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MULTICRITICAL BEHAVIOR OF POLYMERS NEAR AN ADSORBING WALL

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Due to possible technological and biological applications, the statistical mechanics of polymer adsorption has been of longstanding interest. Recently, the problem has been reconsidered both numerically [1,2] and analytically [2,3,4]. This was stimulated mainly by recent advances in the field theory of semi-infinite spin systems [5]. In the following, some of these recent results are presented both for a single long chain with excluded-volume interaction (Sec. 1) and for semidilute solutions in good solvent (Sec. 2) near an adsorbing wall (or surface). As for other critical phenomena the behavior near the adsorption temperature is independent of most details ("universality") and one may discuss simple models.

1. Adsorption of a single chain

a) The adsorption threshold (-temperature)

The concept of an adsorption threshold can be explained most easily for a single chain on a lattice half space (Fig. 1). The chain is made up of N

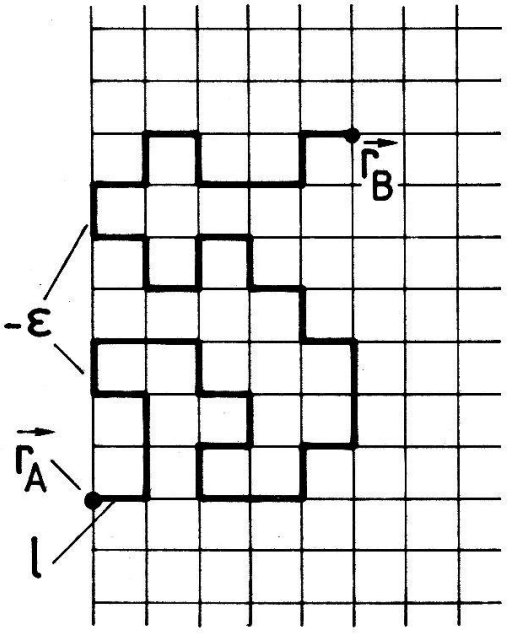

Fig. 1. Chain on a lattice half space.

(nearest neighbor-) links. The statistical ensemble consists of all possible chain configurations on the semi-infinite lattice, where a lattice site may be

occupied only once in a configuration ("real" chain or chain with "excluded-volume" interaction), and one chain end is kept fixed at a certain lattice point $\vec{r}_A$, e.g. at the surface. Each configuration has a Boltzmann-weight $\exp[N_1 \cdot \omega]$ with N_1 the number of links in the surface. Here $\omega = \varepsilon/k_B T$ and $-\varepsilon < 0$ an energy gain per surface link.

Consider the ensemble average $\langle N_1 \rangle$ of N_1 which is a function of N and ω. For dimension $d \geq 2$ of the semi-infinite lattice there exists a finite positive value ω_a such that

$$\lim_{N\to\infty} \langle N_1 \rangle / N \begin{cases} = 0 \\ > 0 \end{cases} \quad \text{for} \quad \omega \begin{matrix} < \\ > \end{matrix} \omega_a \quad , \tag{1}$$

see e.g. Ref. [6], i.e. the chain is nonadsorbed (adsorbed) for $T > T_a$ ($T < T_a$) with $k_B T_a = \varepsilon/\omega_a$.

b) Mapping to a magnetic problem

The mapping [7] of real chain statistics in free space to the n-vector spin model of magnetism can be generalized [8,2] to the real chain problem of Section 1a). In a continuum description this leads to a spin model in the half space $+ = \{z \geq 0\}$ with Hamiltonian

$$\mathcal{H} = \sum_{j=1}^{n} h(\phi_j) + \frac{u}{4!} \int_+ d^d r \left(\sum_{j=1}^{n} \phi_j^2 \right)^2$$
$$h(\phi) = \int_+ d^d r \, \frac{1}{2} \left\{ (\nabla \phi(r))^2 + [t + c\delta(z)] \, \phi^2(r) \right\} \tag{2}$$

for the n-component spin field $\vec{\phi} = (\phi_1, \ldots, \phi_n)$. The phase diagram (Fig. 2) of the

