LETTER TO THE EDITOR

Adsorption of branched polymers at surfaces: exact results for $d = 3$

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Abstract. Exploiting the supersymmetric connection between the statistics of branched polymers and the problem of the Yang–Lee edge singularity, we study universal properties of the adsorption transition of diluted branched polymers in a three-dimensional solution at a hard wall. We calculate various scaling functions for the crossover between the non-adsorbed and adsorbed state exactly. In particular, the crossover exponent is found to be $\phi = \frac{1}{2}$.

In this letter we report on exact results for the adsorption transition of diluted branched polymers in a good solvent at a hard wall. This problem belongs to the same universality class as the statistics of trees and animals near an adsorptive surface of a semi-infinite lattice. It has been known for a number of years [1] that the statistics of large branched polymers in d spatial dimensions can be reduced via a supersymmetric connection to the problem of the Yang–Lee edge singularity in the Ising model in the presence of an imaginary external field in $D = d - 2$ dimensions. A consequence of this connection is that universal properties of correlation functions and other interesting quantities of the branched polymer problem can be calculated, if one knows the corresponding quantities of the Ising model near the Yang–Lee singularities in two dimensions less [2]. It can be shown that this supersymmetric connection holds also for systems with a surface [3]. Thus from the exact results for the critical properties of the one-dimensional semi-infinite Ising chain in imaginary surface and bulk external fields, we get exact results for the adsorption transition of large branched polymers at a wall.

The statistics of a semi-infinite Ising chain in external fields are modelled by the Hamiltonian

$$\mathcal{H} = -\sum_{i=1}^{\infty} K\sigma_i\sigma_{i+1} - H_1\sigma_1 - \sum_{i=2}^{\infty} H\sigma_i. \tag{1}$$

It is a textbook matter [4] to calculate, e.g. by the transfer-matrix method, the free energy, the magnetization $M_i = \langle\sigma_i\rangle$, and the correlation function $C_{ij} = \langle\sigma_i\sigma_j\rangle^{(c)}$ as functions of the parameters K, H and H_1. Going over to imaginary fields $H \to iH$, $H_1 \to iH_1$ the known result for the bulk-magnetization $M = \lim_{i\to\infty} M_i$ is given by

$$M = i/\sqrt{h} \tag{2}$$

where h is defined by

$$h = (e^{2K} \sin H)^{-2} - 1. \tag{3}$$

Equation (2) shows the (one-dimensional) Yang–Lee singularity at $h = 0$. Denoting by $\omega_\pm$ the two eigenvalues of the transfer matrix and by a the lattice constant, the correlation length is given by $\xi = a(\ln(\omega_+/\omega_-))^{-1}$. It diverges at the Yang–Lee singularity as $1/\sqrt{h}$. The critical properties are universal at the full singularity edge and therefore independent of the coupling constant K. Thus we simplify all expressions without losing their universal properties by choosing the 'low temperature' region $K \gg 1$ keeping $\xi_0 = e^{2K}a$ finite. Choosing now ξ_0 as a unit for the length scale, we have a suitable device for performing the continuum limit $a \to 0$. In this limit we find for the surface magnetization and the correlation length

$$M_1 = i\,\frac{(\sqrt{h}+\sqrt{h+1})t+1}{(\sqrt{h}+\sqrt{h+1})-t} \tag{4a}$$

$$\xi = \xi_0\sqrt{(1+h)/4h}. \tag{4b}$$

Here the parameter t is defined by $t = \tan H_1$. The surface magnetization shows the zero-dimensional Yang–Lee singularity at the surface-transition line $t = \sqrt{h}+\sqrt{h+1}$. The surface-bulk multicritical point is given by the parameter values $h = 0$, $t = 1$, and the crossover exponent is read off from (4a) as

$$\phi = \tfrac{1}{2}. \tag{5}$$

Furthermore, we find for the magnetization profile and the correlation function

$$M(z) = (1 - e^{-z/\xi})M + e^{-z/\xi}M_1 \tag{6a}$$

$$C(z, z') = e^{-|z-z'|/\xi}[1 - M(\min(z, z'))^2] \tag{6b}$$

where z denotes the distance from the surface.

