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LETTER TO THE EDITOR

Directed walk models of polymers at interfaces

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Abstract. We report analytical studies of the adsorption-desorption transition of polymers grafted at a penetrable surface, in the 2D and 3D partially directed SAW models. The fraction of adsorbed monomers and the phase diagram of the transition are calculated by the transfer matrix method.

The properties of isolated polymer chains near rigid or penetrable substrates or interfaces have been subject to continuing investigations stimulated both by potential applications and theoretical interest in novel analytical and numerical techniques involved (see reviews by Binder and Kremer (1985), de Gennes (1987), Eisenriegler *et al* (1982) and literature surveyed therein), are eventually also efficient for multichain systems. In this work we use exactly solvable directed self-avoiding walk (SAW) models (Privman *et al* 1988) to study polymers interacting with a symmetric penetrable surface (line in 2D, plane in 3D), previously investigated by numerical techniques and scaling approach (see Nakanishi (1981), Kremer (1985), Ishinabe (1984) and literature cited therein). A continuum field-theoretical model for the asymmetric interface problem has been developed by Wang *et al* (1986).

Experimental realisations of polymers at interfaces (see, e.g., Bloch *et al* 1985) typically involve two different media—a non-symmetric configuration (studied, e.g., by Halperin and Pincus (1986)) which in its critical behaviour at the adsorption-desorption transition is reminiscent of an impenetrable substrate. Directed walk models are relevant for polymers in anisotropic environments induced, e.g., by a weak flow of the solvent parallel to the surface. Experimental realisation of such systems has been described by Lee and Fuller (1985). In general, a sharp transition exists between the high-coverage (at low temperatures) and low-coverage regimes. The symmetric case considered here represents, however, an interesting theoretical limit when there is basically no entropy loss when a grafted (attached at one or both ends) polymer chain is adsorbed at an attractive surface. Thus the desorption transition cannot be induced by temperature increase, but only by making the surface repulsive. This theoretical expectation (Hammersley 1982, Hammersley *et al* 1982) will be checked *exactly* for directed SAW models. Directed models cannot be used to probe possible differences in critical-point exponents for the symmetric and impenetrable surfaces (see Hammersley *et al* 1982, Kremer 1985, Ishinabe 1984) since they have mostly Gaussian-type critical behaviour in both cases (see below, and Privman *et al* (1988)). The global description provided by the exact solution is, however, useful especially in the adsorbed regime (see Privman *et al* (1988) for further discussion).

For a walk of length L , with l steps at the surface, we model the polymer-surface interaction by assigning energy

$$E/k_B T = -Kl \quad (1)$$

with $K > 0$ for the attractive surface case. Thus

$$\kappa \equiv e^K \quad (2)$$

is the Boltzmann factor per adsorbed link (monomer), with $\kappa > 1$ for attraction and $0 < \kappa < 1$ for repulsion. In the grand canonical ensemble, the partition function is given by

$$Z = \sum_{\text{all walks}} \omega^L \kappa^l \quad (3)$$

where the fugacity ω controls the average chain length,

$$\langle L(\omega, \kappa) \rangle = \omega \frac{\partial \ln Z}{\partial \omega} \quad (4)$$

which increases to $\langle L \rangle = \infty$ as ω varies from zero to a model-dependent value, $\omega_\infty(\kappa) < 1$. We follow here the notation of Privman *et al* (1988) where it was generally argued that the fraction of monomers adsorbed at the surface, $P(\kappa)$, is given by

$$P(\kappa) \equiv \left[\frac{\langle l \rangle}{\langle L \rangle} \right]_{\omega \rightarrow \omega_\infty(\kappa)} = - \frac{\kappa}{\omega_\infty(\kappa)} \frac{d\omega_\infty(\kappa)}{d\kappa}. \quad (5)$$

In 2D, we consider a square lattice of unit spacing in the xy plane. The interacting 'surface' is the x axis. Similarly, in 3D a cubic lattice is considered, with the xz plane singled out. The walks start at the origin, and are directed along $+\hat{x}$. Furthermore, in order to avoid unilluminating mathematical complications we consider the *restricted* models where at most one $+\hat{y}$, $-\hat{y}$, $+\hat{z}$ or $-\hat{z}$ step is allowed, following each $+\hat{x}$ step. For each $+\hat{x}$, $+\hat{z}$ or $-\hat{z}$ step (link) at $y=0$, i.e. on the interacting surface, we assign an extra factor κ , as defined above, see equations (1) and (2). (Obviously, there are no $\pm\hat{z}$ steps in 2D.)

