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Topological properties of a two-dimensional polymer chain in the lattice of obstacles

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Abstract. In this work a new method of calculating the topological properties of a polymer chain in the lattice of obstacles on the plane is considered in detail. It is shown that, by applying the method of conformal transformations, it is possible to reduce the problem of calculation of the partition function of the polymer chain in a given topological state with respect to the lattice of obstacles to a much more simple problem of the calculation of the Green function of a free random walk without any topological restrictions on a Riemann surface.

1. Introduction

It is well known that polymer chains in their motion cannot cross each other without chain rupture. The restrictions connected with this property are called topological restrictions. The problem of describing the topological properties of polymer systems on the microscopic level was first formulated in the work by Edwards (1967), where the problem of calculating the polymer chain partition function in the presence of an uncrossable infinite line was solved completely. As was shown by Edwards, this problem is mathematically identical to the problem of the motion of a charged particle in a magnetic field and can be formulated in terms of the path integral method, which is well known in field theory. It was this latter circumstance that stimulated many scientists to work in this field, although it is noteworthy that some other (no less interesting) methods were developed by Prager and Frisch (1967) and by Saito and Chen (1973). In the papers by Brereton and Shah (1980), Tanaka (1982) and Elderfield (1982) the ideas of Edwards were developed to take into account the effects of excluded volume and to construct the gauge-invariant theory of topological restrictions using the Gauss linking number as a topological invariant, but real difficulties were connected with another problem: in concentrated polymer solutions and melts one must take into consideration the topological interactions of a given polymer chain with many neighbours (and not only with one chain). The use of the Gauss invariant in such a situation is not correct because the value of this invariant is known to be equal for topologically different conformations of polymer chains (this fact was first shown by Vologodskii *et al* (1974)). Thus, the microscopic theory of topological interactions came to the problem of the construction of full enough topological invariant which could be used for the safe identification of different topological states in the ensemble of the polymer chains. One of the possible solutions was suggested in the works by Vologodskii *et al* (1974) and Frank-Kamenetskii *et al* (1975), where the special algorithm for the computer analysis of topologically different conformations of the polymer chain was elaborated.

Another approach to the problem of the description of the properties of concentrated polymer solutions and melts where the topological restrictions play a significant role was suggested by de Gennes (1971). The 'polymer chain in a tube' model proposed in this work and the following developments of the method by Doi and Edwards (1978) allowed one to describe dynamical properties of concentrated polymer solutions and melts without the detailed microscopic account for the entanglement effects. Thus, the basic advantages of this model with respect to the microscopic theory were the clear geometrical image and relative simplicity of the mathematical apparatus used.

Recently in the investigation of equilibrium and dynamical properties of concentrated polymer solutions and melts, another model—the 'polymer chain in an array of obstacles' model—has become more and more popular. In my opinion this is due to the fact that, on the one hand, this model is still geometrically simple and, on the other hand, in the framework of this model it is possible to take into account the effects of entanglements in detail. The advantages of this model with respect to the 'polymer chain in a tube' model are most clearly manifested in the investigations of the properties of ring polymer chains in concentrated solutions and melts because in this case the 'polymer chain in a tube' model cannot be applied. Different aspects of the statistical properties of a polymer chain in the array of obstacles were investigated by Helfand and Pearson (1983), Rubinstein and Helfand (1985), Khokhlov and Nechaev (1985), Olvera de la Cruz *et al* (1986), Ternovskii and Khokhlov (1986), Cates and Deutsch (1986), Rubinstein (1986) and Nechaev *et al* (1987). As a rule, in these papers the discrete variant of the model was considered—the polymer chain was represented as a random walk on a lattice; in the centres of some of the cells of this lattice the 'uncrossable for the chain' obstacles were placed.

In this paper the continual consideration of the two-dimensional variant of the problem described above is proposed. The aim of this work is to develop in detail the method of conformal transformations, the basic ideas of which were briefly described in 1985 in the paper by Khokhlov and Nechaev. The method proposed allows us to unite the consideration of this problem with the approach by Edwards. This gives the possibility of investigating the region of applicability of the latter approach and to find the way to the analytical construction of the full topological invariant for the chain in the lattice of obstacles.

The contents of the paper are as follows: § 2 will be devoted to the consideration of statistical properties of the polymer chain in a regular lattice of obstacles on the plane. It will be shown that, with the use of quite simple geometrical ideas, this problem can be reformulated in terms of a free motion on a Riemann surface without any topological restrictions. The case of the dense lattice ($c \ll L$, where c is the spacing of the lattice and L is the contour length of the chain) will be considered in § 3, where the initial problem will be reduced to the calculation of the Green function of a free random walk on the Lobachevsky plane (the Riemann surface of constant negative curvature). In the appendix the case $c \gg L$ (the rare lattice of obstacles) will be analysed and the partition function obtained will be compared with that calculated by Edwards for the interaction of a polymer chain with a single obstacle on the plane.

