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Adsorbed polymers and node-avoiding Levy flights

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Abstract. We discuss the conformation of a linear flexible polymer chain in the vicinity of an attractive wall. We show that the structure in the adsorbing plane may be analysed in terms of a node avoiding Levy flight. This provides a complementary insight to the scaling approach.

1. Introduction

There is renewed interest in the conformation of linear polymer chains in the vicinity of an interacting wall (de Gennes 1979, de Gennes and Pincus 1983, Binder 1983, Eisenriegler *et al* 1982, Eisenriegler 1983). Depending on the quality of the solvent and of the sign of the interaction between the polymer and the wall, one may find depletion (de Gennes 1981), adsorption (de Gennes and Pincus 1983) or wetting (Schmidt and Binder 1987). In this paper we consider a single chain in the vicinity of an attractive wall. Let N be the number of monomers of the polymer and $(-kT\delta)$ the excess energy per monomer on the wall. When δ is positive and large enough (de Gennes 1979), the chain is adsorbed by the wall. The adsorption threshold corresponds to an attractive energy of order kT :

$$\delta_c \sim N^{-\varphi} \quad (1)$$

where φ is a crossover exponent which was calculated by renormalisation group (Diehl and Dietrich 1981) and computer simulations (Ishinabe 1982, 1984, Kremer 1983) and N^φ is the number of monomers on the wall at the threshold.

Below the threshold, the chain behaves as a self-avoiding walk: its radius of gyration R varies as $R \sim N^\nu a$ (Flory 1953, de Gennes 1979) where a is the step length of the polymer.

At and beyond the threshold, the chain is made of a succession of loops with different lengths or sizes connecting monomers on the wall. The distribution of sizes of these loops was recently calculated by de Gennes (1982) and is rather broad. Because there is a distribution of lengths for the distances between two successive monomers on the wall, we will show that the projection of the polymer on the adsorbing surface is equivalent to a node-avoiding Levy flight (NALF). This equivalence will allow us to evaluate the parallel radius of the adsorbed chain. Furthermore, it will enlighten recently proposed scaling laws.

In what follows we first recall the main results on polymer adsorption in § 2 and those on Levy flights in § 3. The analysis of the parallel radius in terms of Levy flights is given in the final section.

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2. Distribution of step lengths in the attractive wall

In this section, we recall the main results on the adsorption of one flexible polymer chain by an attractive wall. For more details, see de Gennes and Pincus (1983) or Eisenriegler *et al* (1982). Consider an attractive wall, with an excess (dimensionless) free energy δ per adsorbed monomer. Above the adsorption threshold (defined by equation (1)), the polymer is adsorbed on the surface. A diffuse layer with an increased density results and a concentration profile $\varphi(z)$ along the direction normal to the wall: $a^{-2}\varphi(z)$ is the monomer concentration per unit surface on the wall at a distance z from the wall. Three regions were considered (de Gennes 1979).

(i) *Proximal*: $a \ll z \ll D$ where a is the step length and

$$D \sim a\delta^{-\nu/\varphi} \quad (2)$$

where ν is the self-avoiding walk exponent (Flory 1953, de Gennes 1979) and the width D of the adsorbed layer is sometimes called the extrapolation length (Binder 1983). In this region

$$\varphi(z) \sim \varphi_s(a/z)^m \quad (3)$$

with

$$\varphi_s \sim \delta^\alpha \quad (4)$$

$$m = (\nu + \varphi - 1)/\nu \quad (5)$$

$$\alpha = \nu(d - 1)/\varphi - 1. \quad (6)$$

(ii) *Central*: $D \ll z \ll R_F$ where

$$R_F \sim N^\nu a \quad (7)$$

is the Flory radius of a single chain. In this region, the layer has a simple self-similar structure, which yields

$$\varphi(z) \sim (a/z)^{(\nu d - 1)/\nu} \quad (8)$$

with d the dimension of space.

(iii) In the *distal* region: $z \gg R_F$, the monomer density decreases exponentially to zero.

Two limits may be considered.

(i) At the threshold, equations (1) and (2) imply that the extrapolation length is of the order of the Flory radius R_F . Thus the central region disappears and the proximal region covers the whole range up to R_F .

(ii) In the opposite limit of strong adsorption ($\delta \sim 1$), D is of the order of the step length, so that the proximal region shrinks out and only the central and distal regions remain.

