

Order in semiflexible polymers at an interface

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In the present paper, the simultaneous effect on a polymer of orientation by a solid surface and strong repulsion at the interface with an incompatible liquid is studied. Semiflexible polymers resist deformations perpendicular to the monomer and have a tendency to align in a given direction in contact with a surface. When a second incompatible liquid is added, a sharp interface between the two liquids forms at a given distance from the substrate. By changing the nature of the second liquid, this second constraint can control the order and force the polymer in the ordered surface layer to assume different conformations. The wormlike chain is used to define the parameters of the system that will determine the resulting conformation. An extended or contracted form is found depending on how the chains interact with the liquid.

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I. INTRODUCTION

The formation of ordered liquid layers near an interface or surface is of fundamental and practical interest [1,2]. A clearer view of liquid-surface interactions and their control would be useful for many practical applications in systems such as lubricants, coatings, detergents and suspensions. Recent experimental work on model systems has proven the existence of order under certain conditions and has studied the effects of temperature and degree of polymerization (DP) [3–5]. Orientational order in polymer systems is observed near a surface or an interface if the polymer chains are sufficiently long and the temperature sufficiently low for the loss of entropy to be balanced by a gain in interaction energy. The chains orient in a preferential direction to the surface. Such orientational effects are well known in liquid crystals and routinely used in industrial applications [6]. In liquid crystals, the anchoring force at the surface fixes the direction of preferred orientation in the bulk by coupling the direction of the molecular axis and the surface plane. In systems without liquid crystal phases, a surface anchoring could cause some orientational order of the monomers in the immediate vicinity of the surface-liquid contact. Strong interaction at the contact between a surface and a polymer liquid is not unusual; in physisorption, steric effects produce efficient packing of the chains, and in chemisorbed systems, chemical bonding develops. In systems with weak orientation-dependent interaction, the polymer must have appreciable resistance to bend deformations in order to straighten under outside influences and the resulting monomer distribution of a flexible chain does not necessarily produce orientational order. Semiflexible polymers that resist deformations perpendicular to the monomer may show a tendency to align in a given direction relative to the surface [7,8]. For example, it was shown that model rigid asymmetric chains can orient parallel to an interface simply due to the coupling between position and direction of a monomer [9].

For a distribution of monomers that depends on the direction of the monomer as well as the position, an anisotropic

chain conformation can emerge. Anisotropic elongation of the monomer density allows us to model the polymers by ellipsoids in numerical simulation studies and in analytical theory [10]. As the anchoring force decays away from the surface into the bulk liquid, the monomer distribution will return to spherical symmetry.

Recently, a second incompatible liquid has been added to control the order of a liquid in contact with a surface [11]. A sharp interface between the two liquids forms at a given distance from the substrate and by changing the nature of the second liquid this second constraint can force the ordered surface layer to assume many different conformations. Depending on how the chains interact with the liquid, an extended or contracted form is observed. In the present paper, the wormlike chain is used to study the simultaneous effect on a polymer of orientation by a solid surface and strong repulsion at the interface with an incompatible liquid and to define the parameters of the system that will determine the resulting conformation.

II. MODEL

The model considers a two-component fluid, the ‘‘surfactant.’’ A and the solvent B , in contact with a substrate W . The structure of the fluid is shown in Fig. 1 and is assumed as follows. There is first a layer of N_A surfactant monomers attached by polar heads to the wall. This is followed at a distance D by the N_B monomers of solvent and, due to incompatibility between the solvent and the surfactant (unfavorable Flory interaction χ), the layers consist of almost pure A or B [9]. Because of the wall, the chains of A have a tendency to align, manifested by an extended conformation. The interactions are modeled by mean field averages, in the layers, of the interactions between the surfactant units U_{AA} , between the solvent units U_{BB} , as well as a contribution from the orientation dependent interaction of surfactant with the wall, V_{AW} . The orientational order of the surfactant is determined by the wall interaction and depends on the DP ($=Z_A$) of the surfactants and on the chain stiffness. In a first step the interactions between A and B in the narrow interface can be neglected. These are usually only weakly dependent on orientation of the monomers except in liquid crystals. The

