Irreversibility and Polymer Adsorption

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(Received 20 September 2002; published 5 February 2003)

Physisorption or chemisorption from dilute polymer solutions often entails irreversible polymer-surface bonding. We present a theory of the resultant nonequilibrium layers. While the density profile and loop distribution are the same as for equilibrium layers, the final layer comprises a tightly bound inner part plus an outer part whose chains make only fN surface contacts where N is chain length. The contact fractions f follow a broad distribution, $P(f) \sim f^{-4/5}$, in rather close agreement with strong physisorption experiments [H. M. Schneider *et al.*, Langmuir **12**, 994 (1996)].

DOI: 10.1103/PhysRevLett.90.056103 PACS numbers: 82.35.–x, 05.40.–a, 68.08.–p

The validity of the laws of equilibrium statistical mechanics hinges on ergodicity, the ability of a system to freely explore its phase space [1]. Many real processes, however, involve irreversible microscopic events such as strong physical or chemical bonding which invalidate ergodicity. Equilibrium then becomes inaccessible and Boltzmann's entropy hypothesis is no longer applicable to calculate observables. Instead, the kinetics must be followed from their very beginning: The accessible region of phase space is progressively diminished as successive irreversible events freeze in an ever-increasing number of constraints. The state of the system at some time depends on the pocket of phase space to which it has become confined.

The adsorption of high molecular weight polymers onto surfaces by its very nature frequently involves this kind of irreversibility (see Fig. 1). When an attractive surface contacts even a very dilute polymer solution, there is a powerful tendency for dense polymer layers to develop [2,3] because sticking energies per chain increase in proportion to the number of monomer units, N. This effect is exploited in many technologies such as coating, lubrication, and adhesion. When the monomer sticking advantage ϵ exceeds k_BT, available experimental evidence indicates that relaxation times become so large that the physisorption processes are effectively irreversible [4]. This is a common situation. Many polymer species attach through strong hydrogen bonds [5] ($\epsilon \gtrsim 4k_BT$) to silicon, glass, or metal surfaces in their naturally oxidized states [4], while DNA and proteins adhere tenaciously to a large variety of materials through hydrogen bonds, bare charge interactions, or hydrophobic forces [6]. In such situations, layer structure is no longer determined by the laws of equilibrium statistical mechanics. The extreme example arises in *chemisorption* [7,8] where covalent surface-polymer bonds develop irreversibly as in applications such as polymer-fiber welding in fiber-reinforced thermoplastics and colloid stabilization by chemical grafting of polymers [9]. Generally, applications prefer the strongest and most enduring interfaces possible, and irreversible effects are probably the rule rather than the exception.

Our aim in this Letter is to understand the effect of irreversibility on the structure of adsorbed polymer layers (see Fig. 1). Polymer adsorption phenomena are a major focus of polymer science, and though a few theoretical and numerical works have addressed irreversibility [8,10,11], the reversible case and the equilibrium layers which result are far better understood [2,3]. Theory [3], consistent with a number of experiments [12], predicts each adsorbed chain in the equilibrium layer has sequences of surface-bound monomers (trains) interspersed with portions extending away from the surface (tails and loops of size s). For good solvents, the loop distribution $\Omega(s) \sim s^{-11/5}$ and net layer density profile $c(z) \sim z^{-4/3}$ are universal. Equilibrium and ergodicity imply every chain is statistically identical. For example, for large N the fraction f of units which are surface bound is the same for all chains to within small fluctuations and is no different to the overall bound fraction, $f = \Gamma_{\text{bound}}/\Gamma$. Here Γ is the total adsorbed polymer mass per unit area and Γ_{bound} the surface-bound part.