2. Polymer chain in the lattice of obstacles: a method of conformal transformations

Let us consider the regular lattice of obstacles on the plane z (see figure 1). Without the loss of generality for simplicity I shall consider the lattice with elementary cell in

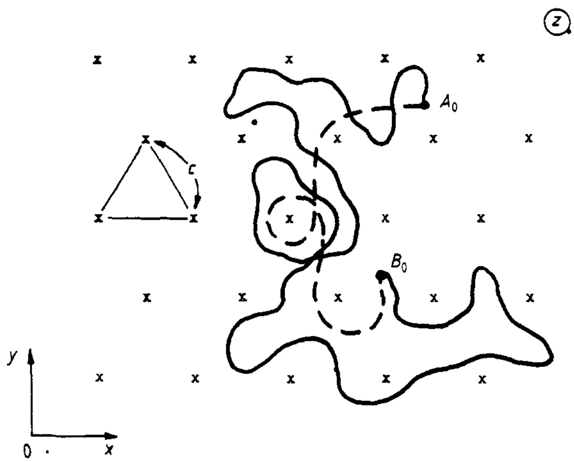

Figure 1. Polymer chain in the lattice of obstacles. The primitive path is shown by a dotted line.

the form of an equilateral triangle with the length of side equal to c. Let us formulate the problem of calculation of the partition function P of the polymer chain of length L and effective segment a, which is placed on the plane z. If the chain has a fixed starting point (A_0) and the end (B_0), in the course of the chain motion (without crossing the edges of the lattice) only these conformations will be available for the chain, which can be transformed into another conformation continuously (without rupture of the chain). These conformations belong to the class of topologically equivalent ones.

The important notion connected with the chain conformation in the lattice of obstacles is the concept of 'primitive path'. A primitive path can be obtained from the actual microscopic trajectory by roughening it up to the scale c (the spacing of the lattice of obstacles) and by deleting all the loops from the rough trajectory, which are not entangled with the obstacles. The configuration of the primitive path determines completely the topological state of the chain and plays the role of full topological invariant for the chain with fixed ends. A more exact definition of the 'primitive path' will be presented at the end of this section.

The main idea of the method used for the calculation of the partition function of the chain in the lattice of obstacles P is as follows: let us suppose that the plane with the regular lattice of obstacles $z(x, y)$ is complex (i.e. each point z of the plane corresponds to a complex number $x+\mathrm{i}y$) and let us find the conformal transformation $z(\tilde{\zeta})$ of this plane to the region $\tilde{\zeta}(\tilde{\xi}, \tilde{\eta})$ such that all obstacles transfer to the boundary of the $\tilde{\zeta}$ region and the internal domain of the $\tilde{\zeta}$ region is free of obstacles. The random walk on the initial z plane transforms under this transformation on some random walk in the $\tilde{\zeta}$ region.

To construct a function $z(\tilde{\zeta})$ it is necessary to find a conformal transformation of the elementary cell of the lattice of obstacles—the triangle ABC of the z plane—to the circular zero-angled triangle $\tilde{A}\tilde{B}\tilde{C}$ of the $\tilde{\zeta}$ plane†. Such a transformation will be performed in two steps.

First let us consider the auxiliary conformal transformation $z(w)$, which transfers the triangle ABC of the z plane to the upper half-plane $\mathrm{Im}\, w > 0$ of the w plane. Let

† For the sake of brevity I also denote the complex plane where the $\tilde{\zeta}$ region is placed by the symbol $\tilde{\zeta}$.

us determine the following correspondence of points: $A \to \tilde{A}$, $B \to \tilde{B}$, $C \to \tilde{C}$ (see figure 2(*b*)). It is obvious that the lower half-plane $\operatorname{Im} w < 0$ corresponds to the triangle ABC' of the z plane. It is easy to be convinced that the non-closed path $O_1 \to O \to O_2$ on the z plane corresponds to the closed path $\tilde{O}_1 \to \tilde{O} \to \tilde{O}_1$ which surrounds point $\tilde{B}$ on the w plane (figure 2(*a*, *b*)). In detail the problem of constructing the Riemann surface for such a transformation $z(w)$ is clarified in a book by Hurwitz and Kourant (1964). The transformation $z(w)$ is defined by the Cristoffel–Schwartz integral:

$$z(w) = \frac{c}{B(\frac{1}{3}, \frac{1}{3})} \int_0^w \frac{d\tilde{w}}{\tilde{w}^{2/3}(1-\tilde{w})^{2/3}} \tag{2.1}$$

where $B(\frac{1}{3}, \frac{1}{3})$ is a beta function. Correspondence of points under transformation (2.1) is as follows:

$$\begin{aligned} &A(z=0) \to \tilde{A}(w=0) \\ &B(z=c) \to \tilde{B}(w=1) \\ &C(z=c\exp(-\mathrm{i}\tfrac{2}{3}\pi)) \to \tilde{C}(w=\infty). \end{aligned} \tag{2.2}$$

Now let us construct the transformation of the upper half-plane $\operatorname{Im} w > 0$ to the circular zero-angled triangle of the $\tilde{\zeta}$ plane. Such a transformation is realised by means of automorphic functions (see, for example, Hurwitz and Kourant (1964) and Golubev (1950)). The differential equation for the $w(\tilde{\zeta})$ function has the form:

$$-\frac{1}{(w'(\tilde{\zeta}))^2}\{w(\tilde{\zeta})\} = \frac{1}{2}\frac{w^2-w+1}{w^2(w-1)^2} \tag{2.3}$$

where $\{w(\tilde{\zeta})\}$ is the so-called Schwartz derivative

$$\{w(\tilde{\zeta})\} = \frac{w'''(\tilde{\zeta})}{w'(\tilde{\zeta})} - \frac{3}{2}\left(\frac{w''(\tilde{\zeta})}{w'(\tilde{\zeta})}\right)^2. \tag{2.4}$$

