Irreversibility and Polymer Adsorption

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Physisorption or chemisorption from dilute polymer solutions often entails irreversible polymer-surface bonding. We present a theory of the non-equilibrium layers which result. 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 \textbf{12}, 994 (1996)].

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The validity of the laws of equilibrium statistical mechanics hinges on ergodicity, the ability of a system to freely explore its phase space \cite{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 Equilibrium then becomes inaccessible and Boltzmann’s entropy hypothesis is no longer applicable to calculate observables.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. \textbf{A}). When an attractive surface contacts even a very dilute polymer solution there is a powerful tendency for dense polymer layers to develop \cite{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 $\epsilon$ exceeds $k_BT$, available experimental evidence indicates that relaxation times become so large that the physisorption processes are effectively irreversible \cite{4}. This is a common situation. Many polymer species attach through strong hydrogen bonds \cite{5} ($\epsilon \gtrsim 4k_BT$) to silicon, glass or metal surfaces in their naturally oxidized states \cite{6}, while DNA and proteins adhere tenaciously to a large variety of materials through hydrogen bonds, bare charge interactions or hydrophobic forces \cite{7}. In such situations layer structure is no longer determined by the laws of equilibrium statistical mechanics. The extreme example arises in chemisorption \cite{8,9} 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 \cite{10}. 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. \textbf{B}). Polymer adsorption phenomena are a major focus of polymer science, and though a few theoretical and numerical works have addressed irreversibility \cite{8,11,12} the reversible case and the equilibrium layers which result are far better understood \cite{1,2,3}. Theory \cite{2}, consistent with a number of experiments \cite{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 $\Gamma$ is the total adsorbed polymer mass per unit area and $\Gamma_{\text{bound}}$ 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 refs. \cite{8} who monitored polymethylmethacrylate (PMMA) adsorption from 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

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig1.png}
\caption{(a) Final irreversible layer structure. Chains highlighted in bold: one belongs to the inner flattened layer ($\omega N$ surface contacts) 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 supersistes (clusters of $n_{\text{cont}}$ empty sites) become dilute. Chains cannot completely zip down. The minimum loop size $s$ just connects two nearest neighbor supersites separated by $l_{\text{sep}}$, i.e. $as^{3/5} = l_{\text{sep}}$.}
\end{figure}
arriving chains had much higher f values than late ar-

vatives. Slow chemisorption allows sufficient time for
chains to explore all configurations given the current
constraints frozen in by earlier reactions. Eq. (4) states
the reaction rate is proportional to the fraction of the
grafted chain’s configurations for which the sth monomer
contacts the surface. Now in cases where \( \theta > 2 \), the
total reaction rate \( R_{\text{total}} \approx \int_{1}^{\infty} ds k(s) \) is domi-
nated by \( s \) of order unity, i.e. monomers near to the first
attached monomer will attach next. Thus, the chain zips
down from the initial graft point. In contrast, for sys-
tems where \( \theta < 1 \) the upper limit dominates \( R_{\text{total}} \), 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 \( \theta \) to other polymer ex-

ponents at hard walls we obtained the exact relation

\[
\theta = 1 + \nu
\]

where \( \nu \approx 3/5 \) is the Flory exponent determining
the polymer bulk coil size \( R_F = aN^\nu \) in good solvent (a
is monomer size). Thus \( 1 < \theta < 2 \) and \( R_{\text{total}} \) is domi-
nated by its lower integration limit. We call this case accele-
rated 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 \( s \), say. 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
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.

During this accelerated zipping down, a characteris-
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the number of surface-bound monomers $\gamma_{\text{bound}}(t)$ grows from 1 to order $N$. We calculated these quantities by solving the detailed loop kinetics. 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, $s_{\text{max}} \approx (Qt)^{5/3}$, i.e. $\Omega(s) \approx (s_{\text{max}}/s)^\alpha/s_{\text{max}}$ for $s \ll s_{\text{max}}$. Assuming $\alpha > 1$, the total number of loops $L(t) \approx s_{\text{max}}$ is dominated by small loops of order unity. Writing $\gamma_{\text{bound}}(t) = N(t/\tau_N)^\beta$ 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, $d\gamma_{\text{bound}}/dt \sim L$, i.e. $\gamma_{\text{bound}} \sim Lt$ 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 $\phi$, $\phi_{\text{surf}} = r \phi$ where the ratio of surface to bulk chain partition functions $r = Z_{\text{surf}}(N)/Z_{\text{bulk}}(N) = 1/N$ was calculated in ref. [14]. Then with $\left[\frac{1}{6}\right] a^2 d\Gamma/dt = QN \phi_{\text{surf}}$ and $\Gamma_{\text{bound}}(t) = \gamma_{\text{bound}}(t/\tau_N)$ we have

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

describing the early chemisorption layer for $t < t_{\text{adsorb}} = Q^{-1} N^{3/5}$. The loop structure of the partially collapsed chains is $\Omega(s) \sim s^{-7/2}$ with maximum size $s_{\text{max}} = (Qt)^{5/3}$. This first phase may be long lived; e.g. for $Q^{-1} = 1$ sec., $N = 10^3$ then $\tau_N \approx 20$ mins. This becomes many hours for smaller $Q$ values which are common.