How are these universal features modified when the adsorption is irreversible? This question was explored in a series of ingenious experiments by the workers of Ref. [4], who monitored polymethylmethacrylate (PMMA)

FIG. 1. (a) Final irreversible layer structure. Chains highlighted in bold: One belongs to the inner flattened layer (ωN surface contacts) and the other to the outer layer ($fN \ll N$ contacts, loop size $s \approx n_{\text{cont}}/f$). (b) Late stage chain adsorption as surface approaches saturation and free supersites (clusters of n_{cont} empty sites) become dilute. Chains cannot completely zip down. The minimum loop size s just connects two nearest neighbor supersites separated by l_{sep}, i.e., $as^{3/5} = l_{\text{sep}}$.

adsorption from a dilute solution onto oxidized silicon via hydrogen bonding with $\epsilon \approx 4k_BT$. Measuring infrared absorption and dichroism, they monitored both $\Gamma(t)$ and $\Gamma_{\text{bound}}(t)$ as they evolved in time and showed that early arriving chains had much higher f values than late arrivers, and these f values were frozen in forever. They modeled [4] this in terms of a picture where early arrivers lie flat and late arrivers, having fewer available surface spots to adsorb onto, are extended. The experimental f values of the asymptotic layer followed a broad distribution, shown in Fig. 2(b). This succinctly quantifies the essential nonergodic characteristic of these nonequilibrium layers: There are now infinitely many classes of chains, each class with its own particular statistics.

In the following, an initially empty surface contacting a dilute polymer solution with good solvent is considered. We will calculate the kinetics of layer formation, $\Gamma_{\text{bound}}(t)$ and $\Gamma(t)$, and the distributions of f values and loop sizes in the evolving and final layer. The two cases of irreversible physisorption and chemisorption must be carefully distinguished. Define Q as the "reaction" rate between a monomer and the surface, given this monomer contacts the surface (see Fig. 3). For physisorption, the attachment of a monomer is virtually instantaneous on reaching the surface so the effective value is diffusion limited, $Q \approx 1/t_a \approx 10^{10}\ \text{s}^{-1}$ typically, where t_a is monomer relaxation time. Chemisorption processes are much slower, with typical values [13] $10^{-2} \lesssim Q \lesssim 10^2\ \text{s}^{-1}$. Consider a chain which, having diffused from bulk to surface, has just made its first attachment, i.e., just one monomer is irreversibly bonded to the surface (see Fig. 3). We first treat the case of chemisorption, where the subsequent attachment of the remaining monomers is a process lasting seconds to hours and is thus experimentally accessible (all N monomers are assumed functionalized).

1. Early stages: single chain adsorption and surface saturation.—How does this chain adsorb down onto the surface? This depends on the exponent θ governing the surface reaction rate $k(s)$ for the sth monomer measured from the initial graft point (see Fig. 3)

$$k(s) \approx QZ_{\text{surf}}(s,N)/Z_{\text{surf}}(N) \approx Q/s^{\theta}, \qquad (s \ll N). \quad (1)$$

Here, $Z_{\text{surf}}(N)$ and $Z_{\text{surf}}(s,N)$ are the chain partition functions given one and two surface attachments, respectively. Slow chemisorption allows sufficient time for chains to explore all configurations given the current constraints frozen in by earlier reactions. Equation (1) states the reaction rate is proportional to the fraction of the grafted chain's configurations for which the sth monomer contacts the surface [8]. Now, in cases where $\theta > 2$, the total reaction rate $\mathcal{R}_{\text{total}} \approx \int_1^N ds k(s)$ is dominated by s of order unity, i.e., monomers near the first attached monomer will attach next. Thus, the chain *zips* down from the initial graft point. In contrast, for systems where $\theta < 1$, the upper limit dominates $\mathcal{R}_{\text{total}}$, i.e., a distant monomer will react next; this implies a much more homogeneous chain *collapse* mechanism (see Fig. 3).