The structure of the chain is made of loops of different sizes joining monomers on the surface. The concentration profile $\varphi(z)$ corresponds to a broad distribution of loop sizes. Let $a^{-2}f(n, \delta)$ be the number per unit area of monomers that belong to the loops made of n monomers. Evaluating the number of monomers per unit surface between the distances z and $z + dz$ provides a relation between $\varphi(z)$ and $f(n, \delta)$:

$$f(n, \delta) dn = \varphi(z) dz. \quad (9)$$

We know that the structure of the chain at the threshold is still isotropic (de Gennes 1979, Eisenriegler *et al* 1982). Thus it is plausible to assume that the loops are isotropic, with bulk behaviour:

$$n \sim (z/a)^{1/\nu}. \tag{10}$$

It is now possible to assume a scaled form for the distribution of loops. It is clear from equations (2), (3), (8) and (10) that $f(n, \delta)$ has different power law behaviours for distances smaller or larger than D . The crossover corresponds to a typical loop size

$$n^* \sim D^{1/\nu} \sim \delta^{-1/\varphi}.$$

Thus we assume

$$f(n, \delta) \sim n^{-\tau} p(n\delta^{1/\varphi}) \tag{11}$$

and using equations (3)-(10), we obtain

$$p(x \rightarrow 0) \sim x^{\tau'} \tag{12a}$$

$$p(x \rightarrow \infty) \sim \text{constant} \tag{12b}$$

with

$$\tau = \nu(d - 1) \tag{13a}$$

and

$$\tau - \tau' = \varphi. \tag{13b}$$

As noted by de Gennes (1982), loops may be divided into two categories.

For small loops, with $1 < n < \delta^{-1/\varphi}$, using (11)-(13), we have

$$f(n, \delta) \sim \varphi_S n^{-\varphi}. \tag{14a}$$

For large loops, with $\delta^{-1/\varphi} < n < N$, we have

$$f(n, \delta) \sim n^{-\nu(d-1)}. \tag{14b}$$

The relative importance of each of these categories depends on the parameter δ : whereas at the threshold only 'small' loops are present, for strong adsorption ($\delta \sim 1$) small loops are no longer present, but it is very important to realise that there are still 'large' loops, and that a finite fraction of the monomers belongs to these loops.

Consider now two successive monomers on the surface. These are linked by a loop. Let l be the distance between these monomers. Because there is a distribution of sizes for the loops, there is a distribution $S(l)$ for the distances. $S(l)$ is related to the *number* distribution of loops:

$$S(l) \frac{dl}{a} = \frac{1}{n} f(n, \delta) dn \tag{15}$$

and, from the isotropy of loops, equation (10)

$$l \sim n^\nu a. \tag{10a}$$

Thus the projection of the adsorbed chain on the surface does not have a constant step length but a rather broad distribution of step lengths $S(l)$. Using equations (11) and (10a) we get two categories of steps: short steps, $a < l < D$,

$$S(l) \sim \delta^\alpha \left(\frac{l}{a}\right)^{-(\nu+\varphi)/\nu} \tag{16a}$$

large steps, $D < l < R_F$,

$$S(l) \sim \left(\frac{l}{a}\right)^{-d} \tag{16b}$$

One can think of the projected structure on the $(d - 1)$ -dimensional surface as a random walk with broad step length distribution $S(l)$. Note that two monomers on the wall cannot be located on the same site, while the links joining them may intersect because they are just projections of the loops. Because $S(l)$ is slowly decaying, we argue that such a walk is a node-avoiding Levy flight (NALF) (Mandelbrot 1975).

3. Node-avoiding Levy flights

Consider, in a $(d - 1)$ -dimensional space, a walk with a step length distribution $S(l)$, for large l :

$$S(l) \underset{l \rightarrow \infty}{\sim} \frac{1}{l^{\sigma+1}} \tag{17}$$

when σ is small (see below and figure 1). Such a walk is called a Levy flight and does not reduce to a self-avoiding walk. In the following, we will be interested in the radius of gyration of such a flight and in its dependence on the number M of steps. In analogy with self-avoiding walks, we assume† (Grassberger 1985)

$$\langle \log R_M \rangle \sim \nu' \log M \tag{18}$$

where the brackets are geometrical averages and R_M the end-to-end distance of the walk.