The problem is solvable by the transfer matrix method (see Privman *et al* 1988). Let $n = y(x)$ and $n' = y(x')$ denote the y values of two consecutive $+\hat{x}$ steps. The transfer matrix elements in 2D are then given by

$$T_{nn'} = \omega^{|n-n'|} \kappa^{\delta_{0n}} (\delta_{0, n-n'} + \delta_{1, |n-n'|}). \quad (6)$$

In 3D, we introduce $m = z(x)$, $m' = z(x')$. We have

$$T_{nm, n'm'} = \omega^{|n-n'| + |m-m'|} \kappa^{\delta_{0n}} (\delta_{0, n-n'} \delta_{0, m-m'} + \delta_{0, n-n'} \delta_{1, |m-m'|} + \delta_{1, |n-n'|} \delta_{0, m-m'}). \quad (7)$$

In either dimension, the partition function can be obtained via

$$Z = Z_0 + V^{(t)} \frac{\omega T^2}{1 - \omega T} W \quad (8)$$

(see Privman *et al* 1988); the uninteresting term Z_0 accounts for configurations with no $+\hat{x}$ steps. V and W are column vectors (with (t) denoting the transpose) carrying the information on the ends of the chain. For instance, in 2D, the end pinned at the origin is accounted for by $W_0 = 1$, $W_{n \neq 0} = 0$. For the other dangling end we select $V_0 = \kappa^{-1}$, $V_{n \neq 0} = 1$. It can be pinned at the substrate by choosing $V_{n \neq 0} = 0$, see further

below. Extensions to 3D are straightforward. The partition function Z in (8) develops a singularity for

$$1 - \omega \lambda_{\max}(\omega, \kappa) = 0 \tag{9}$$

where λ_{\max} is the largest eigenvalue of T . Relation (9) defines $\omega_{\infty}(\kappa)$.

In 2D, the right eigenvector (column vector) Ψ , of T defined in (6), can be either a bound-state type,

$$\Psi_n^{(bs)} = e^{-\mu|n|} \quad \mu > 0 \tag{10}$$

or a continuous oscillating linear combination of $e^{\pm iq n}$ (with different coefficients for $n \geq 0$ and $n \leq 0$). By direct substitution, one finds that the conditions for the bound state are

$$\cosh \mu = \frac{\lambda - 1}{2\omega} \tag{11}$$

$$\kappa(1 + 2\omega e^{-\mu}) = \lambda \tag{12}$$

where $\lambda = \lambda_{bs}$, and one must have $\mu > 0$. One can show that the appropriate solution $\lambda_{bs}(\omega, \kappa)$ exists *provided* $\kappa > 1$, and satisfies $\lambda_{bs}(\omega, \kappa) > 1 + 2\omega$. (The explicit form of λ_{bs} is complicated and is not reproduced here.) The continuous spectrum eigensolutions exist for any κ , and cover the range $1 - 2\omega \leq \lambda \leq 1 + 2\omega$, for $0 \leq q \leq \pi$. Thus, $\lambda_{\max} = \lambda_{bs}$ for $\kappa > 1$, but $\lambda_{\max} = 1 + 2\omega$ for $\kappa \leq 1$. (At $\kappa = 1$, the bound state merges with the continuum.)

In 3D, the form of (7) suggests that the m dependence of the right eigenvector elements Ψ_{nm} is of the form $\Psi_{nm} = A_n e^{iQm} + B_n e^{-iQm}$. However, one can show that the form of the vector W , entering (8), for a dangling-end chain, or a chain with its last step ending at the substrate ($y = 0$) at any z , ensures that only the $Q = 0$ states contribute. The calculation then becomes similar to the 2D case. Specifically, relations (11) and (12) are replaced by

$$\cosh \mu = \frac{\lambda - 1 - 2\omega}{2\omega} \tag{13}$$

$$\kappa(1 + 2\omega + 2\omega e^{-\mu}) = \lambda. \tag{14}$$

One finds that the bound-state solution exists *provided* $\kappa > 1$, with $\lambda_{\max} = \lambda_{bs}(\omega, \kappa) > 1 + 4\omega$. For $\kappa \leq 1$, the $q = 0$ continuous-state eigenvalue is the largest, thus $\lambda_{\max} = 1 + 4\omega$. (The $0 \leq q \leq \pi$, $Q = 0$ eigenvalues cover the range $1 \leq \lambda \leq 1 + 4\omega$, in 3D.)

Equation (9) can be reduced to relatively simple forms both in 2D

$$4\kappa^2 \omega^4 = (1 - \omega\kappa)(2\kappa - \kappa\omega - 1) \tag{15}$$

and in 3D

$$4\kappa^2 \omega^4 = (2\omega^2 \kappa + \omega\kappa - 1)(2\omega^2 \kappa + \omega\kappa - 2\kappa + 1). \tag{16}$$

These relations define $\omega_{\infty}(\kappa)$ for $\kappa > 1$; see figure 1. For $\kappa \leq 1$, however, relation (9) has no κ dependence. Therefore, we get constant values, $\omega_{\infty}(\kappa \leq 1) = \frac{1}{2}$ for 2D and $\frac{1}{8}(\sqrt{17} - 1)$ for 3D, as shown in figure 1, which are, in fact, the same values as for the impenetrable surfaces. Note that, for $\kappa \gg 1$,

$$\omega_{\infty}(\kappa) = \frac{1}{\kappa} - \frac{2}{\kappa^4} - O(\kappa^{-5}) \quad \text{for 2D} \tag{17}$$

$$\omega_{\infty}(\kappa) = \frac{1}{\kappa} - \frac{2}{\kappa^2} + O(\kappa^{-3}) \quad \text{for 3D.} \tag{18}$$

