal chains and for excluded volume chains; numerical simulations based on the bond fluctuation model support the scaling prediction very well. For alternating AB-copolymers adsorption can be described (through a one-step renormalization) as a homopolymer problem at a penetrable interface; scaling is again obeyed well, as we demonstrate through simulations.

1. Introduction

Copolymers built of two monomer species A and B display rich patterns of behaviors. Of much interest are their properties in selective solvents; such solvents are good for one species but poor for the other. Because of the fact that both A and B are on the chain, simple demixing is not possible and, especially for random copolymers, frustrated behaviors can occur. On the other hand block copolymers are widely used for the reinforcement of interfaces between two imiscible polymer melts [1,2] or as "compatibilizer" [3], to improve the mechanical properties of polymer blends. This may be understood from Figure 1, which displays the interfacial potentials for the A- and B-species in the simplest symmetric case, where the A- and B-corresponding potentials are zero in the good solvent and $\chi$ in the poorer solvent, respectively; energy minimization forces the block copolymer to have its A-B covalent bond near the interface, i.e. in Figure 1 at $z = 0$. For a polymer with the A-preferred solvent at $z < z_0$, the potential is:

$$V(z) = \begin{cases} 
\chi \Theta(z - z_0) & \text{for A monomers} \\
\chi \Theta(z_0 - z) & \text{for B monomers}
\end{cases}$$

(1)

Here $\Theta(z)$ defines the Heaviside $\Theta$-function. In equation (1), $\chi$ is only a measure of the interaction with the external medium and does not, distinct from the usual Flory-Huggins picture, include any interchain interactions. The excluded volume effect is accounted for as a hard-sphere repulsion.

Now, while the behavior of homopolymers at interfaces was widely investigated [4-6], the situation for copolymers is still under discussion. Analytical treatments involved ideal chains and special configurations, such as a strict alternation or an annealed disorder [7]. Ideal copolymers with quenched disorder were studied by Garel et al. [8] using a Hartree-type approach;

(*) Author for correspondence (e-mail: sommerju@tpoly.physik.uni-freiburg.de)
(**) Permanent address: Institute of Physics, Academia Sinica, Beijing, China

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Balazs et al. [3] applied a self-consistent field theory [3] and also presented simulation results for different model situations [9,10], see also [11].

In the present article, we put forward a scaling approach valid both for ideal and also for excluded volume (real) chains, generalizing the results of references [12,13]. The results are supported by Monte Carlo simulations using the Bond Fluctuation Model (BFM) [14]. We consider the situation of a single copolymer (dilute surface regime), where the distribution of the A and B along the chain is either periodic or random.

2. Copolymer Models and Simulation Method

As discussed in reference [12] there are basically three different scaling situations for AB-copolymers, depending on their chemical structure. One distinguishes between diblock-copolymers, between random copolymers and between alternating copolymers. Here we confine ourselves to the last two, most interesting cases.

Random copolymers are viewed as an uncorrelated succession of A and B monomers along the chain. In the simulations physical quantities of interest such as the squared radius of gyration, $R^2$, are averaged a posteriori over 100 independent realizations of the AB-disorder. In the case of alternating AB-polymers structural disorder is not present. However, we still use 100 independent realizations of the simulation procedure to obtain good statistics.

We use here the three dimensional bond-fluctuation model (BFM) to simulate polymer chains near a penetrable selective interface. The details of this model, of widespread use can be found for instance in [14]. In the BFM each repeat unit of the polymer chain is represented by an elementary cell of a simple cubic lattice. Brownian-like dynamics is simulated by attempting to move a randomly chosen repeat unit over one nearest neighbor step in a randomly chosen direction. The move is denied whenever a constraint of the polymer conformation (overlapping of monomers, overstretching of bonds, crossing of hard boundaries etc.) is violated. In the BFM version used here the possible bonds between repeat units are taken from a set of 108 vectors [14]. The role of $\chi$ (see Fig. 1) is accounted for through the usual prescription: a monomer jump from the favorable to the unfavorable solvent is only accepted with probability $\exp(-\chi/(kT))$, where $kT$ is the product of Boltzmann's constant and temperature.

