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# A gauge description of topological entanglements in polymers

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**Abstract.** The statistical mechanics of polymer molecules subject to topological constraints is formulated. In particular, the problem of two polymer loops topologically linked is studied in the limit when one of the loops is allowed to fill a macroscopic volume at a finite density. We show that this problem can be recast as a local gauge invariant field theory in the usual limit that the number of components goes to zero. The gauge invariance is a direct consequence of the fact that topological entanglements imposed on the system are conserved.

## 1. Introduction

The statistical mechanics of linear polymer chains have been studied for a long time, and the properties of linear polymer molecules are reasonably well understood (see McKenzie 1976, for a review). In part this has been due to the discovery by de Gennes (1972), des Cloizeaux (1974) and Emery (1975) of the mathematical isomorphism between the polymer problem with excluded volume interactions and a certain classical  $n$ -component field theory (considerably studied in the fields of critical phenomena and elementary particle physics) in the limit  $n \rightarrow 0$ . This present paper is also concerned with identifying the field theoretic problem associated with the statistical properties of ring polymers subject to topological constraints that prevent one ring from penetrating another. From the outset we must distinguish between entanglements as the word is normally used in the polymer literature and topological entanglements which will be the proper subject of this paper. The term 'entanglement constraint' has been used by many authors (see Graessley 1974, for a review) to describe the rather general restrictions on mobility that occur in concentrated solutions and the molten state. The term 'topological entanglements' will be used to describe a topological property existing between different molecules which is necessarily conserved throughout all the configurational changes that the molecule can undergo. As the notion of 'topological entanglements' will occur frequently in this paper, we have simply referred to them as 'entanglements' for the sake of brevity with 'topological' being understood.

In recent years, considerable experimental effort has been directed at these systems. Frisch and Wasserman (1961) (and further references cited therein) have indicated the existence of topologically interlocked polymer rings, commonly known as catenanes in chemical literature, in many polymeric materials.

Wolovsky (1970) and Ben-Efraim *et al* (1970) have demonstrated, by mass spectroscopic analysis, the existence of substantial amounts of catenanes in a certain reaction of cyclododecene.

Wang (1973) has shown that interlocked DNA rings are widely distributed in nature—a fact of some importance in genetics since a DNA catenane cannot finish the replication cycle as the two daughter molecules would be linked with each other.

The statistical properties of entangled polymers are expected to be considerably different from those of linear molecules, as entanglements constitute global constraints on the configurations of molecules even in  $\theta$ -solvents where the excluded volume interaction is absent, leading to a decrease in the configurational entropy and consequently in the free energy of the system, depending on the initial topological state of the system. Therefore, it is necessary to be able to distinguish between the various topological states of the system—i.e. we need an invariant of the system.

Entanglements are specified by topological invariants. Two links which can be transformed into each other by continuous deformations are isotopic; hence they belong to a particular topological classification. A link in one topological class cannot be isotopic to a link in another topological class. Topological entanglements in polymers can occur, either as a consequence of one polymer being linked with another polymer, or as self-knotted configurations—i.e. different parts of the same polymer chain being linked with each other. The various attempts at the formulation of a statistical-mechanical theory of entanglements, incorporating the various types of topological constraints, have been characterised by two fundamentally different approaches. The analytical approach, based on the functional integral model of a polymer chain, and the use of an integral invariant—the Gauss integral—was pioneered by Edwards (1967, 1968) and in the subsequent works of Edwards and his co-workers.

A second approach, based on Monte-Carlo methods, and an invariant from algebraic topology—the so-called Alexander Polynomial—was initiated by Vologodskii *et al* (1974, 1975) and later by des Cloizeaux and Mehta (1979). However, in this paper we shall follow the analytical approach of Edwards, and use field-theoretical methods and the Gauss integral. We shall restrict our discussion to that for closed loops only—as otherwise topological invariants are not, mathematically, well defined. In this approach we shall not consider any self-knotted configurations as no suitable analytical invariants, that can distinguish between various knots, exist. Instead, we shall consider the simplest possible model of entangled polymers—a system of two linked molecules.

