Copolymer adsorption kinetics at a selective liquid-liquid interface:
Scaling theory and computer experiment

A. Corsi,1 A. Milchev,1,2 V.G. Rostiashvili,1 and T.A. Vilgis1

1Max - Planck - Institute for Polymer Research - Ackermannweg 10, 55128 Mainz, Germany
2Institute for Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

(Dated: January 10, 2022)

We consider the adsorption kinetics of a regular block-copolymer of total length \( N \) and block size \( M \) at a selective liquid-liquid interface in the limit of strong localization. We propose a simple analytic theory based on scaling considerations which describes the relaxation of the initial coil into a flat-shaped layer. The characteristic times for attaining equilibrium values of the gyration radius components perpendicular and parallel to the interface are predicted to scale with chain length \( N \) and block length \( M \) as \( \tau_{\perp} \propto M^{1+2\nu} \) (here \( \nu \approx 0.6 \) is the Flory exponent) and as \( \tau_{\parallel} \propto M^{2} \), although initially the rate of coil flattening is expected to decrease with block size as \( \propto M^{-1} \). Since typically \( N \gg M \) for multiblock copolymers, our results suggest that the flattening dynamics proceeds faster perpendicular rather than parallel to the interface. We also demonstrate that these scaling predictions agree well with the results of extensive Monte Carlo simulations of the localization dynamics.

PACS numbers: 36.20.-r, 68.05.-n, 07.05.Tp

The behavior of hydrophobic - polar (HP) copolymers at a selective penetrable interface (the interface which divides two immiscible liquids, like water and oil, each of them being favored by one of the two types of monomers) is of great importance in the chemical physics of polymers. For strongly selective interfaces the hydrophobic and polar blocks of a copolymer chain try to stay on different sides of the interface leading thus to a major reduction of the interfacial tension between the immiscible liquids or melts which has important technological applications, e.g. for compatilizers, thickeners or emulsifiers. Not surprisingly, during the last two decades the problem has gained a lot of attention from experiment [1-3, 4, 5, 6], theory [7-12, 13, 14], as well as from computer experiment [15, 16]. While in earlier studies attention has been mostly focused on diblock copolymers [2, 4, 5] due to their relatively simple structure, the scientific interest shifted later to random HP-copolymers at penetrable interfaces [6, 7, 8, 9, 14]. Until recently though, the properties of regular multiblock copolymers, especially with emphasis to their dependence on block length \( M \), have remained largely unexplored.

In a recent study [12] we showed that the equilibrium properties (structure, diffusion coefficient, etc.) of a regular HP-copolymer at a selective liquid-liquid interface are well described in both regimes of weak and strong localization by a scaling theory in terms of the total copolymer length \( N \) and the block size \( M \). In particular, we demonstrated that: (i) the crossover selectivity decreases with growing block length as \( \chi_c \sim M^{-(1+\nu)/2} \) and the crossover selectivity to the strong localization regime vanishes as \( \chi \sim M^{-1} \), and (ii) the size of the copolymer varies in the weak localization regime as \( R_{g_{\perp}} \sim M^{-\nu}/(1-\nu) \) and \( R_{g_{\parallel}} \sim M^{(2-\nu)/2}/(1-\nu) \), and as \( R_{g_{\perp}} \sim M^{\nu}, \ R_{g_{\parallel}} \sim M^{-(2-\nu)} \) in the case of strong localization (where \( \nu_2 = 3/4 \) is the Flory exponent in two dimensions). We shall use these results in the present communication in which we suggest a theory of the adsorption kinetics of a regular block copolymer at a liquid-liquid interface based on dynamical scaling arguments. To the best of our knowledge so far there have been no attempts to treat this problem analytically or by means of computer simulation.

In our dynamical scaling analysis we consider a coarse-grained model of a multiblock copolymer consisting of \( N \) repeat units which is built up from a sequence of H- and P - blocks each of length \( M \). For simplicity one may take the interface with negligible thickness as a flat plane which separates the two selective immiscible solvents. The energy gain of each repeat unit is thus \( -\chi \), provided it stays in its preferred solvent, and the system is considered in the strong localization limit where \( \chi > \chi_{\infty} \sim M^{-1} \) [15, 16]. We neglect the effect of bulk diffusion on adsorption, and place the center of mass of an unperturbed coil at time \( t = 0 \) at the interface whereby the localization field is switched on. The initial coil will start then relaxing with time into a flat ("pancake") equilibrium configuration in-plane with the interface and the kinetics of relaxation will be determined by the sum of the various forces acting on the copolymer.