The present situation is a self-avoiding polymer at a repulsive wall (we consider pure chemisorption, i.e., we assume a free energy advantage for solvent to contact the wall). It turns out this case is intermediate between zipping and collapse. By relating θ to other polymer exponents at hard walls [14], we obtained the exact relation,

$$\theta = 1 + \nu, \quad (2)$$

where $\nu \approx 3/5$ is the Flory exponent [14] determining the polymer bulk coil size $R_F = aN^{\nu}$ in good solvent (a is monomer size). Thus, $1 < \theta < 2$ and $\mathcal{R}_{\text{total}}$ is dominated by its lower integration limit. We call this case *accelerated zipping* (see Fig. 3). Zipping from the original graft point is accompanied by the occasional grafting of a distant monomer producing a loop of size s, for instance. This occurs after time $\tau_s \approx 1/\int_s^N ds' k(s') \approx Q^{-1}s^{3/5}$. Each such new graft point nucleates further zipping, enhancing the effective zipping speed. Hence, the entire chain adsorbs in a time $t_{\text{adsorb}} = \tau_N \approx Q^{-1}N^{3/5}$, since by this time even the biggest loops have come down. Note this is much less than the pure zipping time $\approx Q^{-1}N$. Thus, pure zipping must have been short circuited by large loop adsorption events before it could have completed its course.

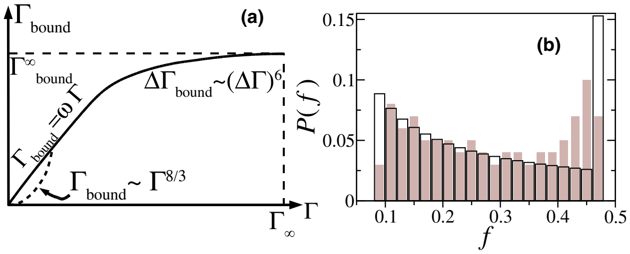

FIG. 2 (color online). (a) Predicted adsorbed polymer mass Γ versus surface-bound part Γ_{bound}. For chemisorption, $\Gamma_{\text{bound}} \sim \Gamma^{8/3}$ initially. (b) Frequency histograms for fraction of bound mass, f. Experiment (grey) from Ref. [4]. Theory (empty), from predicted distribution $P(f) \sim f^{-4/5}$ with $f_{\max} < f \lesssim \omega$, where values for $f_{\max} = 0.9$ and $\omega = 0.47$ were taken from Ref. [4].

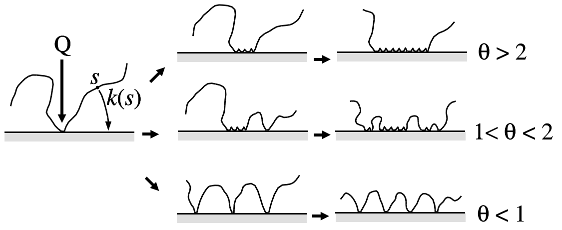

FIG. 3. Chain adsorption commences with formation of an initial monomer-surface bond. For chemisorption, the reaction rate thereafter for the sth monomer from this graft point is $k(s) \sim s^{-\theta}$. Three modes of subsequent chain adsorption are theoretically possible: zipping ($\theta > 2$); accelerated zipping, where occasional big loops nucleate new zipping centers ($1 < \theta < 2$); and uniform collapse ($\theta < 1$). Chemisorption from dilute solution is accelerated zipping ($\theta = 8/5$).

During this accelerated zipping down, a characteristic (unnormalized) loop distribution $\Omega_t(s)$ develops and the number of surface-bound monomers $\gamma_{\rm bound}(t)$ grows from 1 to order N. We calculated these quantities by solving the detailed loop kinetics [15]. These are rather complex, and here we present more accessible scaling arguments which reproduce the same results. Let us postulate that after time t the only relevant loop scale is the largest to have come down, $s_{\rm max} \approx (Qt)^{5/3}$, i.e., $\Omega_t(s) \approx (s_{\rm max}/s)^{\alpha}/s_{\rm max}$ for $s \ll s_{\rm max}$. Assuming $\alpha > 1$, the total number of loops $L(t) \approx s_{\rm max}^{\alpha-1}$ is dominated by small loops of order unity. Writing $\gamma_{\rm bound}(t) = N(t/\tau_N)^{\beta}$, we demand this be independent of N for $t \ll \tau_N$ (imagine sending the chain size to infinity; this would not affect the accelerated zipping propagating outwards from the initial graft point). This determines $\beta = 5/3$. Finally, since there are $L(t)$ nucleating points for further zipping, $d\gamma_{\rm bound}/dt \sim L$, i.e., $\gamma_{\rm bound} \sim Lt$ which fixes $\alpha = 7/5$.