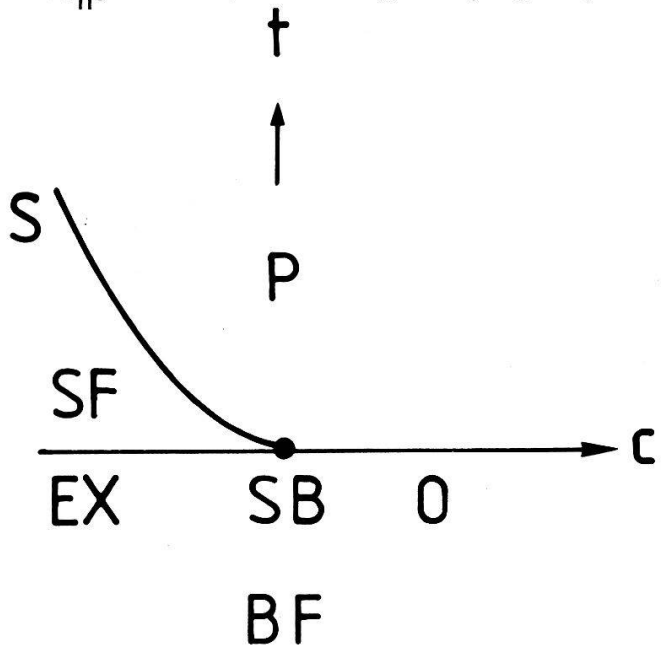

Fig. 2. Phase diagram of spin system in a half space.

spin system shows a paramagnetic phase P and a ferromagnetic phase BF as well as a phase SF with ordered surface and disordered bulk, separated by 3 lines O, S, EX of critical points which join in a multicritical point SB = (c_{SB}, t_b); see Ref. [9] for more details.

The partition function Z of the chain in Sec. 1a) is for large N and small $|\omega-\omega_a|$ then given by the relation [8,2]

$$\int_0^\infty dL\, e^{-L(t-t_b)}\, Z_{L,c-c_{SB}} \sim \lim_{n\to 0} \int d^d r_B \,\langle \phi_1(r_A)\phi_1(r_B)\rangle_{\mathcal{H}} \equiv \chi_1(t-t_b,\, c-c_{SB}) \tag{3}$$

for $(c,t) \in P$ and close to SB. Here

$$L \sim N \quad , \quad c-c_{SB} \sim \omega_a-\omega \sim T-T_a \quad . \tag{4}$$

From now on we suppress the shifts t_b and c_{SB} as well as appropriate powers of a large momentum cutoff $\Lambda \sim \ell^{-1}$ for the field $\vec{\phi}$. Scaling behavior [5,9]

$$\chi_1(t,c) \sim t^{-\gamma_1^{SB}}\, \tilde{\psi}(ct^{-\varphi}) \tag{5}$$

of the spin quantity χ_1 implies a corresponding form

$$Z_{L,c} \sim L^{-1+\gamma_1^{SB}}\, \psi(cL^{\varphi}) \tag{6}$$

for the chain partition function. The scaling form of Z has been verified by Monte Carlo simulations in d=3 [2]. The singular behavior of $\tilde{\psi}$ as (c,t) approaches the boundaries S,O of P determines the behavior of ψ for $L\to\infty$ in the cases $T<T_a$, $T>T_a$; $\tilde{\psi}$ and ψ are regular for small argument. With this information the mean number of surface links can be obtained [2]

$$\langle N_1\rangle \sim \partial_c\, \ell n\, Z \sim (L|c|^{(1/\varphi)-1},\, L^{\varphi},\, c^{-1}) \tag{7}$$

for

$$(T < T_a,\; T = T_a,\; T > T_a)$$

as

$$N \sim L \to \infty \quad .$$

Contrary to earlier conjectures [8,10,11] the exponent φ is not equal to $1-\nu$ as shown first in Ref. [5] (ν appears either in the chain diameter in free space $\sim N^{\nu}$ or the corresponding spin correlation length $\sim t^{-\nu}$). The numerical discrepancy in d=3 is substantial [1,2]: $\varphi \approx 3/5$, $1-\nu \approx 2/5$.