In § 2 we give a rigorous definition of linking numbers in terms of the Gauss integral. Then we show that the constraint imposed on the topology by the requirement of the conservation of the linking number leads, naturally, to a set of symmetry transformations which we ultimately exhibit as a local gauge-invariant field theory. This is in contrast to the usual situation in gauge-field theories where the requirement of local gauge invariance leads to topological conservation laws, e.g. the Wilson loop integral described by Wilson (1974) and Banks *et al* (1977).

In § 3 we set up a model for our entangled system of polymer molecules by identifying a single molecule and replacing the rest by one macroscopically long chain which is taken to fill the macroscopic volume occupied by the system. We then study the topological relation of the identified polymer with the 'background' molecule and the restrictions that this will impose on the conformation of the identified polymer. The conformations of both polymers will be described by the random walk model or equivalently by Wiener distributions and we will explicitly show how the functional integration over the configurations of the background chain can be approximately carried out. This leaves us with the partition sum for the identified molecule, which now assumes an additional self-interacting term due to the entanglement constraint.

In § 4 we derive a ‘Lagrangian’ from which the configurational properties of this self-interacting polymer can be calculated, and show that it has the form of an  $n$ -component gauge-field theory Lagrangian in the limit  $n \rightarrow 0$ . This is in contrast to the work of Stone and Thomas (1978) who have obtained a conventional gauge-field theory, isomorphic to scalar quantum electrodynamics, for a system of topologically unconstrained polymer loops interacting via a Biot–Savart type interaction.

## 2. The Gauss integral and gauge invariance

The problem of deciding whether two closed curves are linked or not is given by an integral formula due to Gauss. Let  $C_\alpha, C_\beta$  be two oriented, non-intersecting, closed, differentiable curves of class  $C^1$  in  $E^3$ . If  $C_\alpha$  is the boundary of a compact, oriented two-dimensional manifold  $M$ , then the linking number  $I\{C_\alpha, C_\beta\}$  is defined to be the intersection number of  $M$  and  $C_\beta$ ; hence it is an integer, and is expressed by the Gauss integral, given by Alexandroff and Hopf (1935), as

$$\begin{aligned}
 I_{\alpha\beta} &= I\{C_\alpha, C_\beta\} \\
 &= \frac{1}{4\pi} \oint_{C_\alpha} \oint_{C_\beta} \dot{r}_\alpha(s_\alpha) \times \dot{r}_\beta(s_\beta) \cdot \nabla(1/|r_\alpha - r_\beta|) ds_\alpha ds_\beta
 \end{aligned}
 \tag{2.1}$$

where  $s_\alpha$  is the arc length on the  $C_\alpha$  curve,  $r(s_\alpha)$  a position vector to a point on the curve and  $\dot{r} = dr/ds$ . The linking number remains invariant under an isotopy of the link; hence it is a topological invariant. However, it is only a first-order topological invariant, since for linked configurations, such as the Whitehead link figure 1(d), a non-boundary link, the linking number is zero.

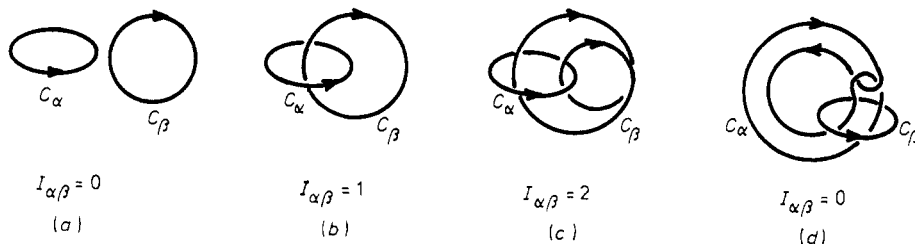


Figure 1.

Higher order link-invariants, such as the Alexander Polynomial, that can distinguish between the configurations of figure 1(a) and 1(d) exist (e.g. Vologodskii *et al* 1974). However, such invariants are group-theoretic in nature, and thus not suitable for the functional integral formalism used in this paper.

In the polymer context, the Gauss integral was first discussed by Delbruck (1962), Edwards (1967) and Iwata (1974). Its limitations as a topological invariant were discussed by Vologodskii *et al* (1974).