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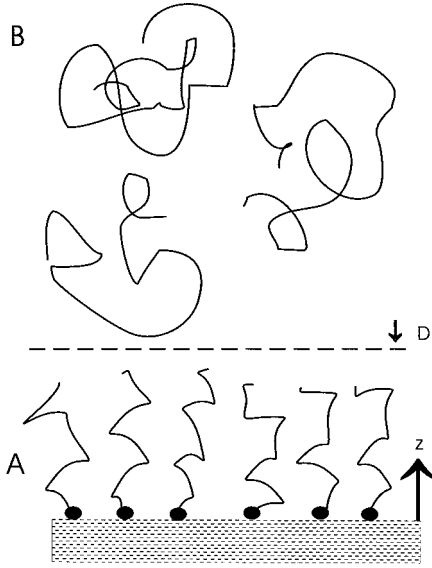


FIG. 1. Schematic representation of the sample with an ordered layer of chains *A* in contact with a substrate *W* and with an interface with an incompatible polymer *B* at distance *D* from the substrate. The *z* axis is perpendicular to the substrate.

thickness of the layer *D* is found then by minimization of the free energy. For a given surfactant and substrate, *D* will be determined by V_{AW} and by the difference between the two interactions U_{BB} and U_{AA} . If the net repulsion $U_{AA} - U_{BB}$ is sufficiently negative, *D* will be large. This means that the system gains energy by increasing the more favorable contribution of *A* at the cost of unfavorable *B*. The surfactant chains resist the elastic deformation and the maximum extension is of the order of the DP. The change in conformation is not just a variation of the radius of gyration but an anisotropic extension perpendicular to the surface. The parameters of the system are the persistence length and the DP of the surfactant chains, and the interactions described above. Experiments vary U_{BB} . If the assumptions are correct, the width of the surfactant layer and the extension of the chains should be larger the larger the repulsion between solvent molecules in the pure solvent layer.

III. CALCULATIONS

The surfactant chain is represented by a semiflexible model [7–9,12]. The wormlike chain model measures deformation of the local tangent to the elastic chain $w(s)$ with an energy $(c_b/2) \int_0^L ds (dw/ds)^2$. The bend elastic constant is c_b and *s* is the length measured along the chain of total length *L*. Stretch deformation is included by a coupling term that forces the polymer chain with monomers at positions $r(s)$ to lie close to the mathematical line with $\vec{w}(s) = d\vec{r}(s)/ds$. The isotropic excluded volume in the mean field approximation [13] donates an energy $\int ds U[r(s)]$. Near the surface, the orientation-dependent wall-monomer interaction contributes an energy $\int ds V(r(s), w(s))$. The usual model for *V* is an expansion in spherical harmonics, limited here to the lowest order quadrupolar term [6,10,14]. All interactions are given per unit segment length.

The probability for a conformation of the chain as given by positions $r(s)$ and orientations $w(s)$ is found from the Boltzmann factor

$$P(\vec{r}(s), \vec{w}(s)) = \exp \left\{ - \int_0^L ds \left[\frac{c_b}{2kT} \left(\frac{d\vec{w}(s)}{ds} \right)^2 + \frac{c_d}{2kT} \left(\vec{w}(s) - \frac{dr(s)}{ds} \right)^2 + \frac{U[\vec{r}(s)]}{kT} + \frac{V(\vec{r}(s), \vec{w}(s))}{kT} \right] \right\}. \quad (1)$$

A useful quantity is the probability $G(r_0, w_0, r, w, L)$ to find the last monomer at *r* with direction *w* for a initial position r_0 and direction w_0 ,

$$G(\vec{r}_0, \vec{w}_0, \vec{r}, \vec{w}, L) = \int d\vec{r}(s) d\vec{w}(s) P(\vec{r}(s), \vec{w}(s)) \delta(\vec{r}(0) - \vec{r}_0) \delta(\vec{w}(0) - \vec{w}_0) \delta(\vec{r}(L) - \vec{r}) \times \delta(\vec{w}(L) - \vec{w}). \quad (2)$$

