# POLYMER AT A WALL

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## 1 Problem

One of the simplest idealizations of a flexible polymer chain consists of replacing it by a random walk on a cubic lattice in three-dimensional space or on a square lattice in two-dimensional space. (This walk is allowed to self-intersect, and it has no "bending energy", i.e. each step is independent of the previous one. Assume that one end of the polymer is tied to a surface. The surface will be considered adsorbing, i.e. every time the polymer (or the random walk) touches the surface its energy decreases by V. A very long polymer will be either localized near the surface, or will be delocalized, depending on the temperature T. Describe the temperature-dependence of the "localization" of the polymer

## 2 The partition function

In this note we concentrate on the case of $2D$ polymers. Basically we deal with a special case of weighted random walk on the lattice $\mathbb{Z}_+ \times \mathbb{Z}$. Consider the partition function for a canonical ensemble of such walks of a fixed length $n$

$$Z_n = \sum_{\text{over all walks of length } n} e^{m\frac{V}{T}}, \qquad (1)$$

where $m$ counts the times a walk touches the wall (the starting point excepted). Denote $\frac{V}{T}$ by $\beta$. Then the mean number of returns to the wall

$$< m >_T = \frac{1}{Z_n} \sum_{\text{over all walks of length } n} m e^{m\frac{V}{T}} = \frac{d}{d\beta} \ln Z_n. \qquad (2)$$

In the following we show that $< m >_T$ may be obtained analytically for the number of steps $n \lessapprox 20$ (with a little help from *Maple*) and good asymptotics may be obtained for $n \gg 1$.

One of the most powerful tools in the theory of simple random walk on $\mathbb{Z}$ is the generating function. As a counterpart in this *Problem* we introduce the generating function of partition functions (GPF)

$$G_Z(t) := \sum_{i=0}^{\infty} Z_i t^i \qquad (3)$$

($Z_0 := 1$), which is a power series in some real $t \geq 0$ and supposed to contain all the information about $\{Z_i\}$.

## 3 An alternative formulation

To take full advantage of the well-developed apparatus of generating functions for the random walk on the line, it would be very convenient to reduce the dimension of the *Problem* to $D = 1$.

Which is in fact possible for two-dimensional polymers and due to the translational invariance of the potential along the wall. It is easy to observe that there is a bijection from the set of all $2D$ random walks of length $n$ restricted to the right-hand half-plane (random walk on $\mathbb{Z}_+ \times \mathbb{Z}$) to the set of all random walks on $\mathbb{Z}_+$ (simple random walk on $\mathbb{Z}$ restricted by the condition $x \geq 0$) of length $N = 2n$. We identify a step in $\mathbb{Z}_+ \times \mathbb{Z}$) walk with *two* steps in $\mathbb{Z}_+$ walk as depicted in the following table:

| $2D$ walk | $1D$ walk |
|---|---|
| $\longrightarrow$ step to the right | $\longrightarrow\longrightarrow$ 2 steps to the right |
| $\longleftarrow$ step to the left | $\longleftarrow\longleftarrow$ 2 steps to the left |
| $\uparrow$ step upward | $\rightleftarrows$ step to the right then step to the left |
| $\downarrow$ step downward | $\leftrightarrows$ step to the left then step to the right. |

We also require that if the original walk starts on the wall, say at $(0;0)$, then its image starts at $x = 1$. Take, for example, the walk in Figure 1.