We now sum over all chains which attached up to time t. The entropic disadvantage to touch the surface reduces the monomer volume fraction at the surface from the far field bulk value ϕ, $\phi_{\rm surf} = r\phi$, where the ratio of surface to bulk chain partition functions $r \equiv Z_{\rm surf}(N)/Z_{\rm bulk}(N) = 1/N$ was calculated in Ref. [14]. Then with [16] $a^2 d\Gamma/dt = QN\phi_{\rm surf}$ and $\Gamma_{\rm bound} = \gamma_{\rm bound}(\Gamma/N)$, we have

$$\Gamma(t)a^2 = \phi Q t, \qquad \Gamma_{\rm bound}(t)a^2 = \phi N^{3/5}(t/\tau_N)^{8/3}, \quad (3)$$

describing the early chemisorption layer for $t < t_{\rm adsorb} = Q^{-1}N^{3/5}$. The loop structure of the partially collapsed chains is $\Omega_t(s) \sim s^{-7/5}$ with maximum size $s_{\rm max} = (Qt)^{5/3}$. This first phase may be long lived; e.g., for $Q^{-1} = 1$ s, $N = 10^3$ then $\tau_N \approx 1$ min. This becomes many hours for smaller Q values which are common.

By time $t_{\rm adsorb}$, zipping is complete and each chain is completely flattened onto the surface with the fraction of adsorbed monomers $f = \omega$. The species-dependent constant ω is of order unity and reflects steric constraints preventing every monomer from actually touching the surface. In practice, we expect broadening of f values about ω due to strong fluctuations, typical of multiplicative random processes characterizing irreversibility. For longer times, each new chain zips down and $\Gamma_{\rm bound}(t) = \omega\Gamma(t)$ with Γ given by Eq. (3). This proceeds until $t_{\rm sat}^{\rm chem} \approx 1/(Q\phi)$ when the surface is virtually saturated with a near monolayer of flattened chains [17].

Consider now physisorption in its early stages. After attachment of its first monomer, the collapse of a single chain into a flattened structure now occurs as rapidly as monomers can diffuse a distance of order R_F, possibly accelerated by the attachments themselves. Thus, we expect the collapse time [11] to be at least as small as the bulk coil relaxation time $\tau_{\rm bulk}$ (of the order of microseconds). Hence, the collapse itself is probably experimentally unobservable, at least with the techniques of Ref. [4]. What is important is that in dilute solutions chains collapse into flattened configurations without hindrance from others. Moreover, we find that the probability a chain arriving from the bulk makes at least one bond before diffusing away is essentially unity even for a nearly saturated surface. It follows that the attachment of chains is diffusion controlled for essentially all times, $a^2\Gamma(t) \approx (\phi/a)(Dt)^{1/2}$, where D is the center of gravity diffusivity. As for chemisorption, $\Gamma_{\rm bound} = \omega\Gamma$ and adsorption produces a virtual monolayer of flattened chains. Surface saturation effects onset after time $t_{\rm sat}^{\rm phys} = \tau_{\rm bulk}(\phi^*/\phi)^2 N^{2/5}$.