The equation for $G(r_0, w_0, r, w, L)$ is derived as usual from the definition given in Eq. (2) [15],

$$\frac{dG}{dL} = \frac{kT}{2c_b} \Delta_{\vec{w}} G - \vec{w} \cdot \frac{d}{d\vec{r}} G + \frac{kT}{2c_d} \Delta_{\vec{r}} G - \frac{1}{kT} \times [U(\vec{r}) - V(\vec{r}, \vec{w})] G. \quad (3)$$

The position and orientation dependence of the end-to-end monomer distribution are coupled. For semiflexible chains, the persistence length $q = c_b/kT$ is a measure of the stiffness of the polymer structure to bend deformations: $q/L \rightarrow \infty$ defines the rigid rod limit, $q/L \rightarrow 0$ defines the limit of flexible chains. To apply Eq. (3) to flexible symmetric chains with no resistance to bend, the distribution of monomers must be independent of orientation and the usual excluded-volume problem reappears.

To derive space-averaged properties for the semiflexible surfactant of DP Z_A and density n_A , the system is divided into two parts as described in the model. The surfactant chains are constrained in the layer of width *D* where wall interaction is also present. The solvent chains of DP Z_B and density n_B fill the remaining part of the sample of width *d*-*D*.

For the surfactant chains, Eq. (3) is averaged over all initial and final positions of monomers in the layer near the wall to obtain

$$G_A(w_0, w, L_A) = [1/D] \int dz G(z_0, w_0, z, w, L_A),$$

which is a solution of

$$\frac{dG_A}{dL_A} = \frac{kT}{2c_b} \Delta_{\vec{w}} G_A - (U_{AA} + V_{AW} Y_{20}(\vec{w})) G_A, \quad (4)$$

The mean-field interaction parameters are the effective excluded-volume interaction (here simply U_{AA} due to exclusion of the solvent) and the effective-wall interaction

as derived from $V(z,w)=V(z)Y_{20}(w)$ with $V_{AW}G_A = \int d(z/D)G(z_0,w_0,z,w,L_A)V(z)/kT$.

The boundary condition $G=0$ is imposed at the limits $z=0,D$ of the layers. As discussed elsewhere [8,12], this equation is solved using eigenfunctions in an expansion in spherical harmonics $Y_{LM}(w)$. The z axis is placed perpendicular to the wall (Fig. 1), the chain ends are assumed to be free symmetrical and invariant to rotation around the chain axis.

Then $G_A(w,w_0,L_A)=\sum\Phi_j^*(w_0)\Phi_j(w)\exp(-E_jL_A)$ with $\Phi_j(w)=\sum a_j^{LM}Y_{LM}(w)$ and the equations for the coefficients are obtained from Eq. (4):

$$\left(-E_j+U_{AA}+\frac{kT}{2c_b}(L+1)L\right)a_j^{LM} + \sum_{L'M'}(-1)^MC(L-M,L'M',20)V_{AW}a_j^{L'M'}=0 \quad (5)$$

with the definition

$$C(LM,L'M',L''M'')=\int dw Y_{LM}(w)Y_{L'M'}(w)Y_{L''M''}(w).$$

Relaxing the initial condition, $\lim_{L_A\rightarrow 0}G_A(\vec{w}_0,\vec{w},L_A)\rightarrow\delta(\vec{w}_0-\vec{w})$, the eigenvalues are calculated for $q/L_A\rightarrow 0$ from a limited expansion to order 2: For $j=1$,

$$E_1=U_{AA}+\frac{kT}{c_b}+V_{AW}C(10,10,20),$$

for $j=0(-),2(+)$

$$E_j=U_{AA}+\frac{1}{2}\left[\frac{3kT}{c_b}+V_{AW}C(2;0,20,20)\right]\left[1\mp\left(1+\frac{4V_{AW}^2C(20,20,00)^2}{\left(\frac{3kT}{c_b}+V_{AW}C(20,20,20)\right)^2}\right)^{1/2}\right]$$