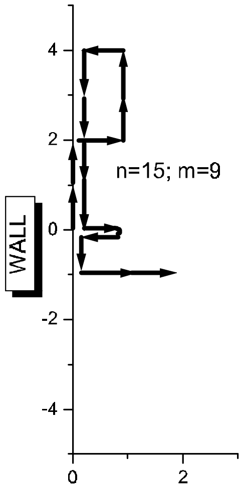


Figure 1

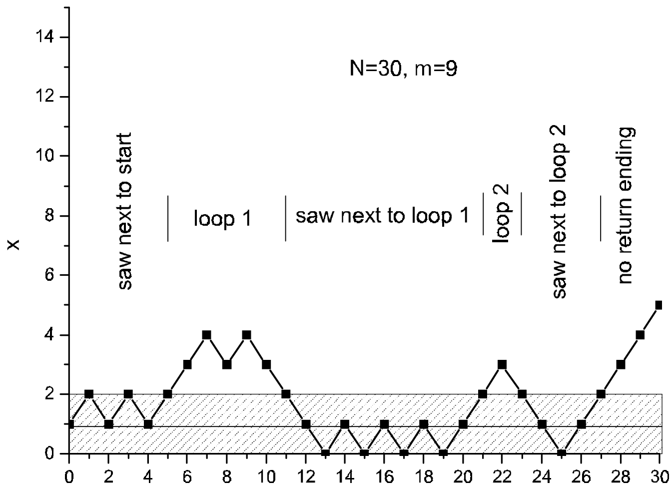


Figure 2

The corresponding walk can be represented by the following series of non-negative integer numbers:

$$1; 2; 1; 2; 1; 2; 3; 4; 3; 4; 3; 2; 1; 0; 1; 0; 1; 0; 1; 0; 1; 2; 3; 2; 1; 0; 1; 2; 3; 4; 5$$

or as a function of time (current step number) as in Figure 2. Note that, though under this reformulation we loose information (in its obvious form) about the position of the polymer chains along the wall, the information about the height is retained, e.g. the number of returns to the wall of an original walk $m$ equals to the number of returns of its image to $x = 1$.

Let us now explain the terminology used in Figure 2. A maximal connected part of a walk confined in the strip $0 \leq x \leq 2$ (shaded area in Figure 2) is called a *saw.* An excursion of a walk to the half-plane $x > 2$ between two consecutive returns to $x = 2$ is called a *loop.* A walk on $\mathbb{Z}_+$ with origin at $x = 1$ starts with a saw of an odd length. Then follows a series of loops (no loops is also possible). Each loop may have or have not a saw attached to it. If there is no saw after a loop we can still consider it a loop-saw combination with a saw of zero length. If after the last loop-saw combination we have some extra length then there is room for the ending, which is an excursion from $x = 2$ upward with no return to $x = 2$.

## 4 GPF

In the reformulated problem (3) can be rewritten as

$$G_Z(t) = \sum_{i=0}^{\infty} \tilde{Z}_{2i} t^i, \tag{4}$$

where $\tilde{Z}_{2i}$ is the partition functions for weighted $\mathbb{Z}_+$ walks of length $2i$. As follows from the discussion above, a walk is weighted be the factor $e^{\frac{V}{T}}$ each time it returns to $x = 1$. Accordingly to the presented description of the structure of the random walk on $\mathbb{Z}_+$ (which we will also call asymmetric random walk in contrast to the simple symmetric walk on $\mathbb{Z}$), the GPF may be decomposed with the help of much simpler GPFs associated with saw, loop and ending types of paths.

### 4.1 Saw -type GPFs

Let us consider random walks on the interval $[0, 2]$ (in other words on the set of three points $\{0, 1, 2\}$) of length $2l$. Each of such walks returns to the point $x = 1$ exactly $l$ times and there are $2^{l-1}$ of them. The partition function, which is just a sum over all such saw-type walks each taken with the same weight $e^{l\beta}$, for any $l \geq 1$ is $2^{l-1}e^{l\beta}$. We need a saw with $l = 0$ to insert it between two consecutive loops, so $\tilde{Z}_0^{saw} = 1$. Then the GPF is

$$\begin{aligned} G_{saw}(t) &= 1 + \sum_{l=1}^{\infty} e^{l\beta} 2^{l-1} t^l = \frac{1}{2} + \frac{1}{2} \sum_{l=0}^{\infty} e^{l\beta} 2^l t^l \\ &= \frac{1}{2} \left( 1 + \frac{1}{1 - 2e^{\beta} t} \right). \end{aligned} \tag{5}$$

The GPF for the starting saw is quite similar except for the fact that its length $2l - 1$ ($l \geq 1$) is odd and as a result $\tilde{Z}_0^{start} = 0$.