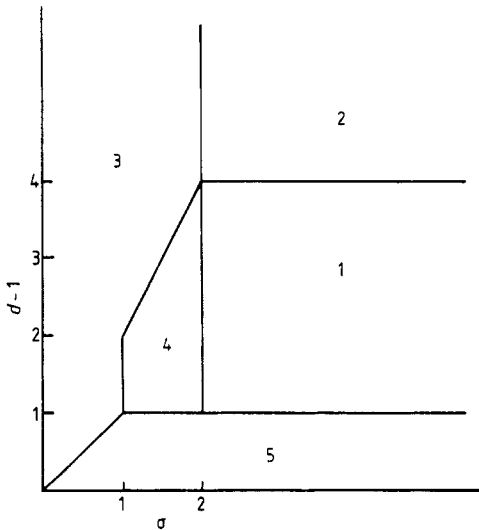


Figure 1. The different regimes for a NALF within a Flory theory. $(d - 1)$ is the space dimension. The probability for a step l is $P(l) \sim l^{-1-\sigma}$. The different regimes are as follows: (1) SAW: $\nu' = 3/(d + 1)$; (2) random walk, $\nu' = \frac{1}{2}$; (3) classical Levy flight, $\nu' = 1/\sigma$; (4) NALF, $\nu' = (2\sigma - 1)/[d\sigma - (d - 1)]$; (5) collapsed, $\nu' = 1/d - 1$. The lines are crossover lines.

† An equivalent definition is that the correlation function varies as $g(q) \sim q^{-1/\nu'}$ in Fourier space.

If $S(l)$ decreases fast enough, namely if $\sigma > 2$, the second moment of the distribution (17) is finite. Then ν' is equal to the Flory exponent ν (Flory 1953) and the flight is equivalent to a self-avoiding walk, or to a random walk depending on the value of d .

When $\sigma < 2$ the second moment of $S(l)$ is infinite and the exponent ν' depends on σ . Halley and Nakanishi (1985) and Grassberger (1985) showed that there is an equivalence between such a flight and a magnetic model with long-range interactions. The latter was considered by Fisher *et al* (1972) and Sak (1978) who showed that the upper critical dimension is

$$d_c - 1 = 2\sigma. \tag{19}$$

Thus when $2\sigma \leq d - 1$ the excluded volume interactions are irrelevant and the flight is classical:

$$\nu' = 1/\sigma. \tag{20}$$

When $2\sigma > d - 1$, these interactions are relevant, and one may calculate ν' within a Flory theory (de Gennes 1979, Flory 1953, Grassberger 1985). Let R be the radius of a NALF made of M steps. The Flory free energy is (de Gennes 1986)

$$F = \left(\frac{R^\sigma}{M}\right)^{1/(\sigma-1)} + \frac{M^2}{R^{d-1}} \tag{21}$$

where the first term is the elastic energy and the second one the interaction contribution. Note the unusual form of the former, which provides the classical behaviour for high space dimensions. The exponent $(\sigma - 1)$ may be understood if one analyses a stretched flight in terms of Pincus blobs (de Gennes 1979, Pincus 1976).

Minimising the free energy with respect to R we find

$$\nu' = \frac{2\sigma - 1}{\sigma d - (d - 1)} \quad d - 1 < 2\sigma. \tag{22}$$

Finally, we note that the fractal dimension has to be smaller than both the space dimension $(d - 1)$ and the unperturbed dimension σ . Thus

$$\nu' = \frac{1}{d - 1} \quad d - 1 < \inf(\sigma, 1). \tag{23}$$

These results are summarised on figure 1 which gives the different regimes in a $(\sigma, d - 1)$ plane.

4. Parallel extension of the polymer

In this section we determine the parallel radius of the chain on the attractive wall. We consider both the adsorption threshold and the strong adsorption regime ($\delta \sim 1$). The discussion is limited to $d = 3$. The two-dimensional case will be considered in the conclusion.

4.1. The adsorption threshold

As noted in § 2, only the proximal and distal regions exist at the threshold. Thus there is a distribution of loop sizes for the adsorbed chain given by equations (11), (12a)

and (13b), and thus a distribution of step lengths for the projection of the polymer on the surface given by relation (16a):

$$S(l) \sim \frac{1}{l^{1+\varphi/\nu}}. \quad (16a)$$

Comparing with equation (17), we find that the projection is a NALF with

$$\sigma = \varphi/\nu \approx 1 \quad (24)$$

with $\varphi \approx \nu \approx \frac{3}{5}$.

From figure 1, we obtain

$$\nu' = \sigma^{-1} \approx 1.$$

At the threshold, the number M of nodes is

$$M \sim N^\varphi.$$

Thus at the threshold, the parallel extension R_{\parallel} of the chain is

$$R_{\parallel} \sim aN^{\varphi\nu'} \approx aN^{3/5} \quad (25)$$

as expected because the chain is assumed to be still isotropic at the threshold. Note that $\sigma = 1$ and $d - 1 = 2$ in figure 1 correspond to a point on the crossover line between classical and critical Levy flights.