and the coefficients are found to be for $j=1, M=0$,

$$a_1^1=1, \quad a_1^0=a_1^2=0,$$

for $j=0,2, M=0, a_j^1=0$

$$(a_j^0)^2=\frac{1}{4\pi}\frac{V_{AW}^2}{(E_j-U_{AA})^2+\frac{V_{AW}^2}{4\pi}},$$

$$(a_j^2)^2=\frac{(E_j-U_{AA})^2}{(E_j-U_{AA})^2+\frac{V_{AW}^2}{4\pi}}.$$

IV. RESULTS

The properties of the surfactant layer of A chains now follow [12]. The monomer density will be considered to be unchanged relative to the bulk. The order of the chain is measured by $S=(1/L_A)\int ds\langle Y_{20}(w(s))\rangle$ with

$$S=\frac{(4\pi)}{Q_A}\sum a_j^0a_j^0,a_j^1,a_j^1C(20,l0,l'0) \times \int_0^{L_A}\frac{ds}{L_A}e^{-E_j s-E_j'(L_A-s)}, \quad (6)$$

where $\langle \rangle$ denotes the average in chain conformations as measured by G . The chain extension perpendicular to the wall is

given by the correlation function of orientation along the chain in the direction perpendicular to the wall,

$$\langle w_{\parallel}^2 \rangle = \int_0^{L_A} ds' \int_0^{s'} ds \langle w_z(s)w_z(s') \rangle = \frac{2}{3}\frac{(4\pi)^2}{Q_A}\sum a_j^0a_j^{l'}a_j^0,a_j^l,a_j^k,a_j^{k'} \times C(10,l'0,k0)C(10,k'0,l0)I_{jj'}$$

$$I_{jj'} = \int_0^{L_A} ds' \int_0^{s'} ds \exp[-E_j s - E_j'(s'-s) - E_j'(L_A-s')]. \quad (7)$$

As discussed in [12], the average chain conformation can be enclosed within an ellipsoid with the long principal axis proportional to $\langle w_{\parallel}^2 \rangle$.

The partition function of the semiflexible A chains is $Q_A = 4\pi[(a_0^0)^2e^{-E_0L_A}+(a_2^0)^2e^{-E_2L_A}]$.

For the flexible solvent B molecules of length L_B , the position-averaged solution of Eq. (4) leads to $G_B=\exp(-U_{BB}L_B),U_{BB}$ being the average isotropic excluded volume interaction between B monomers.

The total free energy of total width d of the system consisting of the surfactant and the solvent is

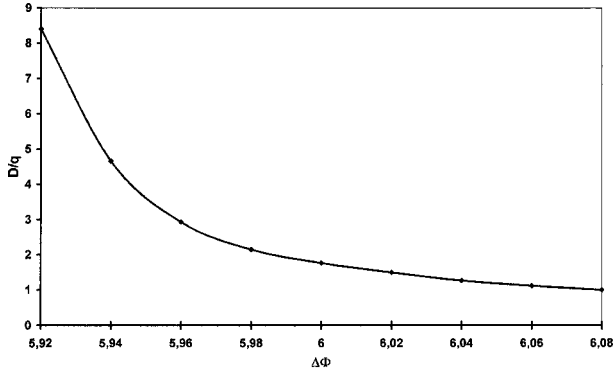


FIG. 2. The thickness D of the ordered layer in the weak interaction limit as a function of potential difference $\Delta\phi$ (in units of kT) for effective anchoring potential with the substrate $v/\lambda = 1$. q is the persistence length of the A chains of total length L_A . The sample thickness is $d = q(0.18 \times 10^3)$.

$$\frac{F}{kT} = \frac{N_A}{Z_A} \left(-\frac{1}{2} U_{AA} L_A + \ln \frac{N_A}{Z_A} - 1 - \ln Q_A \right) + \frac{N_B}{Z_B} \left(\frac{1}{2} U_{BB} L_B + \ln \frac{N_B}{4\pi Z_B} - 1 \right). \quad (8)$$

The extension D of the surfactant layer is calculated by minimization of F with D for equilibrium of surfactant and solvent with their coexisting phases of zero chemical potential.