Equation (2.3) has a solution

$$w(\tilde{\zeta}) = k^2(\tilde{\zeta}) = \frac{\theta_2^4(0|\gamma\, e^{i\pi\tilde{\zeta}})}{\theta_3^4(0|e^{i\pi\tilde{\zeta}})} \tag{2.5}$$

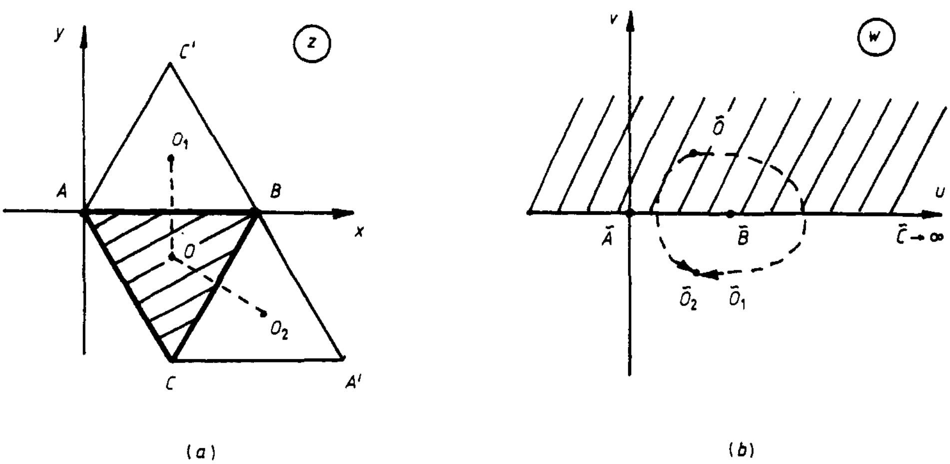

Figure 2. (*a*) Triangles ABC' and $A'BC$ are obtained from the initial triangle ABC by means of reflection with respect to the sides AB and BC. (*b*) The conformal transformation of the triangle ABC to the upper half-plane $\operatorname{Im} w > 0$.

where $k^2(\tilde{\zeta})$ is the modular function, expressed as a ratio of the main periods of the elliptic integral and θ_2, θ_3 are elliptic Jacoby functions (Chandrassekharan 1985). The correspondence of points under transformation (2.5) is as follows:

$$\begin{aligned} &\tilde{A}(w=0) \to \tilde{\tilde{A}}(\tilde{\zeta}=\infty) \\ &\tilde{B}(w=1) \to \tilde{\tilde{B}}(\tilde{\zeta}=0) \\ &\tilde{C}(w=\infty) \to \tilde{\tilde{C}}(\tilde{\zeta}=-1). \end{aligned} \tag{2.6}$$

Thus, combining equations (2.1) and (2.5), the composite transformation $z(\tilde{\zeta})$ transferring the initial triangle ABC of the z plane to the zero-angled circular triangle ABC of the $\tilde{\zeta}$ plane has the form

$$\begin{aligned} z(\tilde{\zeta}) &= \frac{c}{B(\frac{1}{3},\frac{1}{3})}\int_0^{k^2(\tilde{\zeta})} \frac{\mathrm{d}\tilde{w}}{\tilde{w}^{2/3}(1-\tilde{w})^{2/3}} \\ k^2(\tilde{\zeta}) &= \frac{\theta_2^4(0|\mathrm{e}^{\mathrm{i}\pi\tilde{\zeta}})}{\theta_3^4(0|\mathrm{e}^{\mathrm{i}\pi\tilde{\zeta}})}. \end{aligned} \tag{2.7}$$

The correspondence of fundamental domains under transformation (2.7) is shown in figure 3.

The transformation (2.7) solves the problem put above: the whole z plane with the lattice of obstacles transforms to the half-plane $\mathrm{Im}\,\tilde{\zeta}>0$ and all the obstacles transfer to the boundary $\tilde{\eta}=0$ of the region $\mathrm{Im}\,\tilde{\zeta}>0$. Thus, the internal domain $\mathrm{Im}\,\tilde{\zeta}>0$ is free of topological restrictions. This property can be checked in a geometrical way, reflecting the initial triangle ABC on the z plane with respect to its own sides and performing the same transformation with respect to the sides of the triangle $\tilde{\tilde{A}}\tilde{\tilde{B}}\tilde{\tilde{C}}$ on the $\tilde{\zeta}$ plane. Considering arbitrary trial contours (1) and (2) on the z plane and its images $(\tilde{1})$ and $(\tilde{2})$ on the $\tilde{\zeta}$ plane (figure 3(a, b)), it is easy to check the fact that the closed contour (1) which arranged the obstacle (the point A) corresponds to the unclosed contour $(\tilde{1})$, but the closed contour (2) which is not entangled with any of obstacles corresponds to the closed contour $(\tilde{2})$.

Generally one can say that the $\tilde{\zeta}$ region $\mathrm{Im}\,\tilde{\zeta}>0$ is 'expanded' with respect to the initial z plane because the coordinates of endpoints of an arbitrary trajectory in the $\tilde{\zeta}$ region $\mathrm{Im}\,\tilde{\zeta}>0$ determine:

(a) the corresponding coordinates of endpoints on the z plane;

(b) the topological state of a given trajectory on the z plane.