In all simulations a $50 \times 50 \times 100$ lattice was used, and periodic boundary conditions in the $x$ and $y$ directions were applied. The walls of the box in the $z$-direction are rigid. The interface is placed between the lattice coordinates $z = 50$ and $z = 51$. An A-monomer is subject to a repulsive potential when trying to move from $z = 50$ to $z = 51$ and vice versa for

![Diagram](image-url)

Fig. 1. — Schematic illustration of the selectivities for the A-monomers (full line) and B-monomers (dashed line).
the B-species. The range $z \leq 50$ is the favored solvent for the A-species and the range $z > 50$ for the B-species.

3. Random Copolymers

For random copolymers adsorption is controlled by a single scaling variable, as can be shown [8] from an Imry-Ma type argument [15]. We consider an AB-copolymer chain for which the sequence of the A and B is random and uncorrelated. Consider first a chain segment containing $g$ monomers; for $g$ sufficiently large, according to Gauss’ law, one species is in average in excess by roughly $\sqrt{g}$ monomers. Such a segment experiences an energy of $\chi \sqrt{g}$ when found in the “wrong” solvent, a situation which for $\chi \sqrt{g} > kT$ hardly happens. Now, the next segment has with probability $1/2$ the other species in excess; then these two segments will tend to be at the interface. In this picture one finds for $g$, the average number of monomers in a segment, that $g \sim (kT)^2 / \chi^2$, and that $N/g$, the total number of such segments (“blobs”) at the interface is proportional to $N \chi^2 / (kT)^2$. One expects the basic physical properties to be controlled by the number of blobs per chain rather than by the variables $\chi$, $kT$ and $N$ separately. In this spirit one introduces

$$\theta = \sqrt{N} \chi / (kT) \sim \sqrt{N/g}$$

as scaling variable. Scaling with respect to $\theta$ was demonstrated analytically for ideal chains in references [8,12]. Here we show through Monte-Carlo simulations that this also holds for real chains. We note that $\theta$ has the same form for ideal and for real chains. Already in reference [9] it was suggested that the average loop length is the same for ideal and excluded volume chains.

We take the interface perpendicular to the $z$-direction, and consider $R_{gz}$, the averaged radius of gyration in the direction perpendicular to the interface:

$$R_{gz}^2 = \sum_{i=1}^{N} (z_i - \bar{z})^2 / N$$

where $z_i$ are the $z$-components of the position vectors and $\bar{z} = \frac{1}{N} \sum_{i=1}^{N} z_i$. Using $\theta$ we write:

$$R_{gz}/(l N^{\nu}) = f(\sqrt{N} \chi / (kT)) = f(\theta)$$

where we take into account that the chain is in the scaling regime with respect to the excluded volume. Now for very low values of $\chi$ the chain remains isotropic: $R_{gz} \sim R_0 / \sqrt{3}$ with $R_0 \sim N^{\nu}$ ($\nu = 1/2$ for ideal chains and approximately 0.588 for real chains). In equation (4) we choose $l$ such that $f(0) = 1$. When $\chi$ (i.e. $\theta$) becomes larger $R_{gz}$ decreases. For $\theta$ large $R_{gz}$ should become independent of $N$ since then the blobs stick at the interface; cutting the chain in pieces smaller than $N$ (but larger than $g$) does not change much its shape, i.e., $R_{gz} \sim N^0$ for $\theta$ large. Furthermore assuming that $f(\theta)$ displays power law behavior (i.e. scales) leads to $f(\theta) = \theta^m$, and with equation (1) to $\nu + m/2 = 0$, i.e. to $m = -2\nu$. Hence

$$R_{gz}/(l N^{\nu}) \sim (\sqrt{N} \chi / (kT))^{-2\nu} = \theta^{-2\nu}$$

for $\theta$ large.

In Figure 2 we show for random copolymers $R_{gz}$ as a function of $\theta = \sqrt{N} \chi / (kT)$, for several values of $N$, $N = 16, 32, 64$ and 128. From low to moderate values of $\chi$ the results for different $N$ follow a common pattern, a fact which proves the scaling assumption. Deviations from scaling are found only for $\chi$ large: such $\chi$ values imply that each A-B covalent bond sticks to the interface between the solvents without need for further chain organization, so that $R_{gz}$
gets to be near to one bond-length. In this strong adsorption regime the plots of Figure 2 level off and scaling breaks down. This happens for a \( \chi \)-value around 6 irrespectively of \( N \). Hence the scaling regime with respect to \( \theta \) is larger for longer chains. The data of Figure 2 display around \( \theta_c \approx 10 \) a cross-over behavior from the nearly unperturbed region (\( f(\theta) \approx 1 \), \( \theta < \theta_c \)) to a decaying power-law, scaling behavior (for \( \theta \geq \theta_c \)). This crossover regime is rather narrow. From a best fit to the data in the scaling regime (e.g., Eq. (5)) we obtain numerically \( m = -1.112 \pm 0.10 \). This gives \( \nu = 0.56 \pm 0.05 \), which is quite close to the accepted 0.588 for real chains in good solvents.