To illustrate the results, the wall-surfactant interaction is modeled by a simple exponential $V(z) = -v \exp(-\lambda z)$. In this case, the layer average is calculated as $V_{AW} \approx -v/\lambda D$.

For $q/L_A \ll 1$, the approximate solution of D/d in the limit of weak interactions (D/L_A small) is found on minimization of (8):

$$\frac{D}{q} = \frac{v}{\lambda} \frac{C(20,20,20)}{\left(1 + \frac{\Delta\phi}{kT} + \ln \frac{vq}{\lambda d} C(20,20,20) \right)}, \quad (9)$$

where $\Delta\phi$ is the difference in free energy between A and B molecules, including the entropy of the semiflexible chains (N_A^0 and N_B^0 are the number of A or B monomers needed to fill the entire sample of thickness d):

$$\frac{\Delta\phi}{kT} = \frac{1}{2} U_{AA} L_A + \ln \frac{N_A^0}{4\pi Z_A} - \frac{n_B}{n_A} \frac{Z_A}{Z_B} \left[\frac{1}{2} U_{BB} L_B + \ln \frac{N_B^0}{4\pi Z_B} \right]. \quad (10)$$

Experiments explore differences in the repulsive interaction in the solvent [11]. A large repulsion in A relative to B repulses the chains at the interface. The chains curl up to reduce D and the anisotropic chain extension. This is counteracted by the effect of the repulsive wall interaction (Fig. 2). Strong repulsion of intermolecular interaction in B increases the extent of the ordered layer of A . The thickness of the ordered layer depends on the ability of the rigid surfactant to expand as measured by q and $DP L_A$. The strength of the chain-wall interaction can be obtained from the slope of $D(L_A)$, as can be seen in Eq. (9). The anisotropy of the single chain con-

formation depends on D and an example of order parameter and chain extension are given in Table I for the ordered A layer in contact with an incompatible polymer B . All anisotropy disappears at high temperature and the extent of the ordered layer drops to zero.

The model can be adapted to a pure polymer liquid near a repulsive orienting wall, also shown in Table I. The two layers consist of the ordered surface chains with ellipsoidal distribution of monomers and the bulk chains with a spherical symmetry. For small effective repulsion from the wall, the extension in contact with the disordered liquid is found from Eq. (10) with $\Delta\phi = 0$. In order to find an appreciable ordered layer, the wall effect must be of the order of the total monomer-monomer interaction in a chain.

V. DISCUSSION

As suggested by the experiments, the results presented above show that chain order at a surface can be regulated by adding an incompatible solvent to the system. The bulk chains must be rigid but by themselves need not display orientational interactions and do not form liquid crystal phases. The parameters of the system are accessible to experimental measurement. The persistence length has been given for many different systems [16,17], and the isotropic mean field interactions can be fitted to phase diagrams, although a dependence of the effective fields on density is possible. The wall interaction is more of a problem. In the experiments on surfactants, polar heads bind the chains to the substrate and the chains are strongly asymmetric in structure and chemical reactivity. Numerical simulation for the single chain or a number of chains in the presence of a wall could be used to calculate the effective interaction in simple systems and to test the form and strength of the anchoring force. The simple exponential model used here for the chain-interface interaction has been applied successfully to many surface problems in simple liquids [14,18]. More complex models [1,19] could be used but will not change the qualitative results.

The method can be applied to calculate the surface properties of semiflexible polymers over the whole range of stiffness from flexible to rigid and $0 < q/L < \infty$ as described in [12]. The calculation requires numerical diagonalization of

TABLE I. The thickness D/q of the ordered liquid layer, the orientational order parameter S , and the anisotropy of chain extension $e = \langle w_{\parallel}^2 \rangle / 2/3 L_A q$ within the ordered layer $z < D$ for A chains in contact with liquid B and in contact with pure A . The effective anchoring potential is $v/\lambda = 1$. The persistence length of the A chains is q and $L_A/q = 2$. In the incompatible liquid B the total chain length is $L_B = L_A$ and the density is $n_B = n_A$, the potential difference is $(U_{AA} - U_{BB})q = -6$. The sample thickness is $d = q(0.18 \times 10^3)$.