For our purpose it is most convenient to write the Gauss integral formula (2.1) as

$$I_{\alpha\beta} = \oint_{C_\alpha} \mathbf{A}(r_\alpha) \cdot dr_\alpha = \oint_{C_\alpha} \mathbf{A}(r_\alpha) \cdot \dot{r}_\alpha(s_\alpha) ds_\alpha
 \tag{2.2}$$

where we have defined a vector field

$$\mathbf{A}(\mathbf{r}_\alpha) = \frac{1}{4\pi} \oint_{C_\beta} d\mathbf{r}_\beta \times \nabla(1/|\mathbf{r}_\alpha - \mathbf{r}_\beta|). \quad (2.3)$$

We note that if  $C_\beta$  represented a line of magnetic flux, then  $\mathbf{A}(\mathbf{r}_\alpha)$  would represent the vector potential due to this flux line.

Equations (2.2) and (2.3) exhibit an important symmetry transformation, for, under an isotopic deformation of  $C_\beta$  such that

$$C_\beta \rightarrow C'_\beta \quad \text{and} \quad I_{\alpha\beta} \rightarrow I'_{\alpha\beta} = I_{\alpha\beta},$$

we have

$$\mathbf{A}(\mathbf{r}_\alpha) \rightarrow \mathbf{A}'(\mathbf{r}_\alpha) = \mathbf{A}(\mathbf{r}_\alpha) + \nabla\Omega(\mathbf{r}_\alpha) \quad (2.4)$$

where  $\Omega(\mathbf{r}_\alpha)$  is the solid angle subtended by the curve  $C_\beta - C'_\beta$  at  $\mathbf{r}_\alpha$ .

Equation (2.4) is recognised in electromagnetism as a local gauge transformation of the vector potential. It arises directly from conformational changes that preserve the linking number.

If the deformation is not isotopic, and  $C_\beta$  is allowed to cut through the curve  $C_\alpha$ , then the linking number  $I_{\alpha\beta}$  will change by an amount  $\pm 1$ ; hence the Gauss integral jumps by a value  $\pm 4\pi$ .

We will represent polymer configurations by the two curves  $C_\alpha$  and  $C_\beta$ . The following two properties of the vector field  $\mathbf{A}$  are easily derived from the definition (2.3). The first expresses the fact that the curve  $C_\beta$  is closed:

$$\nabla \cdot \mathbf{A} = 0 \quad (2.5)$$

whilst the second result locates the source of the  $\mathbf{A}$  field:

$$\nabla \times \mathbf{A}(\mathbf{R}) = \oint_{C_\beta} ds_\beta \dot{\mathbf{r}}_\beta(s_\beta) \delta(\mathbf{r}_\alpha - \mathbf{R}) = \mathbf{U}^\beta(\mathbf{R}). \quad (2.6)$$

$\mathbf{U}^\beta(\mathbf{R})$  is the density of the  $\beta$ -chain monomer bond vectors at space point  $\mathbf{R}$ .

The conservation of the linking number between the two polymers  $C_\alpha$  and  $C_\beta$  to a value  $m$ ,  $m \in \mathbb{Z}$ , is expressed by the Kronecker delta, which can be parametrised by:

$$\begin{aligned} \delta[I_{\alpha\beta} - m] &= \frac{1}{2\pi} \int_{-\pi}^{+\pi} dg \exp\{ig(I_{\alpha\beta} - m)\} \\ &= \frac{1}{2\pi} \int_{-\pi}^{+\pi} dg \exp\left\{ig \oint_{C_\alpha} \mathbf{A} \cdot d\mathbf{r}_\alpha - m\right\}. \end{aligned} \quad (2.7)$$

The term  $\exp\{ig \oint_{C_\alpha} \mathbf{A}(\mathbf{r}_\alpha) \cdot d\mathbf{r}_\alpha\}$  plays a significant role in gauge-field theories and may be identified with the Wilson loop integral (Wilson 1974) used extensively in gauge theories of confinement. We shall discuss this in greater detail in § 4.