$$\begin{aligned} G_{start}(t) &= \sum_{l=1}^{\infty} e^{(l-1)\beta} 2^{l-1} t^l \\ &= \frac{t}{1 - 2e^{\beta} t} \end{aligned} \tag{6}$$

### 4.2 Loop-type GPFs

Note that we have already isolated all the weight factors in $G_{saw}(t)$ and $G_{start}(t)$. This done, the only problem with the loop-type GPF is asymmetry. The partition function for a canonical ensemble of loops of length $2l$ in the symmetric random walk is just the well-known probability of a first return to the origin at time $2l$ (see any good book on Probability theory) multiplied by $2^{2l}$. The generating function of the latter is $1 - \sqrt{1 - t}$ so the generating function of the former is $1 - \sqrt{1 - 4t}$. Our loops are asymmetric, i.e. only loops above $x = 0$ are allowed, which gives a factor $\frac{1}{2}$. Finally requiring $G_{loop}(0) = 0$, we have

$$G_{loop}(t) = \frac{1}{2} \left( 1 - \sqrt{1 - 4t} \right). \tag{7}$$

Similarly the ending-type GPF is connected with the generating function $\frac{1}{\sqrt{1-t}}$ of another well known class of simple walk probabilities, namely the probabilities of no return to the origin. What should be taken into consideration here is that an ending-type walk has an odd length $2l + 1$ and that the last step (if $l \geq 1$, see discussion in 4.3) gives a factor 2 into the partition function and thus compensate for the asymmetry factor $\frac{1}{2}$. If there is no ending ($l = 0$) the last step is still there and we require $G_{end}(0) = 2$, which yields

$$G_{end}(t) = 1 + \frac{1}{\sqrt{1 - 4t}}. \tag{8}$$

### 4.3 Decomposition

We have chosen the above GPS's values at $t=0$ the way that allows us to decompose $G_Z(t)$ as follows:

$$G_Z(t) = G_{start}(1 + G_{loop}G_{saw} + (G_{loop}G_{saw})^2 + (G_{loop}G_{saw})^3 + \cdots)G_{end}, \tag{9}$$

where 1 in the brackets accounts for all walks without any loop, $G_{loop}G_{saw}$ – for all walks with a single loop and so on. Using (6), (7), (5) and (8) we can compute

$$G_Z(t) = \frac{2t}{1 - 3e^\beta t + \sqrt{1-4t}(1 - e^\beta t)}\left(1 + \frac{1}{\sqrt{1-4t}}\right). \tag{10}$$

It should be admitted that (10) in a way ignores boundary effects. One could notice that obtaining (8) we supposed that the final position of a walk lies outside the interval $[0, 2]$, since if it does not the factor of the last step into partition function will not be 2 but rather $1 + e^\beta$ or $2e^\beta$ depending on whether the walk ends in a loop or a saw. The exact formula for $G_Z(t)$ is still possible to compute and we just state it here for the sake of completeness:

$$G_Z(t) = \frac{2e^\beta t}{1-2e^\beta t} + \frac{1}{1 - 3e^\beta t + \sqrt{1-4t}(1-e^\beta t)}\left(\frac{1}{\sqrt{1-4t}} - 1\right)\left(2t + \frac{\sqrt{1-4t}(e^\beta + 1 - 2e^\beta t)}{1-2e^\beta t}\right). \tag{11}$$

But since it gives the same asymptotics as (10) (for example, the singularity $t = \frac{1}{2e^\beta}$ is always farther from 0 than the other singularities of both (10) and (11) ) being much more complicated, in the following we use (10).

At this point we can already compute $< m >_T$ for some relatively large $n$. The GPF $G_Z(t)$ may be expanded in Taylor series, the coefficients of which and the coefficients of (3) coincide:

$$Z_n = \frac{1}{n!}G_Z^{(n)}(0).$$

Then (2) reads as

$$< m >_T = \frac{d}{d\beta}\ln G_Z^{(n)}(0). \tag{12}$$

*Maple* can analytically compute $< m >_T$ using (10) and (12) for up to $n \cong 20$ and the corresponding curves for $n = 5, 10$ and 20 are depicted in Figure 3 with thin solid lines.