In the $\tilde{\zeta}$ region the theorem of conformal invariance of Brownian motion is valid and therefore in the $\tilde{\zeta}$ region $\mathrm{Im}\,\tilde{\zeta}>0$ a stochastic process corresponding to the initial random motion on the z plane will be obtained as well (Ito and McKean 1965, McKean 1969). Under the conformal transformation the Laplace operator transforms in the following way:

$$\Delta_z = \frac{1}{|z'(\tilde{\zeta})|^2}\Delta_{\tilde{\zeta}} \tag{2.8}$$

where

$$\Delta_z = \frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2} \qquad \Delta_{\tilde{\zeta}} = \frac{\partial^2}{\partial \tilde{\xi}^2}+\frac{\partial^2}{\partial \tilde{\eta}^2} \qquad z'(\tilde{\zeta}) = \frac{\mathrm{d}z}{\mathrm{d}\tilde{\zeta}}.$$

Taking into account the fact that the $\tilde{\zeta}$ region is free of topological restrictions (i.e. obstacles) the equation for partition function P in the $\tilde{\zeta}$ region can be written in the

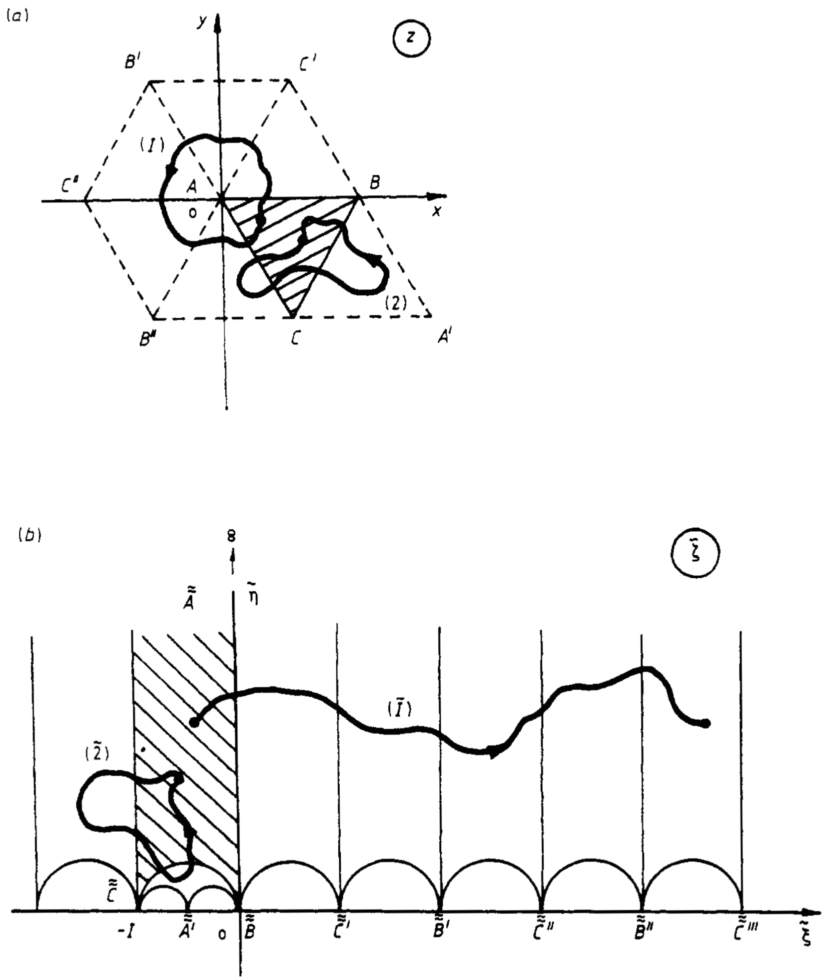

Figure 3. The correspondence of fundamental domains under conformal transformation (2.7).

usual form:

$$\tfrac{1}{4}a\Delta_{\tilde{\zeta}}P(\tilde{\zeta}, L) = \left|\frac{dz}{d\tilde{\zeta}}\right|^2 \frac{\partial}{\partial L} P(\tilde{\zeta}, L). \tag{2.9}$$

The derivative $dz/d\tilde{\zeta}$ can be obtained from (2.7) and its final expression is

$$\left|\frac{dz}{d\tilde{\zeta}}\right|^2 = c^2\beta^2|\theta_1'(0|e^{i\pi\tilde{\zeta}})|^{8/3} \tag{2.10}$$

where

$$\beta = \frac{1}{\pi^{1/3}B(\frac{1}{3}, \frac{1}{3})}$$

and

$$\theta_1'(0|\ldots) \equiv \left.\frac{d\theta_1(\lambda|\ldots)}{d\lambda}\right|_{\lambda=0} = \pi\theta_0(0|\ldots)\theta_2(0|\ldots)\theta_3(0|\ldots).$$