2. Late stages: the tenuously attached outer layer.— Both chemisorption and physisorption processes fill the surface with completely collapsed chains, albeit in very different time scales $t_{\rm sat}^{\rm chem}$ and $t_{\rm sat}^{\rm phys}$. By this stage, the distribution of surface-bound fractions is sharply peaked at $f = \omega$. However, as saturation is approached, free surface sites become scarce and late-arriving chains can no longer zip down completely. Suppose each chain-surface adhesion point consists in $n_{\rm cont}$ attached monomers. The precise value of $n_{\rm cont}$ is sterically determined and is expected to be strongly species dependent. Then the surface density of free "supersites" (unoccupied surface patches large enough to accommodate $n_{\rm cont}$ monomers) is $\rho_{\rm super} \approx \Delta\Gamma_{\rm bound}/n_{\rm cont}$, where $\Delta\Gamma_{\rm bound} \equiv \Gamma_{\rm bound}^{\infty} - \Gamma_{\rm bound}$ is the density of available surface sites and $\Gamma_{\rm bound}^{\infty}$ is the asymptotic density of bound monomers. Now as the surface approaches saturation so the density of supersites becomes small, $\rho_{\rm super} \ll 1/(n_{\rm cont}a^2)$, and their mean separation $l_{\rm sep} \approx \rho_{\rm super}^{-1/2}$ becomes so large that a late-arriving chain cannot find contiguous supersites to complete its accelerated zipping down. The minimum loop size s which can come down is that just large enough to connect two free supersites, i.e., $as^{3/5} = l_{\rm sep}$ whence $s = (n_{\rm cont}/a^2\Delta\Gamma_{\rm bound})^{5/6}$. Thus, the final adsorbed state of chains arriving at this stage [see Fig. 1(b)] consists of trains of $n_{\rm cont}$ monomers separated by loops of order s units. For these chains $\partial\Delta\Gamma_{\rm bound}/\partial\Delta\Gamma = f \approx n_{\rm cont}/s$ for large s, where $\Delta\Gamma$ is the deviation from the asymptotic coverage Γ^{∞}. Integrating this process up to saturation,

$$a^2\Delta\Gamma_{\rm bound} = n_{\rm cont}(a^2\Delta\Gamma/6)^6, \qquad P(f) = Af^{-4/5}, \quad (4)$$

where $f \ll 1$ and A is a constant of order unity [18]. Adding this broad distribution of f values to the peak centered at $f = \omega$ from the early stages gives the total distribution, shown in Fig. 2(b). It agrees rather closely with the experimental one of Ref. [4] shown in the same figure. The predicted $\Gamma_{\rm bound}(\Gamma)$ profile [see Fig. 2(a)] is also very close to the measured profile [4].

Equation (4) describes a tenuously attached outer layer (small f values) formed by late-arriving chains, adding to the dense flattened layer formed at earlier times. The loop distribution of this diffuse outer layer is obtained from $s\Omega(s)ds/\Gamma^{\infty} = P(f)df$, whence

$$\Omega(s) \approx a^{-2}s^{-11/5}, \qquad c(z) \sim z^{-4/3}, \quad (5)$$

where the density profile followed from $c = \Omega s ds/dz$ evaluated at $z = as^{3/5}$.

Finally, the kinetics of the total and bound coverages during the late stages are modified by saturation effects. For chemisorption, the rate of attachment is directly proportional to the density of available surface sites, $\dot{\Gamma} \sim \Delta\Gamma_{\text{bound}} \sim (\Delta\Gamma)^6$ so $\Delta\Gamma \sim t^{-1/5}$ and $\Delta\Gamma_{\text{bound}} \sim t^{-6/5}$. In the physisorption case as discussed, diffusion control always pertains, $\Gamma \sim t^{1/2}$, and thus the bound fraction saturates as $\Delta\Gamma_{\text{bound}} \sim (1 - \text{const} \times t/t_{\text{sat}}^{\text{phys}})^6$.