## 5 Asymptotics

It is quite easy to find singularities of the expression (10) for $G_Z(t)$. For $e^\beta < \frac{4}{3}$ we have a single singularity in the complex $t$-plane: $t = t_0 = \frac{1}{4}$ of the form $G_Z(t) \sim \frac{1}{\sqrt{t_0 - t}}$. For $e^\beta > \frac{4}{3}$ there is $t_0$ and

$$t_1 = -1 + \frac{1 + \sqrt{e^{2\beta} - e^\beta}}{e^\beta} \tag{13}$$

(which is always closer to the origin than $t_0$) of the form $G_Z(t) \sim \frac{1}{t_1 - t}$. If $e^\beta = \frac{4}{3}T$, $t_1$ and $t_0$ coincide but the singularity is still a pole $G_Z(t) \sim \frac{1}{t_0 - t}$. Note that $G_Z(t)$ may be analytically continued on $\mathbb{C}\setminus[\min(t_0, t_1), \infty)$. It enables us to employ *Singularity analysis* [P. Flajolet and A. Odlyzko. Singularity analysis of generating functions. *SIAM Journal on Discrete Mathematics 3*, 2:216-240, 1990] to derive the asymptotics of $Z_n$ for $n \gg 1$, which using (3) yields:

- for $e^\beta < \frac{4}{3}$:

$$Z_n \simeq \frac{1}{\sqrt{\pi n}}\frac{F(t_0)}{t_0^{n+\frac{1}{2}}}, \tag{14}$$

where $F(t) = G_Z(t)\sqrt{t_0 - t}$;

- for $e^\beta > \frac{4}{3}$:

$$Z_n \simeq \frac{F(t_1)}{t_1^{n+1}}, \tag{15}$$

where $F(t) = G_Z(t)(t_{1-}t)$;

- for $e^\beta = \frac{4}{3}$:

$$Z_n \simeq \frac{F(t_0)}{t_0^{n+1}}, \tag{16}$$

where $F(t) = G_Z(t)(t_{0-}t)$.

- In general, *Singularity analysis* gives asymptotic Taylor coefficients for functions of the form $H(t) = \frac{f(t)}{(t_0-t)^\alpha}$, where $f(t)$ is supposed to be 'good enough':

$$\frac{1}{n!}H^{(n)}(0) \simeq \frac{n^{\alpha-1}}{\Gamma(\alpha)}\frac{f(t_0)}{t_0^{n+\alpha}}. \tag{17}$$

### 5.1 $e^\beta > \frac{4}{3}$

In this case $F(t_1)$ happens to be quite complicated but luckily we can do without it if we just want to compute the asymptotic of $< m >_T$ for $n \gg 1$. Using (2),(15) and (13) and keeping only the leading term we have

$$\begin{aligned} < \quad m >_T &\simeq \frac{d}{d\beta}\left(\ln F(t_1) - (n+1)\ln t_1\right) \\ \simeq \quad -n\frac{d}{d\beta}\ln t_1 &= \frac{n}{2}\frac{e^{-\beta}(2\sqrt{1-e^{-\beta}}-1)}{\sqrt{1-e^{-\beta}}(e^{-\beta}+\sqrt{1-e^{-\beta}}-1)}, \end{aligned} \tag{18}$$

or for the mean number of returns to the wall per step

$$\frac{< m >_T}{n} \simeq \frac{1}{2}\frac{e^{-\beta}(2\sqrt{1-e^{-\beta}}-1)}{\sqrt{1-e^{-\beta}}(e^{-\beta}+\sqrt{1-e^{-\beta}}-1)}. \tag{19}$$

As the temperature ($T = \frac{U}{\beta}$) decreases, $\frac{<m>_T}{n}$ asymptotically approaches 1.(see Figure 3). This asymptotic apparently does not work at $\beta = \ln\frac{4}{3}$ but for any positive $\varepsilon$ it works for $\beta > \ln\frac{4}{3} + \varepsilon$ for all $n$ starting from some $N_\varepsilon$.