By time $t_{\text{adsorb}}$ zipping is complete and each chain is completely flattened onto the surface with fraction of adsorbed monomers $f = \omega$. The species-dependent constant $\omega$ 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 $\omega$ due to strong fluctuations, typical of multiplicative random processes characterizing irreversibility. For longer times each new chain zips down and $\Gamma_{\text{bound}}(t) = \omega \Gamma(t)$ with $\Gamma$ given by eq. (6). This proceeds until $t_{\text{chem}}^\text{sat} \approx 1/(\phi \phi)$ when the surface is virtually saturated with a near-monolayer of flattened chains.

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 $\tau_{\text{bulk}}$ to be at least as small as the bulk coil relaxation time $\tau_{\text{bulk}}$ (of order microseconds). Hence the collapse itself is probably experimentally unobservable, at least with the techniques of ref. [14]. 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 center of gravity diffusivity. As for chemisorption, $\Gamma_{\text{bound}} = \omega \Gamma$ and adsorption produces a virtual monolayer of flattened chains. Surface saturation effects onset after time $t_{\text{sat}}^\text{phys} = \tau_{\text{bulk}}(\phi/\phi)^2 N^{2/5}$.

(2) Late stages: the tenuously attached outer layer. Both chemisorption and physisorption processes fill the surface with completely collapsed chains, albeit in very different timescales $t_{\text{chem}}^\text{sat}$ and $t_{\text{phys}}^\text{sat}$. 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 $n_{\text{cont}}$ attached monomers. The precise value of $n_{\text{cont}}$ 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 $n_{\text{cont}}$ monomers) is $\rho_{\text{super}} = \Delta \Gamma_{\text{bound}}/n_{\text{cont}}$ where $\Delta \Gamma_{\text{bound}} \equiv \Gamma_{\text{bound}} - \Gamma_{\text{bulk}}$ is the density of available surface sites and $\Gamma_{\text{bound}}$ is the asymptotic density of bound monomers. Now as the surface approaches saturation so the density of supersites becomes small, $\rho_{\text{super}} \ll 1/(n_{\text{cont}} a^2)$, and their mean separation $l_{\text{sep}} \sim \rho_{\text{super}}^{-1/2}$ 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. $a^2/3 = l_{\text{sep}}$ whence $s = (n_{\text{cont}}/a^2 \Delta \Gamma_{\text{bound}})^{1/6}$. Thus the final adsorbed state of chains arriving at this stage (see fig. 2(b)) consists of trains of $n_{\text{cont}}$ monomers separated by loops of order $s$ units. For these chains $\Delta \Gamma_{\text{bound}}/\partial \Delta \Gamma = f \approx n_{\text{cont}}/s$ for large $s$, where $\Delta \Gamma$ is the deviation from the asymptotic coverage $\Gamma_{\infty}$. Integrating this process up to saturation,

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

where $f \ll 1$ and $A$ is a constant of order unity [38]. Adding this broad distribution of values $P(f)$ 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 $\Gamma_{\text{bound}}(\Gamma)$ profile (see fig. 2(a)) is also very close to the measured profile [4].

Eq. (6) 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

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

where the density profile followed from $c = \Omega ds/dz$ 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, $\Gamma \sim \Delta \Gamma_{\text{bound}} \sim (\Delta \Gamma)^6 \; \text{so} \; \Delta \Gamma \sim t^{-1/5}$ 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 $\Delta \Gamma_{\text{bound}} \sim (1 - \text{const.} \; t/t_{\text{sat}}^{\text{phys}})^6$.

In conclusion, we found that irreversible adsorption of polymer chains leads to final non-equilibrium 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 order 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 compared to the non-equilibrium layer where the rearrangement of chains on the surfaces leads to characteristic force profiles.

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[15] The loop kinetics are $\dot{\Omega} = \int_0^s ds' \Omega(s')k(s|s') - \int_0^s ds' \Omega(s)k(s'|s)$ where $k(s|s')$, the rate $s'$-loops generate 2 loops $s$ and $s' - s$, has the small $s$ behavior of eq. (5).
[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 $t = t_{\text{ad}}$ is $\Gamma(t_{\text{ad}})/N \approx (\phi/\phi^*)/R_p^2$ where $\phi^* = N^{-1/3}$ 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 $P(f) = 1/(\Gamma_{\text{cont}} \Gamma_{\text{bound}} \Gamma_{\text{cont}} - f)$ where prime denotes differentiation with respect to $\Gamma$. The prefactor is $A \approx 6/(5a^2 \Gamma_{\text{cont}} [n_{\text{cont}}]^{1/5})$. 