Substituting equation (2.10) into (2.9) I obtain the equation for partition function $P(\tilde{\zeta}, \tilde{\zeta}_0, L)$, determining the probability of the fact that the polymer chain ends are placed in points $\tilde{\zeta}$ and $\tilde{\zeta}_0$ as

$$\tfrac{1}{4}a\Delta_{\tilde{\zeta}}P(\tilde{\zeta}, \tilde{\zeta}_0, L) = \beta^2|\theta_1'(0|\mathrm{e}^{\mathrm{i}\pi\tilde{\zeta}})|^{8/3}\frac{\partial}{\partial L}P(\tilde{\zeta}, \tilde{\zeta}_0, L). \tag{2.11}$$

The primitive path can be defined now as the image of the segment $|\tilde{\zeta} - \tilde{\zeta}_0|$ after transformation of (2.7) to the initial z plane. In particular, the partition function $P(\tilde{\zeta}_0, \tilde{\zeta}_0, L)$ where the value $\tilde{\zeta}_0$ is connected with the known transformation (2.7) with the value z_0 determines the probability of the fact that the polymer chain, in which both ends are placed at the point z_0 has a zero primitive path (i.e. the polymer chain is not entangled with either of the obstacles of the lattice).

3. Long polymer chain in the lattice of obstacles: random motion on the Lobachevsky plane

Let us turn to (2.11) and to investigate a behaviour of a function $P(\tilde{\zeta}, \tilde{\zeta}_0, L)$ in the limit $c \ll L$ let us use the symmetry properties of the problem considered.

First of all let us perform the conformal transformation, which transforms the upper half-plane $\mathrm{Im}\,\tilde{\zeta} > 0$ to the interior of a circle $|\zeta| < 1$ on the plane ζ (see figure 4):

$$\tilde{\zeta}(\zeta) = \mathrm{e}^{-\mathrm{i}\pi/3}\frac{\zeta - \mathrm{e}^{\mathrm{i}2\pi/3}}{\zeta - 1} - 1. \tag{3.1}$$

The correspondence of points $\tilde{A}, \tilde{B}, \tilde{C}$ on the $\tilde{\zeta}$ plane and its images A, B, C on the ζ plane is as follows:

$$\begin{aligned} &\tilde{A}(\tilde{\zeta} = \infty) \to A(\zeta = 1) \\ &\tilde{B}(\tilde{\zeta} = 0) \to B(\zeta = \exp(-\mathrm{i}2\pi/3)) \\ &\tilde{C}(\tilde{\zeta} = -1) \to C(\zeta = \exp(\mathrm{i}2\pi/3)). \end{aligned} \tag{3.2}$$

Figure 4 shows the correspondence of fundamental domains under transformation (3.1). Comparing figures 4(*b*) and (*c*) it is easy to understand that the modular function shown in figure 4(*b*) has the form of a Cayley tree (figure 4(*c*)). This circumstance was briefly noted by Khokhlov and Nechaev (1985).

Let us consider the polymer chain in an open circle $|\zeta| < 1$. If the starting point of the chain is placed at the origin $\zeta = 0$ and its end placed at some arbitrary point ζ_{end} then the coordinates $\zeta_{\mathrm{end}}(\xi_{\mathrm{end}}, \eta_{\mathrm{end}})$ determine: (*a*) the coordinates of the endpoint of the chain on the initial z plane; (*b*) the configuration of the primitive path ($|\zeta_{\mathrm{end}}|$ is the length of the primitive path in coordinates ξ, η, connected with the known transformations (2.7) and (3.1) with coordinates x, y). Rewriting equation (2.9) in ξ, η coordinates, the following equation is valid:

$$\tfrac{1}{4}a\Delta_{\zeta}P(\zeta, L) = Z\frac{\partial}{\partial L}P(\zeta, L) \tag{3.3}$$

where

$$Z \equiv \left|\frac{\mathrm{d}z}{\mathrm{d}\zeta}\right|^2 = \frac{3c^2\beta^2}{|1-\zeta|^4}\left|\theta_1'\left[0\middle|\exp\left(\mathrm{i}\pi\exp(-\mathrm{i}\pi/3)\frac{\zeta - \exp(\mathrm{i}2\pi/3)}{\zeta - 1}\right)\right]\right|^{8/3} \tag{3.4}$$

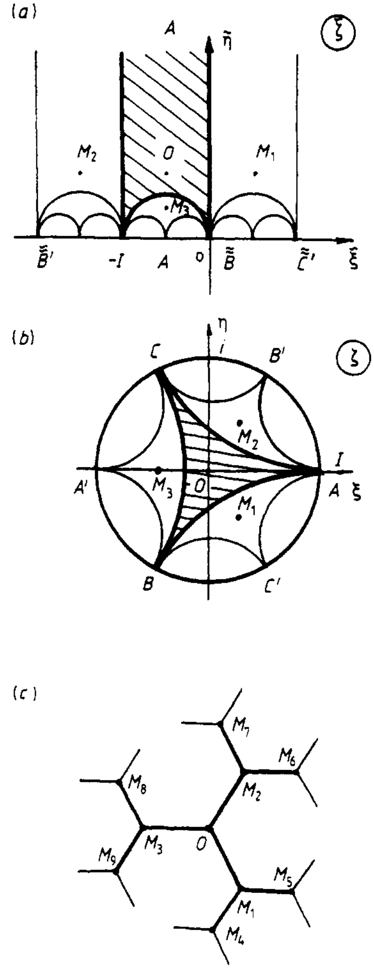

Figure 4. The illustration of the transformation $\tilde{\zeta} \to \zeta$ (see (3.1)); on figure 4(b) is shown the elliptic modular function, which topological structure has a form of a Cayley tree (figure 4(c)).