Similar procedure may be applied to calculate the heat capacity

$$c = \beta^2\frac{d^2 \ln Z_n}{d\beta^2} = \beta^2\frac{d < m >_T}{d\beta}. \tag{20}$$

For the heat capacity per step using (18) we have

$$\frac{c}{n} \simeq -\beta^2\frac{d^2\ln t_1}{d\beta^2}. \tag{21}$$

### 5.2 $e^{\beta} < \frac{4}{3}$

Formula (14), where

$$F(t_0) = \frac{1}{4 - 3e^{\beta}},$$

and (2) yield

$$< m >_T \simeq \frac{3e^{\beta}}{4 - 3e^{\beta}} \tag{22}$$

and

$$c \simeq \beta^2 \frac{12e^{\beta}}{(4 - 3e^{\beta})^2}. \tag{23}$$

Note that for $V = 0$ we have $< m >= 3$.

### 5.3 $e^{\beta} = \frac{4}{3}$

This case is aggravated by the fact that we cannot compute the derivative of $Z_n$ with respect to $\beta$. Note, instead, that

$$\begin{aligned} < \quad m >_T = \frac{\frac{d}{d\beta} Z_n}{Z_n} = \frac{\frac{d}{d\beta} G_Z^{(n)}(0)}{G_Z^{(n)}(0)} \\ = \frac{(\frac{d}{d\beta} G_Z)^{(n)}(0)}{G_Z^{(n)}(0)} \end{aligned} \tag{24}$$

and

$$\begin{aligned} c &= \beta^2 \frac{d}{d\beta} \frac{(\frac{d}{d\beta} G_Z)^{(n)}(0)}{G_Z^{(n)}(0)} = \beta^2 \left( \frac{(\frac{d^2}{d\beta^2} G_Z)^{(n)}(0)}{G_Z^{(n)}(0)} - \frac{((\frac{d}{d\beta} G_Z)^{(n)}(0))^2}{(G_Z^{(n)}(0))^2} \right) \\ &= \beta^2 \left( \frac{(\frac{d^2}{d\beta^2} G_Z)^{(n)}(0)}{G_Z^{(n)}(0)} - < m >_T^2 \right). \end{aligned} \tag{25}$$

The $n \gg 1$ asymptotics (17) and the expression (10) for $G_Z$ lead to the following results:

$$< m >_T \simeq 3\sqrt{\frac{n}{\pi}}, \tag{26}$$

$$\frac{c}{n} \simeq \frac{9(\pi - 2)}{2\pi} (\ln \frac{4}{3})^2. \tag{27}$$

One interesting feature of (26) is that it differs from $< m >$ for the simple symmetric $1D$ walk by a factor $\frac{3}{2}$. This is due to the fact that we do not have the symmetric walk here but rather the $\mathbb{Z}$ walk weighted at $x = 1$ by the factor $\frac{4}{3}$ and at $x = 0$ by $\frac{1}{2}$.

# 6 Discussion

Let us now discuss what happens at $e^{\beta} = \frac{4}{3}$ in the limit $n \to \infty$. We have already mentioned that we expect our two asymptotic branches to work very close to $e^{\beta} = \frac{4}{3}$ for large enough $n$. This means that for any small positive $\varepsilon$ we can use (21) and (23) to calculate the limits of $\frac{c}{n}$ at $\beta = (\ln \frac{4}{3} + \varepsilon)$ and $(\ln \frac{4}{3} - \varepsilon)$ respectively. Thus we have