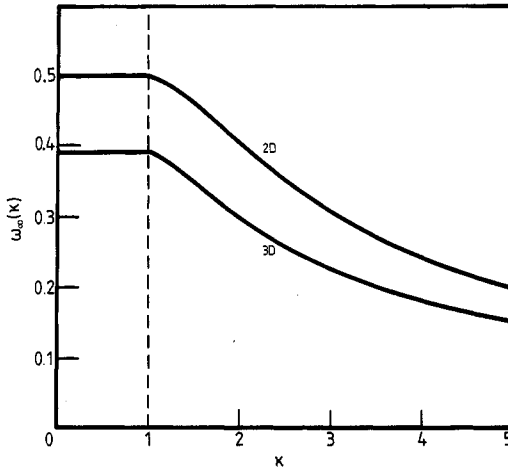


Figure 1. Phase diagram for the adsorption-desorption transition. The vertical broken line indicates the boundary of the adsorbed-chain regime at $\kappa > 1$. The values of $\omega_\infty(\kappa \leq 1)$ are $\frac{1}{2}$ and $\frac{1}{8}(\sqrt{17}-1)$ for 2D and 3D, respectively.

For fixed κ , the form of the singularity of Z in (8) as $\omega \rightarrow \omega_\infty^-$ defines the critical exponents γ_1 , for chains with dangling ends, and γ_{11} , for chains ending at the surface, via $Z \sim [\omega_\infty(\kappa) - \omega]^{-\gamma_1}$ or $[\omega_\infty(\kappa) - \omega]^{-\gamma_{11}}$. In the adsorbed regime ($\kappa > 1$), the bound state dominates, and we get $\gamma_1 = \gamma_{11} = 1$. In the desorbed state ($\kappa < 1$), a careful analysis (not detailed here) of the small- q eigenstate contributions to (8) yields $\gamma_1 = \frac{1}{2}$, $\gamma_{11} = -\frac{1}{2}$, identical to the impenetrable surface results (see Privman *et al* 1988). On the borderline ($\kappa = 1$), we get the multicritical values $\gamma_1 = 1$, $\gamma_{11} = \frac{1}{2}$. These values are new and, interestingly, satisfy the scaling relation $2\gamma_1 - \gamma_{11} = \gamma + \nu_\perp$, with the bulk values $\gamma = 1$ and $\nu_\perp = \frac{1}{2}$, as advanced by Privman *et al* (1988), inspired by the isotropic scaling results (see Binder and Kremer 1985).

The adsorption ratio $P(\kappa)$ can be calculated by using relation (5). The results are summarised in figure 2. For $\kappa \gg 1$, we have

$$P_{2D}(\kappa) = 1 - \frac{6}{\kappa^3} - \frac{8}{\kappa^4} - \frac{10}{\kappa^5} - \dots \quad (19)$$

$$P_{3D}(\kappa) = 1 - \frac{2}{\kappa} + \frac{12}{\kappa^2} - \frac{86}{\kappa^3} + \dots \quad (20)$$

In both cases, $P(\kappa)$ vanishes linearly at the sharp adsorption threshold, at $\kappa = 1$, which is a typical mean-field (Gaussian) behaviour (see, e.g., Hammersley *et al* 1982). These authors presented numerical evidence for the general validity of a $\kappa \equiv 1$ threshold for all $d \geq 2$, for a large class of symmetric adsorption models. Near the transition, the pinning in 3D is stronger than in 2D; see figure 2. However, for larger κ values, there is a suppression of adsorption in 3D, reminiscent of a similar effect for impenetrable surfaces.

In summary, we have presented directed SAW model results for the polymer adsorption at penetrable surfaces, indicating the existence of the adsorbed state for arbitrary weak attracting interactions, in 2D and 3D. In either dimension, $P(\kappa)$ vanishes linearly at the transition though the detailed κ dependence is basically different throughout the adsorbed region.

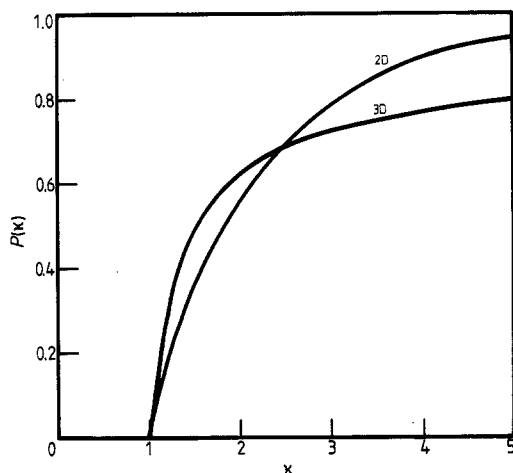


Figure 2. The fraction of adsorbed monomers, $P(\kappa)$, in 2D and 3D.

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