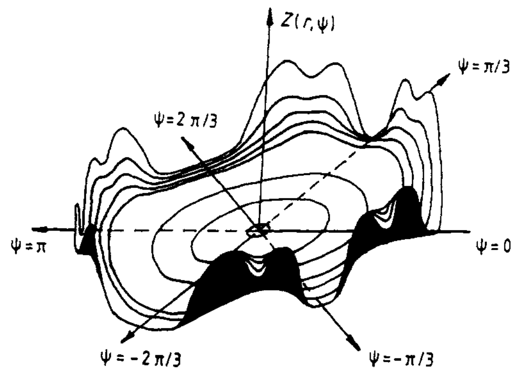

Figure 5. The relief of the function $Z(r, \psi)$ (see (3.4)).

The geometrical structure of the surface $Z(r, \psi)$ (r and ψ are the polar coordinates in the circle $|\zeta|<1$) is presented in figure 5. Equation (3.4) can be replaced by an essentially more simple relation, which allows us to solve (3.3) exactly. One must neglect the changing of the value $Z(r, \psi)$ inside the circular triangle (see figure 4(b)) and replace the function $Z(r, \psi)$ by the value in the centre of the circle triangle considered, Z_m†. After rather complicated transformations using the properties of Jacoby θ functions (Chandrassekharan 1985) I obtain the approximation

$$Z_m \equiv \left|\frac{\mathrm{d}z}{\mathrm{d}\zeta}\right|^2_{\zeta=\zeta_m} = 3c^2\beta^2 \left|\theta_1'\left\{0 \left| \exp\left[\mathrm{i}\pi\left(\frac{1}{2}+\mathrm{i}\frac{\sqrt{3}}{2}\right)\right]\right.\right\}\right|^{8/3} \frac{1}{|1-\zeta_m\bar{\zeta}_m|^2} \tag{3.5}$$

where

$$\zeta_m = r_m \exp(\mathrm{i}\psi_m) \qquad \bar{\zeta}_m = r_m \exp(-\mathrm{i}\psi_m).$$

Thus, in the vicinity of the centres of circle triangles equation (3.4) has the form of equation (3.5). In figure 6 the function $Z_m(r)$ is compared to the data of numerical calculation of the function $\langle Z(r)\rangle_\psi$, where $\langle \ldots \rangle_\psi$ means the angle-average of the function $Z(r, \psi)$. In the limit $|\zeta_m| \to 1$ the relative deviation between both curves tends to zero (see figure 6). Therefore when I do not take an interest in the details of a modular figure on scales lower than the spacing of the lattice (i.e. the length of the chain is much greater than the spacing of the lattice $L \gg c$) for calculations, (3.5) instead of (3.4) can be used. It is noteworthy that (3.5) determines the metrics of the Lobachevsky plane (Hurwitz and Kourant 1964, Golubev 1950).

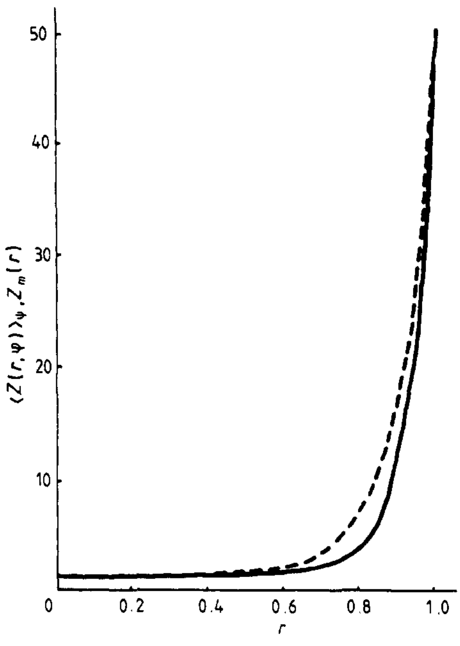

Figure 6. The function $\langle Z(r)\rangle_\psi$ is shown by the full curve and the function $Z_m(r)$ by the broken curve.

† In other words I suppose all the values $Z(r, \psi)$ inside, for example, the triangle $A'BC$ (see figure 4(b)) being approximately equal to the value $Z(r_{m_3}, \psi_{m_3})$ where the point m_3 is the centre of the triangle considered.

If for some problems it is necessary to take into account the detailed metric structure of a modular figure, then (3.3) and (3.4) can be solved numerically.

Substituting (3.5) into (3.3) I obtain the equation describing the random motion on the Lobachevsky plane in the Poincaré model

$$\tfrac{1}{4}a\Delta_{r,\psi}P(r,\psi,L)=\tfrac{3}{2}c^2\beta^2\alpha\frac{1}{(1-r^2)^2}\frac{\partial}{\partial L}P(r,\psi,L) \tag{3.6}$$

where

$$\Delta_{r,\psi}=\frac{1}{2}\frac{\partial}{\partial r}\left(r\frac{\partial}{\partial r}\right)+\frac{1}{r^2}\frac{\partial^2}{\partial\psi^2}\qquad\text{and}\qquad \alpha=\left|\theta_1'\left\{0\left|\exp\left[\mathrm{i}\pi\left(\frac{1}{2}+\mathrm{i}\frac{\sqrt{3}}{2}\right)\right]\right.\right\}\right|^{8/3}.$$

I would pay attention once more to the fact that r—the distance between the chain ends on the Lobachevsky plane—means physically the length of the primitive path expressed in the units of the spacing of the lattice of obstacles.