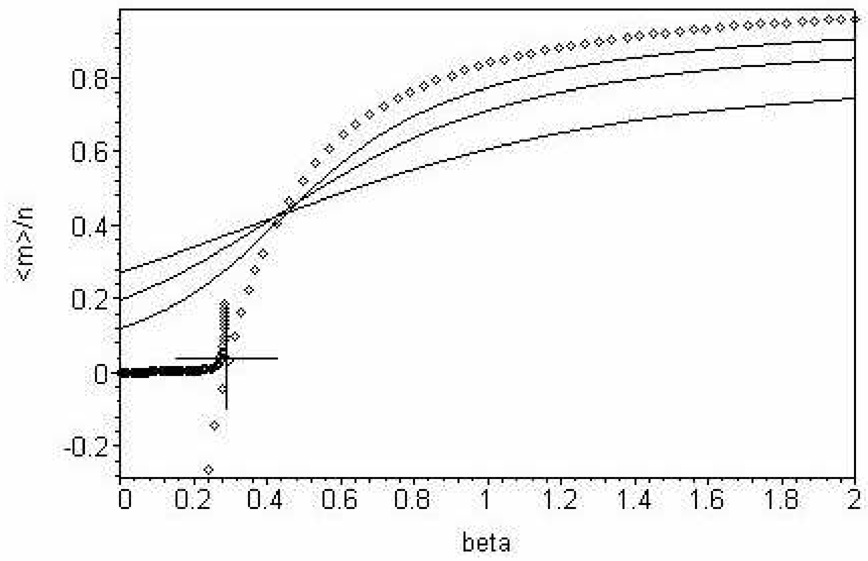


Figure 1: The mean number of returns to the wall per step $\frac{<m>_T}{n}$ as a function of $\beta$. With points the two asymptotic branches (18) and (22) are depicted for $n = 2000$. They should be glued together at the asymptotic (26) (cross). The thin lines are Maple generated analytical solutions for $n = 5, 10, 20$ (the closest to the asymptotic branches is $n = 20$ and so on).

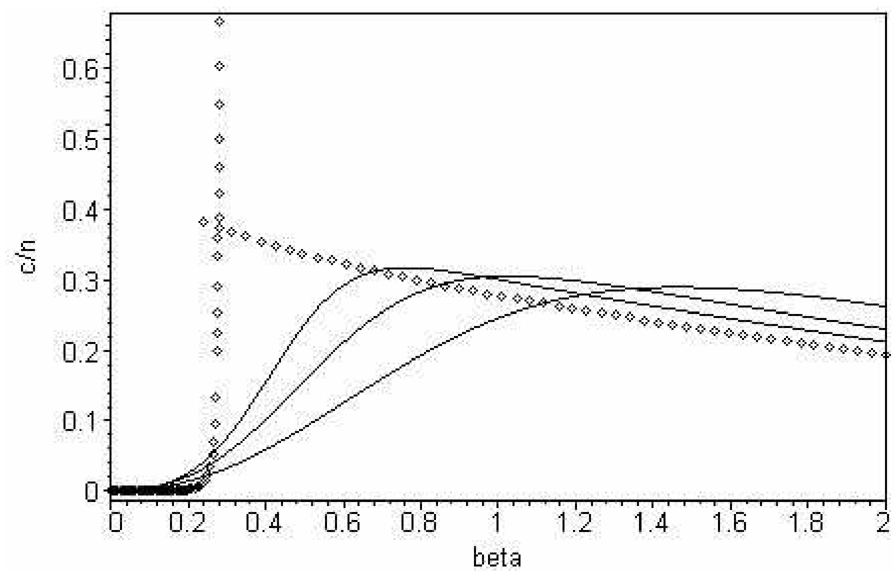


Figure 2: The heat capacity per step $\frac{c}{n}$ as a function of $\beta$. With points the two asymptotic branches (21) and (23) are depicted for $n = 2000$. The thin lines are Maple generated analytical solutions for $n = 5, 10, 20$ (the closest to the asymptotic branches is $n = 20$ and so on).

$$\lim_{n\to\infty} \frac{c}{n} = 0$$

for $\beta = \ln \frac{4}{3} - \varepsilon$ and

$$\lim_{n\to\infty} \frac{c}{n} \approx 0.372 \tag{28}$$

for $\beta = \ln \frac{4}{3} + \varepsilon$.

At the same time (27) gives $\frac{c}{n} \approx 0.135$ exactly at $\beta = \ln \frac{4}{3}$. This shows that at $\beta = \ln \frac{4}{3}$ we have a transition of second order with the jump of $\frac{c}{n}$ given by (28).