	$A+B$	$A+A$
D/q	1.7	90
$S \times 10$	0.25	0.005
e	1.08	1.001

the eigenvalue matrix of Eq. (5). The larger the number of spherical harmonics, the higher the precision. In the bulk, an expansion in eight spherical harmonics yielded a precision $<10^{-3}$. As the chains become more flexible or longer, the expansion in eigenfunctions can be approximated by a smaller number of terms. In the bulk liquid, the one eigenvalue expansion is a good approximation in the range $L/q > 1$. With this in mind, the expansion was limited here to the first three terms that made an analytical solution possible.

Density and order parameter profiles arising from the position-dependent distribution of monomers can be calculated in principle [9]. Total spatial separation of the two components does not occur in systems with partial compatibility and mutual interpenetration could influence the chain conformation by chemical bonding or other effects. Minimization of the free energy functional by analytical or numerical means yields profiles for the monomer density and the

orientational order parameter. For physical reasons, the profiles are expected to be continuous. In another approach, a simple form for the profiles is assumed and the resulting free energy is minimized with respect to profile parameters. The actual interfacial profiles are not easily accessible to experiment but the present model can be expected to give the correct trends for derived average properties. In strongly incompatible $A+B$ mixtures, the interface is sharp in order to reduce the contact between monomers of different components. This may not be true for the contact between the ordered surface layer of pure A and the remaining isotropic bulk.

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- [1] J. Israelachvili, *Intermolecular and Surface Forces* (Academic, San Diego, 1991).
 - [2] J. A. Zasadzinski, R. Viswanathan, L. Madsen, J. Gamaes, and D. K. Schwartz, *Science* **263**, 1726 (1994).
 - [3] E. B. Sirota and X. Z. Wu, *J. Chem. Phys.* **105**, 7763 (1996).
 - [4] Y. Ouchi, M. M. Feller, T. Moses, and Y. R. Shen, *Phys. Rev. Lett.* **68**, 3040 (1992).
 - [5] X. Z. Wu, B. M. Ocko, H. Tang, E. B. Sirota, S. K. Sinha, and M. Deutsch, *Phys. Rev. Lett.* **75**, 1332 (1995).
 - [6] B. Jérôme, *Rep. Prog. Phys.* **54**, 392 (1991).
 - [7] P. G. de Gennes, *Rep. Prog. Phys.* **32**, 187 (1969).
 - [8] F. Jähnig, *J. Chem. Phys.* **70**, 3279 (1979).
 - [9] D. Morse and G. Fredericksen, *Phys. Rev. Lett.* **73**, 3235 (1994); W. E. McMullen and K. F. Freed, *J. Chem. Phys.* **92**, 1413 (1990); K. M. Hong and J. Noolandi, *Macromolecules* **14**, 727 (1981).
 - [10] P. B. Miranda, V. Pflumio, H. Saijo, and Y. R. Shen, *Chem. Phys. Lett.* **264**, 387 (1997); *J. Am. Chem. Soc.* **120**, 12 092 (1998).
 - [11] A. Ten Bosch, *J. Chem. Phys.* **108**, 2228 (1998).
 - [12] L. Varichon and A. Ten Bosch, *J. Chem. Phys.* **100**, 1708 (1994); *Makromol. Chem., Theory Simul.* **2**, 851 (1993).
 - [13] M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1988).
 - [14] F. Celestini and A. Ten Bosch, *Z. Phys. D* **28**, 293 (1993).
 - [15] K. F. Freed, *Adv. Chem. Phys.* **22**, 1 (1972); A. Ten Bosch, *Physica A* **262**, 396 (1999).
 - [16] S. Aragon, *Macromolecules* **20**, 370 (1987).
 - [17] A. Dubault, R. Ober, M. Veyssie, and B. Cabane, *J. Phys. (France)* **46**, 1227 (1985).
 - [18] F. Celestini and A. Ten Bosch, *Phys. Rev. E* **50**, 1836 (1994).
 - [19] B. M. Law, *Phys. Rev. E* **48**, 2760 (1993).