After transformation to the new variable

$$\mu=\tfrac{1}{2}c\ln[(1+r)/(1-r)]$$

the usual diffusion equation on the surface of constant negative curvature has the form (Karpelevich *et al* 1959, Gerzenstein and Vasiljev 1959, Molchanov 1975)

$$\tfrac{1}{4}a\tilde{\Delta}P(\mu,\psi,L)=\tfrac{3}{2}\beta^2\alpha(\partial/\partial L)P(\mu,\psi,L) \tag{3.7}$$

where $\tilde{\Delta}$ is the Beltrami-Laplace operator

$$\tilde{\Delta}=\frac{1}{(\det g)^{1/2}}\frac{\partial}{\partial x^i}\left((\det g)^{1/2}g^{ik}\frac{\partial}{\partial x_k}\right). \tag{3.8}$$

The metric tensor $\|g^{ik}\|$ has the form

$$\|g^{ik}\|=\left\|\begin{matrix}1 & 0\\ 0 & \dfrac{c^2}{4}\sinh^2\dfrac{2\mu}{c}\end{matrix}\right\|. \tag{3.9}$$

The solution of (3.7) is

$$P(\mu,N)=\frac{\exp[-(\lambda^2/4)N]}{(2\pi a^2N)^{3/2}}\int_{2\mu/c}^{\infty}\frac{x\exp(-x^2/4\lambda^2N)}{(\cosh x-\cosh 2\mu/c)^{1/2}}\,\mathrm{d}x \tag{3.10}$$

where $N=L/a$ and $\lambda^2=2/(3\beta^2\alpha)a^2/c^2$. Considering the limit $\mu/c\gg 1$ it is easy to obtain the relation

$$P(\mu,N)\simeq\frac{1}{4\pi Na^2}\exp\left[-\frac{1}{4\lambda^2N}\left(\lambda^2N+\frac{2\mu}{c}\right)^2\right] \tag{3.11}$$

which corresponds to one obtained earlier in the discrete case (see, for example, Khokhlov and Nechaev (1985))†. The function $P(\mu,N)$ can be used for calculation of any conformational characteristics of polymer chains in a given topological state with respect to the lattice of obstacles. In particular, the probability that the closed polymer chain does not become entangled with either obstacle on the plane is

$$P(\mu=0,N)=\frac{\exp(-\frac{1}{4}\lambda^2N)}{(2\pi a^2N)^{3/2}}\int_0^{\infty}\frac{x\exp(-x^2/4\lambda^2N)}{\sqrt{2}\sinh(x/2)}\,\mathrm{d}x\simeq\frac{\mathrm{erfc}(\frac{1}{2}\lambda\sqrt{N})}{4\pi a^2N} \tag{3.12}$$

† The probability of the fact that the length of the primitive path is equal to μ is $\tilde{P}(\mu,N)=P(\mu,N)\sinh 2\mu/c$. One must compare just this relation to the relation of the paper mentioned above.

(compare this equation with corresponding relations obtained by Helfand and Pearson (1983) and Khokhlov and Nechaev (1985)).

Thus the problem of investigating statistics of a long closed polymer chain in an array of obstacles is reduced to the much more simple problem of investigating effective random motion on the Lobachevsky plane; and the influence of the lattice of obstacles on chain statistics is reduced to the effective changing of metrics of the initial plane.

The case of a short polymer chain $L \ll c$ is considered in the appendix.

4. Conclusion

The method proposed in the present paper allows one to reduce the problem of investigating topological properties of a polymer chain in a regular lattice of obstacles to the study of metric properties of Riemann surfaces, free of obstacles, obtained as a result of conformal transformation from the initial plane. It is obvious that the method proposed does not limit the consideration of the simplest lattice of obstacles and can be generalised to solve more complicated topological problems. Moreover I hope that the application of general geometrical ideas to this branch of the statistical physics of macromolecules is very useful for the construction of the microscopic theory of topological restrictions in concentrated polymer solutions and melts.

Acknowledgments

I am very grateful to Drs A Yu Grosberg and F F Ternovskii for fruitful discussions of the problem; to Drs S A Molchanov, D D Sokolov and V N Tutubalin for elucidation of some mathematical questions; and especially to Dr A R Khokhlov for his interest in this work.