### 3. The statistical mechanics of entanglement

Ideally we would like to treat  $N$  polymer loops with specified topological constraints between each pair of loops. This appears to be a formidable problem so we have identified one polymer molecule, say  $\{\mathbf{r}_\alpha(s)\}$ , and replaced the rest of the molecules in the system by one very long 'effective' molecule  $\{\mathbf{R}_\beta(s)\}$  which will be referred to as the

background chain. For both molecules we assume random flight statistics, so that the configurational probability of a polymer chain  $\mathbf{r}(s) = \{\mathbf{r}(s): 0 \leq s \leq L, \text{ step length } l\}$  is given by the Wiener measure

$$P[\mathbf{r}(s)]\mathcal{D}\mathbf{r} = \mathcal{N}\mathcal{D}\mathbf{r} \exp\left\{-\frac{3}{2l} \int_0^L \dot{\mathbf{r}}^2(s) ds\right\} \tag{3.1}$$

with

$$\mathcal{N}^{-1} = \int \mathcal{D}\mathbf{r} \exp\left\{-\frac{3}{2l} \int_0^L \dot{\mathbf{r}}^2(s) ds\right\} \tag{3.2}$$

and  $\mathcal{D}\mathbf{r}$  represents functional integration. It is well known that the measure (3.1) satisfies the diffusion equation:

$$\left(\frac{\partial}{\partial L} - \frac{l}{6} \nabla_r^2\right)P(\mathbf{r}, L) = 0. \tag{3.3}$$

For any property  $F_{\alpha\beta} \equiv F[\{\mathbf{r}_\alpha(s)\}, \{\mathbf{R}_\beta(s)\}]$  of the two polymers, the value of  $F_{\alpha\beta}$ , averaged over all the configurations of the two polymers, is given by

$$\langle F[\{\mathbf{r}_\alpha(s)\}, \{\mathbf{R}_\beta(s)\}] \rangle = \frac{1}{Z(0)} \frac{\partial}{\partial \lambda} Z(\lambda, L, m)|_{\lambda=0} \tag{3.4}$$

where

$$Z(\lambda, L, m) = \int \mathcal{D}\mathbf{r}_\alpha \mathcal{D}\mathbf{r}_\beta P(\mathbf{r}_\alpha) P(\mathbf{R}_\beta) \delta[I_{\alpha\beta}, m] \exp\{\lambda F[\{\mathbf{r}_\alpha\}, \{\mathbf{R}_\beta\}]\}. \tag{3.5}$$

Using the parametrisation (2.7) for the Kronecker delta function and (3.1) for the  $P(\mathbf{r})$ ,  $Z(\lambda, L, m)$  can be expressed as

$$Z(\lambda, L, m) = \frac{1}{2\pi} \int_{-\pi}^{\pi} dg \exp\{-igm\} Z(\lambda, L, g) \tag{3.6}$$

where

$$\begin{aligned} Z(\lambda, L, g) = & \int \mathcal{D}\mathbf{r}_\alpha \mathcal{D}\mathbf{R}_\beta \delta[\mathbf{r}_\alpha(0) - \mathbf{r}_\alpha(L_\alpha)] \delta[\mathbf{r}_\beta(0) - \mathbf{r}_\beta(L_\beta)] \exp\{igI_{\alpha\beta}\} \\ & \times \exp\left\{-\frac{3}{2l} \int_0^{L_\alpha} \dot{\mathbf{r}}_\alpha^2 ds - \frac{3}{2l} \int_0^{L_\beta} \dot{\mathbf{R}}_\beta^2 ds\right\} \exp\{\lambda F[\{\mathbf{r}_\alpha\}, \{\mathbf{R}_\beta\}]\}. \end{aligned} \tag{3.7}$$

The Dirac delta function in this result expresses the condition for the molecules to form loops.

In this paper we will be concerned only with the properties of the identified chain  $\alpha$ , so that

$$F[\{\mathbf{r}_\alpha\}, \{\mathbf{R}_\beta\}] = F[\{\mathbf{r}_\alpha\}].$$

Hence we can try to do the averaging over the configurations of the background chain  $\mathbf{R}$ .

In attempting the functional integral over  $\{\mathbf{R}_\beta\}$  an immediate difficulty presents itself with the term  $I_{\alpha\beta}[\mathbf{r}_\alpha, \mathbf{R}_\beta]$  in (3.7), as it cannot be evaluated in any closed form.