4.2. Strong adsorption

The number of monomers on the wall may be written in the scaled form

$$M = N^\varphi f(\delta N^\varphi) \quad (26)$$

where $f(x)$ is an unknown function. Its behaviour far from the threshold may be obtained by noting that a finite fraction of the monomers is on the wall

$$M \sim N.$$

Assuming a power law behaviour for $f(x)$, we obtain

$$M \sim N\delta^{(1-\varphi)/\varphi}. \quad (27)$$

For strong adsorption, $\delta \sim 1$, the number of steps is proportional to N .

As discussed in § 2, only the central and distal regions exist in this regime. Thus the distribution of step lengths for the projection of the polymer is

$$S(l) \sim \left(\frac{l}{a}\right)^{-3}. \quad (16b)$$

Thus we have a NALF with $\sigma = 2$. As discussed above, this value for σ corresponds to a marginal case between SAW and NALF where both the Flory exponent and relation (22) are valid. Therefore we find

$$R_{\parallel} \sim N^{3/4}a. \quad (28)$$

It is important to realise that although the parallel radius is proportional to the two-dimensional Flory radius—with eventual logarithmic corrections—the chain is still three dimensional: a finite fraction of the monomers are in the long loops extending in the solution. The radius of the chain in the normal direction is still proportional to $R_F \sim aN^{3/5}$.

4.3. Intermediate case: $N^{-\varphi} \ll \delta \ll 1$

For intermediate energies or temperatures, the number of monomers on the surface is given by relation (27). One may reduce this case to the strong adsorption case discussed by introducing adsorption blobs, made of n monomers such that

$$\delta n^\varphi \sim 1. \tag{29}$$

The radius of these blobs is of the order of the extrapolation length, defined by equation (2):

$$\xi \sim n^{3/5} a \sim \delta^{-1} a \tag{30}$$

$$\xi \sim D.$$

If we take these blobs as elementary units, the resulting chain, made of N/n units of length ξ each, is in a strong adsorption regime. Using relation (28) we obtain for this intermediate case

$$R_{\parallel} \sim \left(\frac{N}{n}\right)^{3/4} \xi \tag{31}$$

$$R_{\parallel} \sim N^{3/4} \delta^{1/4} a.$$

Equation (31) was previously derived by Eisenriegler *et al* (1982) using scaling arguments. The same remark applies as in the previous subsection: the radius of the chain in the direction normal to the surface is of the order of the Flory radius.

5. Discussion

We have shown that the parallel extension of an adsorbed chain may be discussed in terms of node-avoiding Levy flight. For the three-dimensional case we considered so far, this discussion confirms all the results derived previously.

Now we consider the case of a two-dimensional chain with an adsorbing line: if we make the same analysis as above, we know that at the threshold the number of adsorbed monomers is

$$M \sim N^\varphi. \tag{32}$$

If we assume a distribution of loops, and thus of step sizes, we still have a Levy flight and

$$R_{\parallel} \sim aM^{\nu'} \sim aN^{\nu'\varphi}. \tag{33}$$

Assuming the structure is still isotropic at the threshold implies

$$\nu' = \nu/\varphi = 1/\sigma. \tag{34}$$

Thus the corresponding point in figure 1 has to be in region 3. This in turn implies

$$\sigma \leq 1 \tag{35}$$

and thus

$$\sigma \leq \nu = \frac{3}{4}. \tag{36}$$

This upper bound, $\varphi = \frac{3}{4}$, is in agreement with recent numerical results (Kremer 1983, Ishinabe 1984).

The present scaling approach, however, might be questioned in this two-dimensional case, and for low space dimensions more generally: let us return for instance to relation (8) for the concentration profile in the central region. If we then consider the excess concentration in this region:

$$\Gamma_c \sim \int \varphi(z) dz \sim \int_D^{R_F} z^{-(\nu d-1)/\nu} dz \quad (37)$$

$$\sim N^{1/4} \quad d = 2. \quad (37a)$$

More generally, as soon as the exponent in the integrand of (37) is smaller than unity, Γ_c depends on the upper limit R_F rather than on the lower one, D , and thus a divergence appears in (37a). Within a Flory theory, $\nu = 3/(d+2)$, we find that this is the case with low space dimensions:

$$d < d_i \equiv \frac{5}{2}. \quad (38)$$

Because of this divergence, one might question the definition of the profile $\varphi(z)$ as given by equations (3)–(8).

As a conclusion, we have shown that the parallel structure of an adsorbed linear polymer may be considered as a node-avoiding Levy flight. In the three-dimensional case, this equivalence reveals useful to describe the structure constituted by the anchoring points on the surface. In the case of a two-dimensional system with an adsorbing line, this leads to an upper bound $\varphi = \frac{3}{4}$ for the crossover exponent, but the whole scaling approach might be questioned.

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