In order to estimate the driving force of the flattening process, one may recall [15, 16] that the effective attractive energy \( \epsilon \) (per diblock) in the strong localization limit is \( \epsilon \approx \chi M \). In this case the diblock (i.e. a segment consisting of one H- and one P-block) plays the role of a blob and the overall attractive free energy \( F_{\text{attr}} \propto \epsilon N \propto \chi N \) where \( N \approx N/M \) is the total number of blobs. Thus the effective driving force perpendicular to the interface is \( f_{\perp}^{\text{attr}} \approx -\chi N/R_{\perp} \) where \( R_{\perp} \) denotes the perpendicular component of the radius of gyration. This force is op
posed by a force of confinement due to the deformation of the self-avoiding chain into a layer of thickness \( R_\perp \). The corresponding free energy of deformation is simply estimated as \( E_{\text{conf}} \sim N(b/R_\perp)^{1/\nu} \) where \( b \) is the Kuhn segment size \[1\]. For the respective force then one gets \( f_{\text{conf}} \sim N b^{1/\nu}/R_\perp^{1/\nu+1} \).

The equation of motion for \( R_\perp \) follows from the condition that the friction force which the chain experiences during the motion in the direction perpendicular to the interface is balanced by the sum of \( f_{\text{attr}} \) and \( f_{\text{conf}} \). In the case of Rouse dynamics, each chain segment experiences independent Stokes friction so that the resulting equation of motion has the form

\[
\zeta_0 N \frac{dR_\perp}{dt} = -\frac{N \nu}{R_\perp} \frac{1}{R_\perp^{1/\nu+1}} ,
\]  

(1)

where \( \zeta_0 \) is the friction coefficient per segment.

During the flattening process, the chain spreads parallel to the interface due to the excluded volume interaction. Within the Flory mean field arguments, the corresponding free energy \( E_v \approx v N^2/(R_\parallel R_\perp) \) where \( v \) is the second virial coefficient and \( R_\parallel \) is the gyration radius component parallel to the interface. The corresponding driving force is \( f_{\text{def}} = -R_\parallel/(bN) \).

Taking into account the balance of forces in the parallel direction, the equation of motion for \( R_\parallel \) takes then the following form

\[
\zeta_0 N \frac{dR_\parallel}{dt} = v N^2 / R_\parallel R_\perp - \frac{R_\parallel}{bN} ,
\]  

(2)

Evidently, the excluded volume interactions provide a coupling between the relaxation perpendicular and parallel to the interface. Thus Eqs. \( 1 \) and \( 2 \) describe the relaxation kinetics of a multiblock copolymer configuration at a selective liquid-liquid interface. One may readily verify that the equilibrium solutions which follow from these equations are

\[
R_\perp^{\text{eq}} \simeq b M^\nu ,
\]  

(3)

and

\[
R_\parallel^{\text{eq}} \simeq (vb)^{1/4} M^{-\nu/4} N^{\nu^2} .
\]  

(4)

This coincides with the equilibrium expressions for \( R_\perp \) and \( R_\parallel \) derived earlier from purely scaling consideration \[1\]. The only difference is in the power of the \( M \) dependence in eq. \( 4 \) which looks like \( M^{-\nu/4} \) instead of \( M^{-(\nu_2-\nu)} \) in ref. \[15\] albeit numerically the values of both exponents coincide: \( \nu/4 \simeq (\nu_2-\nu) \simeq 0.15 \).