Now we are in a position to calculate polymer quantities in dimension $d = 3$ by an inverse Laplace transformation $1/(2\pi i)\int_{-i\infty}^{i\infty} dH\, e^{-HN}\ldots$ of $M(z)$ and $C(z, z')$. Here, up to a scale factor, N is the number of monomers of the branched polymer. Since $N \gg 1$, only a small region around the critical value of H is effectively used by the integration, if we deform the integration path around the branch point singularities of the integrands. Thus we can approximate H by $H \approx H_c - e^{-2K}h/2$. $H_c \approx e^{-2K}$ is a non-universal quantity. We renormalize N by the factor $e^{-2K}/2$ and define

$$Z_N(z) = \frac{1}{2\pi i}\int_{-i\infty}^{i\infty} dh\, e^{hN}M(z) \tag{7a}$$

$$Z_N(z, z') = \frac{1}{2\pi i}\int_{-i\infty}^{i\infty} dh\, e^{hN}C(z, z'). \tag{7b}$$

In particular, the inverse Laplace-transformed bulk magnetization $Z_N = Z_N(\infty)$ yields, up to a non-universal exponential factor λ^N, the number $\mathscr{A}_N$ of possible three-dimensional configurations of a branched polymer or animal made from N monomers or sites: $\lambda^N Z_N/N \sim \mathscr{A}_N \sim N^{-\theta}\lambda^N$ with $\theta = \tfrac{3}{2}$. We denote by $\mathscr{A}_N(n_1|z_1, n_2|z_2, \ldots)$ the number of such polymer configuration with n_i monomers in the two-dimensional layer at a distance z_i from the surface. Then we get from the supersymmetric connection, the relation

$$\sum_{\substack{n_i = 0 \\ (\text{all } i)}}^{\infty} n_1 \ldots \mathscr{A}_N(n_0|0, n_1|z_1, \ldots)\, e^{\varepsilon n_0} \sim Z_N(z_1, \ldots)\lambda^N. \tag{8}$$

The adsorption energy ε for a monomer at the surface is proportional to the field H_1. Thus near the critical value ε_c, we have $\varepsilon - \varepsilon_c \sim t - 1$.

Now we get from equations (6) and (7) our fundamental results

$$Z_N(z) = \frac{1}{\sqrt{\pi N}} \{1 + e^{-\zeta^2}[1 - 2\sqrt{\pi}\Gamma\, e^{(\Gamma+\zeta)^2}\, \text{erfc}(\Gamma+\zeta)]\} \tag{9a}$$

$$Z_N(z, z') = \text{erfc}(\zeta - \zeta') - 2\,\text{erfc}(\zeta) + \text{erfc}(\zeta + \zeta') + 4\,e^{(\Gamma+\zeta)^2 - \zeta^2}\,\text{erfc}(\Gamma+\zeta) + 8\Gamma\,e^{-(\zeta+\zeta')^2}$$

$$\times [(\Gamma + \zeta + \zeta')\,e^{(\Gamma+\zeta+\zeta')^2}\,\text{erfc}(\Gamma + \zeta + \zeta') - 1/\sqrt{\pi}]. \tag{9b}$$

Here the last equation for $Z_N(z, z') = Z_N(z', z)$ is written down for $z \geq z'$ and erfc denotes the error function: $\text{erfc}(x) = (2/\sqrt{\pi}) \int_x^\infty \exp(-y^2)\, dy$. If z is measured in units of ξ_0, the variables ζ and Γ are defined by $\zeta = z/\sqrt{N}$ and $\Gamma = (1 - t)\sqrt{N} \sim (\varepsilon_c - \varepsilon)\sqrt{N}$. The expressions (9a), (9b) have the same structure as the corresponding quantities in the problem of the surface adsorption of ideal linear polymers as presented in the work of Eisenriegler *et al* [5]. Thus we follow their discussion.