However, we can write this term from (2.1) as

$$I_{\alpha\beta} = \int d\mathbf{R} \mathbf{J}(\mathbf{R}) \cdot \mathbf{U}^\beta(\mathbf{R}) \tag{3.8}$$

where  $\mathbf{U}^\beta(\mathbf{R})$  is the density of bond vectors of the  $\beta$ -chain defined by equation (2.6), and

$$\mathbf{J}(\mathbf{R}) = \int d\mathbf{R}' \nabla(1/|\mathbf{R} - \mathbf{R}'|) \times \mathbf{U}^\alpha(\mathbf{R}'). \quad (3.9)$$

An approximation that enables us to make further analytic progress is to replace

$$\langle \exp\{igI_{\alpha\beta}\} \rangle_{\{\mathbf{R}_\beta\}} \approx \exp\{-\frac{1}{2}g^2 \langle I_{\alpha\beta}^2 \rangle_{\{\mathbf{R}_\beta\}}\}. \quad (3.10)$$

This is tantamount to treating the density of the  $\beta$ -chain bond vectors as Gaussian random variables, so that

$$\begin{aligned} \langle \exp\{igI_{\alpha\beta}\} \rangle_{\{\mathbf{R}_\beta\}} &= \left\langle \exp\left\{ig \int d\mathbf{R} \mathbf{J} \cdot \mathbf{U}^\beta\right\} \right\rangle_{\{\mathbf{R}_\beta\}} \\ &\approx \exp\left\{-\frac{1}{2}g^2 \int d\mathbf{R} d\mathbf{R}' \mathbf{J}(\mathbf{R}) \cdot \mathbf{J}(\mathbf{R}') \langle \mathbf{U}^\beta(\mathbf{R}) \cdot \mathbf{U}^\beta(\mathbf{R}') \rangle_{\{\mathbf{R}_\beta\}}\right\}. \end{aligned} \quad (3.11)$$

Therefore we have replaced the configurational average over the background chain by an average over the bond vector densities  $\mathbf{U}^\beta(\mathbf{R})$  with the distribution

$$P\{\mathbf{U}^\beta\} \mathcal{D}\mathbf{U}^\beta = \mathcal{N}_{\mathbf{U}^\beta}^{-1} \mathcal{D}\mathbf{U}^\beta \exp\left\{-\frac{3}{2} \int d\mathbf{R} d\mathbf{R}' \mathbf{H}^{-1}(\mathbf{R}, \mathbf{R}') \mathbf{U}^\beta(\mathbf{R}) \cdot \mathbf{U}^\beta(\mathbf{R}')\right\} \quad (3.12)$$

where  $\mathcal{N}_{\mathbf{U}^\beta}$  is the normalisation, and

$$\begin{aligned} \mathbf{H}(\mathbf{R}, \mathbf{R}') &= \langle \mathbf{U}^\beta(\mathbf{R}) \cdot \mathbf{U}^\beta(\mathbf{R}') \rangle_{\{\mathbf{R}_\beta\}} \\ &= \oint_{C_\beta} ds ds' \langle \dot{\mathbf{r}}_\beta(s) \cdot \dot{\mathbf{r}}_\beta(s') \delta(\mathbf{r}_\beta - \mathbf{R}) \delta(\mathbf{r}_\beta' - \mathbf{R}') \rangle_{\{\mathbf{r}_\beta\}}. \end{aligned} \quad (3.13)$$

The original Gaussian distribution (3.1) for  $\{\mathbf{r}_\beta\}$  is used to calculate the RHS of (3.13). For a long chain ( $L_\beta \rightarrow \infty$ ) which we imagine to fill a macroscopic volume, so that the density of the background monomers is finite, we find that

$$\langle \mathbf{U}^\beta(\mathbf{R}) \cdot \mathbf{U}^\beta(\mathbf{R}') \rangle_{\{\mathbf{R}_\beta\}} = \rho l^2 \delta(\mathbf{R} - \mathbf{R}') \quad (3.14)$$

where  $\rho$  is the density of monomers. Thus the distribution of bond vector densities (3.12) becomes

$$P\{\mathbf{U}^\beta\} \mathcal{D}\mathbf{U}^\beta = \mathcal{N}_{\mathbf{U}^\beta}^{-1} \mathcal{D}\mathbf{U}^\beta \exp\left\{-\frac{3}{2\rho l^2} \int d\mathbf{R} [\mathbf{U}^\beta(\mathbf{R})]^2\right\}. \quad (3.15)$$