4. Alternating Copolymers

An important, ordered situation is a strictly alternating copolymer: In this case in any subgroup of monomers the excess of one species over the other cannot be larger than unity, regardless of the subgroup’s length \( g \). Hence we cannot expect now an organization in majority-blobs as before; the previous Imry-Ma-type argument does not apply. However, a weaker organization mechanism is still operative. Consider an AB-subunit directly at the interface. Oriented such that both monomers are immersed in their favored solvents, the interaction energy of the subunit is \( 2\chi \) less than that for the opposite orientation. The situation is similar to that of a spin in an external field. We consider first the case when \( \chi/(kT) \) is smaller than unity so that the individual AB-units are only weakly oriented at the interface. When they are at the interface and not in the bulk, the AB-units gain a small amount of free energy \( \epsilon \), which equals [12, 13]:

\[
\epsilon = a\chi^2/(kT) ,
\]

where \( a \) is a numerical constant of order unity. The problem maps thus on the de Gennes model for the adsorption of homopolymers at a penetrable interface [4]: Our chain may be viewed as consisting of \( N/2 \) AB-units, each of which gains at the interface an effective energy \( \epsilon \). The reference state (\( \epsilon = 0 \)) is simply the free chain in the bulk and the adsorption is controlled by the

![Figure 2](image-url)
free energy per chain, which for an only slightly disturbed chain is proportional to $N^{1-\nu}\epsilon$ [13]. One has as a dimensionless energy variable $N^{1-\nu}\epsilon/(kT)$, so that we take as scaling variable

$$\eta = N^{(1-\nu)/2}\chi/(kT),$$

which is now $\nu$-dependent. Note that for alternating copolymers $\eta$ is different for ideal and for excluded volume chains, a fact which is different from the structure of $\theta$ in equation (2) and from the conclusion of reference [9]. Evidently the general scaling behavior changes when going from random to alternating AB-copolymers. Focusing on $R_{gz}$, we have in analogy to equation (4):

$$R_{gz}/(lN^\nu) = g(\eta) = g(N^{(1-\nu)/2}\chi/(kT))$$

To obtain the asymptotic behavior we proceed as in the previous section: we assume scaling, i.e., $g(\eta) = \eta^\rho$. Thus

$$R_{gz}/(lN^\nu) = (N^{(1-\nu)/2}\chi/(kT))^\rho$$

Requiring that $R_{gz}$ becomes independent of $N$ for large $\chi$ leads now to

$$\rho = -2\nu/(1-\nu).$$

Finally, when $\chi$ gets to be very large the whole chain lies near the interface and scaling breaks down.

Figure 3 displays our results for $R_{gz}$ obtained from simulations, where the chosen chain lengths are $N = 64, 128$ and $256$. We had to use longer chains than in Figure 2 because now the repeat units comprise two monomers and because the localization mechanism is weaker than before. The lattice size was also chosen larger than before, again in order to avoid artificial self-overlaps. We again remark, as in Figure 2, that scaling works well for small and moderately large $\eta$. Here the cross-over value $\eta_c$ between the regimes is around 4. A best fit
5. Conclusions

We have checked by Monte Carlo simulations that simple scaling ideas can explain the adsorption behavior of copolymers at selective interfaces. In particular for random AB-copolymers the scaling variable is the same for ideal and for excluded volume chains. We succeeded in showing numerically that for real chains scaling holds well. It holds regardless of the chain's character (ideal or real), because it is obviously based on simple grounds (flexible chain, Gaussian limit theorem).

For strictly alternating chains the effective adsorption energy of a AB-unit at a weakly selective interface, equation (6), again does not depend on the character (ideal or real) of the chain. Here, however, the character comes into play already for the scaling parameter $\eta$, see equation (7), which depends on $\nu$. Our numerical results confirm this scaling, which we exemplify using $R_{g2}$. We close by noting that the procedure used here can be extended to the case of many chains following the lines developed for homopolymers [16].

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References