2. Semidilute solutions

Semidilute solutions (strong overlap between neighboring chains) can be mapped [4] unto the "coexistence" limit $t<0$, $H\to 0$ of a spin system in a magnetic field H with Hamiltonian

$$\mathcal{H}_H = \mathcal{H} - H \int_+ d^d r\, \phi_1(r) \quad . \tag{8}$$

This corresponds to the magnetic phase BF in Fig. 2. The local monomer density ρ at a point $r=(r_\parallel, z)$ is determined via

$$\rho(z,\rho_b,c) = \lim_{H\to 0} \lim_{n\to 0} \langle \vec{\phi}^2(r_\parallel, z)\rangle_{\mathcal{H}_H} \tag{9}$$

by the local energy density $\langle \vec{\phi}^2\rangle$ of the spin system. Here $t<0$ is adjusted such that the right hand side of (9) for $z\to\infty$, i.e. the bulk spin-energy density, equals a given bulk monomer density ρ_b

$$\rho(z\to\infty,\rho_b,c) \equiv \rho_b \sim |t|^{d\nu-1} \quad . \tag{10}$$

Scaling behavior of the $n\to 0$ spin energy density [4] implies a form

$$\rho(z,\rho_b,c) = \rho_b \cdot F(z/\xi_b, z/\xi_c) \;;\quad z,\xi_b,\xi_c \gg \ell \tag{11}$$

with ℓ a microscopic length, e.g. $\sim$ range of monomer-wall interaction, and two macroscopic lengths

$$\xi_b \sim |t|^{-\nu} \quad , \quad \xi_c \sim |c|^{-\nu/\varphi} \quad . \tag{12}$$

The length ξ_c already appears in the problem of Sec. 1, where the single chain for $T<T_a$ extends over a length ξ_c perpendicular to the wall [2].

Consider in particular $T=T_a$, i.e. $\xi_c=\infty$, where F in (11) depends only on one variable. The density at the surface depends upon $|t|$ in the form [4]

$$\rho(z=0,\rho_b,c=0) \equiv \rho_1(\rho_b,c=0) \sim |t|^{(d-1)\nu-\varphi} \tag{13}$$

consistent with a surface free energy $f_s \sim |t|^{(d-1)\nu}\, \psi_s(c|t|^{-\varphi})$ and $\rho_1 \sim \partial_c f_s$. Matching the t-dependence of (11) for $\ell \ll z \ll \xi_b$ to that of (13) leads to

$$\rho \sim \rho_b \cdot (z/\xi_b)^a \;;\quad c = 0 \;,\quad \ell \ll z \ll \xi_b \tag{14}$$

with

$$a = -1 + (1-\varphi)/\nu \quad . \tag{15}$$

According to Ref. [5] $a\neq 0$ in contrast to the earlier conjectures [8,10,11].

The numerical values [1,2] for φ in d=3 lead to a ≈ -0.3. The power-law behavior of ρ in (14) persists even for $T \neq T_a$ as long as $\ell \ll z \ll \xi_b, \xi_c$. Ref. [4] gives a detailed comparison with the behavior conjectured in Ref. [11].

The result (14),(15) following from the behavior of the local field theory (8) confirms a conjecture in Ref. [3] based on the behavior of the monomer density close to the wall for a single chain (Sec. 1) which was shown [2] to follow also the power law in Eq. (14) with the exponent (15).

I take the opportunity to describe this behavior for the single chain (of Sec. 1) in more detail. Consider the monomer number M(z) in a layer of width dz a distance z apart from the wall. For $T<T_a$ and $L \to \infty$

$$M(z) \sim \begin{cases} \langle N_1 \rangle \cdot z^a \\ 0 \end{cases} \quad \text{for} \quad \begin{cases} \ell \ll z \ll \xi_c \\ \xi_c \ll z \end{cases} \tag{16}$$

with $\langle N_1 \rangle$ from Eq. (7). On integrating (16) from $z=\ell$ to $z=\xi_c$, the leading contribution is consistently independent of $c \sim T-T_a$ and proportional to L, i.e. to the total monomer number. For $T=T_a$, Eq. (16) also holds if ξ_c is replaced by a length $\xi_b^{(s)} \sim L^{\nu}$, proportional to the chain diameter in free space, and the integral again is $\sim L$. For $T>T_a$ and large L, i.e. $\xi_c \ll \xi_b^{(s)}$, the behavior of M(z) is more complicated

$$M(z) \sim \begin{cases} \langle N_1 \rangle \cdot z^a \\ z^{(1/\nu)-1} \\ 0 \end{cases} \quad \text{for} \quad \begin{cases} \ell \ll z \ll \xi_c \\ \xi_c \ll z \ll \xi_b^{(s)} \\ \xi_b^{(s)} \ll z \end{cases} \tag{17}$$

and shows a minimum near $z=\xi_c$.

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