$Z_N(z)\lambda^N$ is proportional to the number of polymer configurations with one monomer rooted in the layer z under the influence of the surface adsorption energy ε. As remarked above, this quantity changes over for $z \to \infty$ to the animal number $N\mathscr{A}_N$ in the bulk, independent of ε. In the general case we have to distinguish between the three cases non-adsorbed ($\varepsilon < \varepsilon_c$), critical ($\varepsilon = \varepsilon_c$), and adsorbed ($\varepsilon > \varepsilon_c$). Because $N \gg 1$, these cases correspond to the limiting values of the scaling variable $\Gamma \gg 1$, $\Gamma = 0$ and $-\Gamma \gg 1$. We find

$$Z_N(z) = \frac{1}{\sqrt{\pi N}} \begin{cases} (1 - e^{-\zeta^2}) + \Gamma^{-1}[2\zeta + \Gamma^{-1}]e^{-\zeta^2} & \Gamma \gg 1 \\ (1 + e^{-\zeta^2}) & \Gamma = 0 \\ 1 + 4\sqrt{\pi}|\Gamma|\,e^{|\Gamma|(|\Gamma|-2\zeta)} & -\Gamma \gg 1. \end{cases} \tag{10}$$

For $\varepsilon < \varepsilon_c$, $Z_N(z)$ approaches the bulk value $1/\sqrt{\pi N}$ for z large compared to the correlation length $\xi \sim \sqrt{N}$. However, this is not the case for $\varepsilon > \varepsilon_c$ ($-\Gamma \gg 1$), where $\sqrt{\pi N}\, Z_N(z) - 1 \sim |\Gamma| \exp[(z_0 - z)/\Delta z_0]$ which defines two more lengths $\Delta z_0 \sim (\varepsilon - \varepsilon_c)^{-1}$ and $z_0 \sim N(\varepsilon - \varepsilon_c)$ with the orders of magnitude $\Delta z_0 \ll \xi \ll z_0$. If one moves the root towards the surface, at the characteristic distance $z = z_0$ the physical properties change rapidly within a small interval of width Δz_0 around z_0 from bulk to adsorbed behaviour.

In general, we have the relation $\int_0^\infty dz\, Z_N(z, z') = 2N Z_N(z')$, which follows from the dissipation-fluctuation theorem of the Ising model by the inverse Laplace transformation (7a), (7b). Therefore we find for the monomer density in the layer z, if the polymer is rooted in the layer z'

$$\rho_N(z|z') = Z_N(z, z')/2Z_N(z'). \tag{11}$$

If the root is fixed at the surface, equations (9a), (9b) yield

$$Z_N(0) = \frac{2}{\sqrt{\pi N}} \{1 - \sqrt{\pi}\Gamma\, e^{\Gamma^2}\, \text{erfc}(\Gamma)\} \tag{12a}$$

$$Z_N(z, 0) = 4\,e^{-\zeta^2}\{[1 + 2\Gamma(\Gamma + \zeta)]\,e^{(\Gamma+\zeta)^2}\,\text{erfc}(\Gamma + \zeta) - 2\Gamma/\sqrt{\pi}\}. \tag{12b}$$

From these expressions we find the asymptotic forms of the monomer density of a surface rooted polymer

$$\rho_N(z|0) = \sqrt{N} \begin{cases} 2\,e^{-\zeta^2}(\zeta + \Gamma^{-1}) & \Gamma \gg 1 \\ \sqrt{\pi}\, \text{erfc}(\zeta) & \Gamma = 0 \\ 2|\Gamma|\,e^{-2|\Gamma|\zeta} & -\Gamma \gg 1. \end{cases} \tag{13}$$

The interpretation in terms of the cases non-adsorbed, critical, and adsorbed is obvious. Note that in the adsorbed case, the thickness of the polymer at the surface is given by the length $\Delta z_0 \sim (\varepsilon - \varepsilon_c)^{-1}$. The number of polymer configurations rooted in the surface follows from the asymptotic form of $Z_N(0)$ in the three cases

$$Z_N(0) = \frac{1}{\sqrt{\pi N}} \begin{cases} \Gamma^{-2} & \Gamma \gg 1 \\ 2 & \Gamma = 0 \\ 4\sqrt{\pi}\,|\Gamma|\,e^{\Gamma^2} & -\Gamma \gg 1. \end{cases} \tag{14}$$