In conclusion, we found that irreversible adsorption of polymer chains leads to final nonequilibrium layers exhibiting both similarities and profound differences compared to their equilibrium counterparts. The layer is a sum of a surface monolayer plus a diffuse outer part of thickness of the order of the bulk coil size with density profile $c(z) \sim z^{-4/3}$ and loop size distribution $\Omega(s) \sim s^{-11/5}$. Interestingly, these features are identical to those predicted for equilibrium layers, including the precise exponent values. Prefactors are different, however, and we anticipate different values for physisorption and chemisorption. To determine these necessitates accounting for topological constraints and fluctuations in empty surface site densities and other quantities, effects absent from our model. Note that, although we did not explicitly treat excluded volume interactions between an adsorbing chain and those previously adsorbed, we expect these to be unimportant because an empty site is correlated with a reduced surface loop density at that location.

What is very different about irreversible layers is that individual chains in the layer are not statistically identical: A given chain either belongs to the surface-bound part and has order N surface contacts, or else the diffuse outer part. In the latter case, the number of contacts, fN, is generally much less than N and its loop distribution is almost monodisperse with loop size $s \sim 1/f$. In equilibrium layers, there is just one class of chain; parts of each chain lie bound to the surface, other parts extend into the outer layer and its loop distribution is the same as the layer's. In contrast, for irreversible layers there are an infinite number of classes, each with its own f value. The weighting for different values is universal, $P(f) \sim f^{-4/5}$ for small f. Practically, these differences have important implications for the physical properties of irreversible layers; for example, the outer layer is much more fragile than the protected inner flattened layer. From a fundamental point of view, these systems provide a measurable example of how irreversible events progressively diminish the available phase space volume and modify the entropy algorithm. For an equilibrium layer with $\epsilon > kT$, this gives [3] $F \approx F_{\text{trans}} + F_{\text{osm}} + F_{\text{train}}$ for the free energy. Here, $F_{\text{trans}} = -k_B T \int ds \Omega(s) \ln[a^2 \Omega(s)]$ derives from loop translational entropy, $F_{\text{train}} = E_{\text{train}} - TS_{\text{train}}$ is the contribution from trains, and F_{osm} is the osmotic part due to the solvent-swollen loops in the outer part of the brush. By comparison, for the nonequilibrium layers both trains and loops are immobilized on the surface, $F_{\text{trans}} = S_{\text{train}} = 0$. The free energy is thus increased, $F \approx F_{\text{osm}} + E_{\text{surf}}$. Its modified structure is expected, for example, to profoundly modify the interaction between polymer-covered surfaces as compared to the equilibrium case where the rearrangement of chains on the surfaces leads to characteristic force profiles [3].

This work was supported by the National Science Foundation, Grant No. DMR-9816374.

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[15] The loop kinetics are $\dot{\Omega}_t = \int_s^N ds' \Omega_t(s') k(s|s') - \int_0^s ds' \Omega_t(s) k(s'|s)$, where $k(s|s')$, the rate s' loops generate two loops s and $s' - s$, has the small s behavior of Eq. (1), $k(s|s') \to k(s) \sim s^{-\theta}$ for $s \ll s'$.

[16] Although chain ends are more likely to touch the surface than a typical interior monomer, we find the latter dominate since there are order N of them.

[17] The surface density of chains at $t = t_{\text{adsorb}}$ is $\Gamma(t_{\text{adsorb}})/N \approx (\phi/\phi^*)/R_F^2$, where [3] $\phi^* = N^{-4/5}$ is the overlap threshold. Thus, for dilute conditions ($\phi < \phi^*$) a chain zips down flat before others arrive to interfere.

[18] The distribution was obtained from $P(f) = 1/(\Gamma^\infty[\Delta\Gamma''_{\text{bound}}]_{\Delta\Gamma'_{\text{bound}}=f})$, where prime denotes differentiation with respect to $\Delta\Gamma$. The prefactor is $A \approx 6/(5a^2\Gamma^\infty[n_{\text{cont}}]^{1/5})$.