For the full solution of the equations of motion it is convenient to rescale the variables as \( x \equiv R_\perp/(b M^\nu) \), \( y \equiv R_\parallel/(vbN^3) \) so that eqs. \( 1 \) and \( 2 \) can be written in the dimensionless form

\[
\frac{dx}{dt} = \frac{1}{x^{1/\nu+1}} - \frac{1}{x} ,
\]  

(5)

and

\[
\frac{dy}{dt} = \frac{1}{x} - y .
\]  

(6)

The characteristic times for relaxation perpendicular and parallel to the interface in eqs. \( 5 \) - \( 6 \) should then scale as \( \tau_\perp \simeq \zeta_0 b^2 M^{1+2\nu} \), and \( \tau_\parallel \simeq \zeta_0 b^2 N^2 \).

Eq. \( 6 \) can be solved exactly:

\[
\frac{x^2(t)}{2} \left[ 1 - F(2\nu, 1; 1 + 2\nu; x^{1/\nu}(t)) \right] - \frac{x^2(0)}{2} \left[ 1 - F(2\nu, 1; 1 + 2\nu; x^{1/\nu}(0)) \right] = -\frac{t}{\tau_\perp} ,
\]  

(7)

where \( F(\alpha, \beta; \gamma; z) \) is the hypergeometric function and \( x(0) = R_\perp(0)/b M^\nu \) is the initial value. In the early stage of relaxation (i.e. at \( t < \tau_\perp \)) one has \( x \gg 1 \) and the solution, eq. \( 7 \), with \( R_\perp(0) \approx b N^\nu \) reduces to

\[
R_\perp^2(t) = R_\perp^2(0) - \frac{t}{\zeta_0 M} ,
\]  

(8)

so that the perpendicular collapse of the chain should last proportionally to the block length \( M \). In the opposite limit of late stage kinetics, \( t \gg \tau_\perp \), and \( x \gg 1 \), that is, close to equilibrium, the relaxation of \( R_\perp(t) \) is essentially exponential with \( \tau_\perp \propto M^{2.2} \).

Moreover, as typically \( N \gg M \), one expects that \( \tau_\parallel \gg \tau_\perp \), i.e. the chain coil collapses first in the perpendicular direction to its equilibrium value and after that slowly extends in the parallel direction. In this case one can use \( x(t) \approx x^{\text{eq}} = 1 \) in eq. \( 7 \) and derive the resulting solution for the parallel component of \( R_\parallel \) as

\[
y(t) - 1 = [y(0) - 1] \exp(-t/\tau_\parallel) ,
\]  

(10)

where the initial value \( y(0) < 1 \). As one may see in Fig. \( 1 \) the time evolution of \( R_\perp \) and \( R_\parallel \) which follows from the solution of the system of differential equations \( 5 \) - \( 6 \), resembles qualitatively rather well the simulation data even though one should bear in mind that the time axis for the former is in arbitrary units (scaling always holds up to a prefactor) whereas in the simulation time is measured in MC steps (MCS) per monomer (i.e., after all monomers have been allowed to perform a move at random). The relaxation of \( R_\parallel \) looks somewhat slower and, as our data for longer chains show, this effect becomes much more pronounced with growing number of blocks.

For the Monte Carlo simulations we use an off-lattice bead-spring model that has been employed previously for
ell effective bond, which can vary in between 128 and block size M.

The numerical solution of eqs. (5)-(6) for a copolymer of length N
is the distance between the beads, and the parameters are chosen as:

\[ \tau_r (t) = \tau_0 + \chi/2. \]

The inset shows the typical behavior of \( R_{\perp} \) at different block lengths, indicating dynamics is then followed until the chain reaches its new equilibrium configuration at the interface. Since we are interested in the behavior of these chains in the limit of strong localization, we have chosen \( \chi = 2 \chi_c \), where \( \chi_c \) is the crossover selectivity as obtained in Ref. [15]. We use periodic boundary conditions in the plane of the interface while there are rigid walls in the z-direction, where the simulation box extends from \( z = -32 \) to \( z = 32 \). Typically we studied chains with lengths \( 32 \leq N \leq 512 \) and block lengths \( 1 \leq M \leq N/8 \) whereby all measurements have been averaged over 1024 different and independent equilibrated starting configurations.