Now, the animal numbers for surface rooted branched polymers can be defined in analogy to the bulk animals: $\mathscr{A}_{N,1} \sim \lambda^N Z_N(0)/N$. In the non-adsorbed case we find $\mathscr{A}_{N,1} \sim N^{-\theta_1}\lambda^N$ with an exponent $\theta_1 = \frac{5}{2} = \theta + 1$. The last relation between the bulk and surface exponents was found for all dimensions by De'Bell *et al* [6] for lattice trees by rigorous arguments. In the critical case $\varepsilon = \varepsilon_c$, the animal numbers are $\mathscr{A}_{N,1} \sim N^{-\theta_a}\lambda^N$ with $\theta_a = \frac{3}{2}$. In general dimensions below eight, the exponent θ_a depends on the bulk exponent θ and the crossover exponent ϕ. We have derived the relation

$$\theta_a = \frac{d-3}{d-2}(\theta - 1) + (2 - \phi) \tag{15}$$

using field-theoretic renormalization group methods [3]. In the adsorbed case $\varepsilon > \varepsilon_c$, we find $\mathscr{A}_{N,1} \sim \mathscr{A}'_N \sim N^{-\theta'}\lambda'^N$ with $\theta' = 1$. This result shows that the adsorbed branched polymers are indeed quasi-two-dimensional animals. In general θ' is the exponent in $(d-1)$ bulk-dimensions.

Now we consider the number $\mathscr{A}_N(n)$ of possible configuration of branched polymers with n monomers at the surface made from N monomers. The various moments of $\mathscr{A}_N(n)$ are defined by $m_p = \lambda^{-N} \sum_{n=0}^{\infty} n^p \mathscr{A}_N(n)\,e^{\varepsilon n}$ up to the non-universal factor λ^N. We have $m_1 \sim Z_N(0)$, $m_2 \sim Z_N(0,0)$, etc. The moments can be derived by successive differentiation with respect to the variable $\varepsilon - \varepsilon_c \sim -\Gamma/\sqrt{N}$. The general relation is $\partial Z_N(z)/\partial\Gamma = -Z_N(z,0)/2\sqrt{N}$, etc. Defining the generating function $F_N \sim m_0$ with $\partial F_N/\partial\Gamma = -Z_N(0)/2\sqrt{N}$, we get

$$F_N = \frac{1}{2N}\,e^{\Gamma^2}\,\mathrm{erfc}(\Gamma). \tag{16}$$

Mean values may be defined by $\langle n^p \rangle = m_p/m_0$. The ratio of the second and the first moment is proportional to the monomer density $\rho_N(0|0)$. The asymptotic expressions can be read off from equation (13)

$$\langle n^2 \rangle/\langle n \rangle \sim \begin{cases} 2/(1-t) & \varepsilon < \varepsilon_c \\ \sqrt{\pi N} & \varepsilon = \varepsilon_c \\ 2(t-1)N & \varepsilon > \varepsilon_c. \end{cases} \tag{17}$$

A final result which we can infer from the generating function is the number of possible configuration of branched polymers at the surface. We find from equation (16)

$$\mathscr{A}_N(n) = aN^{-3/2}\,e^{-bn^2/N - cn}\lambda^N \tag{18}$$

where a, b, c, and λ are non-universal constants.

This ends our exact results in three dimensions. It would be interesting to compare these results, for example, with Monte Carlo simulations. We are aware of only one such simulation [7]. The authors 'measure' a type of specific heat $(\langle n^2 \rangle - \langle n \rangle^2)/N$. Since the exact crossover exponent is $\phi = \frac{1}{2}$, it is easily shown that this quantity is not

characteristic for the adsorption transition discussed above. It may be possible that the authors have found another adsorption transition, which leads to more compact objects than animals in two dimensions [3].

References

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