Appendix. A short polymer chain near the obstacle ($L \ll c$)

To investigate a solution of (2.11) in the vicinity of the point $\tilde{\tilde{A}}$ ($\eta_{\tilde{\tilde{A}}} = \mathrm{Im}\,\tilde{\zeta}_{\tilde{\tilde{A}}} = \infty$) (see figure 3($b$)) let us consider the limit $\tilde{\eta} \to \infty$ in (2.10). Presenting Jacobi θ functions in power series the following relation is valid:

$$\theta_1'[0|\exp(\mathrm{i}\pi\tilde{\zeta})] = \pi \sum_{n=-\infty}^{\infty} (-1)^n (2n+1) \exp[\mathrm{i}\pi(n+\tfrac{1}{2})^2 \tilde{\zeta}] \tag{A1}$$

and, therefore,

$$\theta_1'\{0|\exp[\mathrm{i}\pi(\tilde{\xi}+\mathrm{i}\tilde{\eta})]\}|_{\tilde{\eta}\to\infty} \simeq \pi \exp(-\tfrac{1}{4}\pi\tilde{\eta}) \exp\left(\mathrm{i}\frac{\pi}{4}\tilde{\xi}\right). \tag{A2}$$

Substituting (A2) into diffusion equation (2.11) on the $\tilde{\zeta}$ plane I obtain the equation

$$\begin{aligned} &\frac{a}{4}\left(\frac{\partial^2}{\partial\tilde{\xi}^2}+\frac{\partial^2}{\partial\tilde{\eta}^2}\right) P(\tilde{\xi}, \tilde{\eta}, \tilde{\xi}_0, \tilde{\eta}_0, L) \\ &\qquad = \beta^2\pi^2 \exp\left(-\frac{2\pi}{3}\tilde{\eta}\right)\frac{\partial}{\partial L} P(\tilde{\xi}, \tilde{\eta}, \tilde{\xi}_0, \tilde{\eta}_0, L). \end{aligned} \tag{A3}$$

Equation (A3) can be deduced from the initial (2.9) using the conformal reflection $\tilde{\zeta}_1(z)$

$$\tilde{\zeta}_1(z)=\frac{3}{\pi \mathrm{i}}\ln\left(\frac{\mathrm{i}z}{3\beta}\right)\equiv\frac{3}{\pi \mathrm{i}}\ln z+\text{constant}. \tag{A4}$$

In polar coordinates $z=\rho\,\mathrm{e}^{\mathrm{i}\varphi}$ equation (A4) transforms to the system

$$\begin{aligned}\rho&=3\beta\exp\left(-\frac{\pi}{3}\tilde{\eta}\right)\\ \varphi&=\frac{\pi}{3}\tilde{\xi}-\pi.\end{aligned} \tag{A5}$$

A number of turns of the chain n around the obstacle on the z plane plays the role of Gauss topological invariant and is equal to the angle distance $\Delta\varphi=\varphi_{B_0}-\varphi_{A_0}$ (see figure 7). Performing transformation (A5) and taking into account the fact that to one turn to the angle 2π correspond six successive reflections of the triangles with the angles $\pi/3$ (see figure 7(a)) I obtain the final equation in polar coordinates on the z plane:

$$\frac{a}{4}\left[\frac{1}{\rho}\frac{\partial}{\partial\rho}\left(\rho\frac{\partial}{\partial\rho}\right)+\frac{1}{\rho^2}\frac{\partial^2}{\partial\varphi^2}\right]P_0(\rho,\varphi,\rho_0,\varphi_0,L)=\frac{\partial}{\partial L}P_0(\rho,\varphi,\rho_0,\varphi_0,L). \tag{A6}$$

In (A6) $0\leqslant\varphi<2\pi$ and $P_0(\ldots)$ denotes the probability for the chain with fixed ends having an entanglement with the obstacle of order $n=0$ (Saito and Chen 1973). The probabilities of different orders of entanglements are connected among themselves as follows:

$$\begin{aligned}P_0(\rho,\rho_0,\varphi,\varphi_0,L)&\equiv P_0(\rho,\rho_0,\varphi-\varphi_0,L)\\ &=P_1(\rho,\rho_0,\varphi-\varphi_0+2\pi,L)=\ldots\\ &=P_n(\rho,\rho_0,\varphi-\varphi_0+2\pi n,L).\end{aligned} \tag{A7}$$

Equations (A6) and (A7) are solved in the paper by Saito and Chen (1973) and in two dimensions the solution is

$$P_n(\rho,\rho_0,\varphi-\varphi_0,L)$$
$$=\frac{1}{\pi La}\exp\left(-\frac{\rho^2+\rho_0^2}{La}\right)\int_{-\infty}^{\infty}I_{|\nu|}\left(\frac{2\rho\rho_0}{La}\right)\exp\{[2\pi n-(\varphi-\varphi_0)]\,\mathrm{i}\nu\}\,\mathrm{d}\nu. \tag{A8}$$

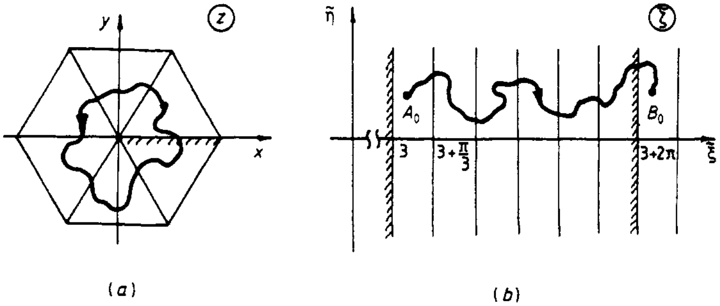

Figure 7. The correspondence of the domains under the transformation (A4).

Thus, in the limit $c \gg L$ only the solitary obstacle interacted with the polymer chain instead of the whole lattice can be considered. Only in this limit the Gauss linking number can be considered as a full topological invariant and can be used for the safe classification of different topological states of the chain.

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