From Fig. 2 one may readily verify that the initial collapse of \( R_{\perp} \) with time closely follows the predicted rate \( \propto M^{-1} \) according to eq. (3) in the limit of \( N,M \gg 1 \). Moreover, for sufficiently large block size M the N-dependence of this initial rate disappears so that asymptotically this initial perpendicular collapse is governed by the length M only. In contrast, during the late stages of localization at the interface one observes on Fig. 3 the expected, cf. eq. (4), characteristic scaling of
\( \tau_1 \propto M^{1+2\nu} \) which progressively improves as the asymptotic limit is approached. Note that the fits of \( \tau_1 \) are taken only after the initially unperturbed coil has sufficiently relaxed. \( R_{\perp}(t)/R_{\perp}(0) \leq 1/e \). As expected, the initial dependence of \( \tau_1 \) on \( N \) is seen to vanish as \( M \) and \( N \) become sufficiently large, in agreement with eq. \( \text{[9]} \).

Eventually, in Fig. 4 we display the measured scaling of the characteristic time for spreading along the interface, \( \tau_{\parallel} \), with block size \( M \) for different chain lengths \( 32 \leq N \leq 512 \). Apart from some scatter of data for too small \( N = N/M \), one recovers nicely the relationship \( \tau_{\parallel} \propto N^2 \) whereby, once again, the initial \( M \)-dependence gradually diminishes as \( N \gg 1 \).

In summary, it appears that the simple scaling theory of copolymer adsorption on a selective liquid-liquid interface captures well the most salient features of the problem as a comparison with extensive MC simulation data demonstrates. In this letter we focus our consideration on the case of Rouse dynamics whereby hydrodynamic effects are neglected. Therefore the present approach should be appropriate to the case of an interface between immiscible polymer melts. The case of the so-called Zimm dynamics which accounts for hydrodynamic effects will be discussed in an extended paper.

Acknowledgments AM acknowledges the support and hospitality of the Max-Planck Institute for Polymer Research in Mainz during this study. This research has been supported by the Sonderforschungsbereich (SFB 625).

**References**

[1] B. J. Clifton, T. Cosgrove, R. M. Richardson, A. Zarabkhsh, and J. R. P. Webster, Physica B 248, 289(1998).
[2] G. Rother, and G. F. Findenegg, Colloid Polym. Sci. 276, 496(1998).
[3] R. Wang, and J. B. Schlenoff, Macromolecules 31, 494(1998).
[4] P. Omarjee, P. Hoerner, G. Riess, V. Cabuili, and O. Mondain-Monval, Eur. Phys. J. E 4, 45(2001).
[5] J.-U. Sommer and M. Daoud, Europhys. Lett. 32, 407 (1995).
[6] J.-U. Sommer, G. Peng and A. Blumen, J. Phys. II (France) 6, 1061 (1996); J. Chem. Phys. 105, 8376 (1996).
[7] T. Garel, D.A. Huse, S. Leibler and H. Orland, Europhys. Lett. 8, 9 (1998).
[8] X. Chatellier and J.-F. Joanny, Eur. Phys. J. E 1, 9(2000).
[9] N.A. Denesyuk and I.Ya. Erukhimovich, J. Chem. Phys. 113, 3894 (2000).
[10] A. C. Balazs, and C. P. Semasko, J. Chem. Phys. 94, 1653(1990).
[11] R. Israels, D. Jasnow, A.C. Balazs, L. Guo, G. Krausch, J. Sokolov, and M. Rafailovich, J. Chem. Phys. 102, 8149 (1995).
[12] J.-U. Sommer, G. Peng and A. Blumen, J. Chem. Phys. 105, 8376(1996).
[13] Y. Lyatskaya, D. Gersappe, N.A. Gross, and A.C. Balazs, J. Chem. Phys. 100, 1449 (1996).
[14] Z. Y. Chen, J. Chem. Phys. 111, 5603 (1999); 112, 8665 (2000).
[15] A. Corsi, A. Milchev, V.G. Rostiashvili, and T.A. Vilgis, J. Chem. Phys. 122, 094907(2005).
[16] E. Leclerc and M. Daoud, Macromolecules 30, 293(1997).
[17] P.-G. de Gennes, Scaling Concepts in Polymer Physics,
Cornell University Press, N.Y., 1979.

[18] K. Binder and A. Milchev, J. Computer-Aided Mater.