We recall from (2.6) that  $\mathbf{U}^\beta$  is the source of the vector field  $\mathbf{A}(\mathbf{R})$ ; consequently the functional integration over the bond vector densities  $\mathbf{U}^\beta$  can be replaced by functional integration over the  $\mathbf{A}$  field (integration being restricted over those fields that satisfy  $\nabla \cdot \mathbf{A} = 0$ ).

Then,

$$P\{\mathbf{U}^\beta\} \mathcal{D}\mathbf{U}^\beta = \frac{\mathcal{D}\mathbf{A} \exp\{-\mathcal{L}[\mathbf{A}]\} \delta(\nabla \cdot \mathbf{A})}{\int \mathcal{D}\mathbf{A} \delta(\nabla \cdot \mathbf{A}) \exp\{-\mathcal{L}[\mathbf{A}]\}} \quad (3.16)$$

where

$$\mathcal{L}[\mathbf{A}] = (3/2\rho l^2) \int d\mathbf{R} (\nabla \times \mathbf{A})^2.$$

Now using the definition (2.3) for  $I_{\alpha\beta}$ , we may finally write

$$\langle \exp\{igI_{\alpha\beta}\} \rangle_{\{\mathbf{R}_\beta\}} \simeq \left\langle \exp\left\{ig \oint \mathbf{A} \cdot d\mathbf{r}\right\} \right\rangle_{\{\mathbf{A}\}} \tag{3.17}$$

where  $\langle \dots \rangle_{\{\mathbf{A}\}}$  is given by equation (3.16).

The partition sum (3.7) may, then, be written as

$$\begin{aligned} Z(\lambda, L, g) = \mathcal{N}_{\mathbf{A}}^{-1} &\int \mathcal{D}\mathbf{r}_\alpha \mathcal{D}\mathbf{A} \delta[\mathbf{r}_\alpha(0) - \mathbf{r}_\alpha(L_\alpha)] \\ &\times \exp\left\{-\frac{3}{2l} \int_0^{L_\alpha} \dot{\mathbf{r}}_\alpha^2 ds + \lambda F\{\mathbf{r}_\alpha\}\right\} \\ &\times \exp\left\{ig \oint_{C_\alpha} \mathbf{A} \cdot d\mathbf{r}_\alpha\right\} \delta(\nabla \cdot \mathbf{A}) \exp\{-\mathcal{L}[\mathbf{A}]\} \end{aligned} \tag{3.18}$$

with

$$\mathcal{N}_{\mathbf{A}}^{-1} = \int \mathcal{D}\mathbf{r}_\alpha \mathcal{D}\mathbf{A} \delta(\nabla \cdot \mathbf{A}) \exp\left\{-\frac{3}{2l} \int_0^{L_\alpha} \dot{\mathbf{r}}_\alpha^2 ds - \mathcal{L}[\mathbf{A}]\right\}. \tag{3.19}$$

Equation (3.18) will form the starting point in the next section for deriving the relationship between this problem of an entangled molecule and an  $n \rightarrow 0$  component gauge-field theory. However, to complete this section we wish to remark that the functional integration over the  $\{\mathbf{A}\}$  field is just a standard Gaussian functional integral. Consequently it can be evaluated to give:

$$\left\langle \exp\left\{ig \oint \mathbf{A} \cdot \dot{\mathbf{r}} ds\right\} \right\rangle_{\{\mathbf{A}\}} = \exp\left\{-\frac{1}{2}g^2 \int ds ds' W[\mathbf{r}(s), \mathbf{r}(s')]\right\} \tag{3.20}$$

where

$$W[\mathbf{r}(s), \mathbf{r}(s')] = \sum_{ij} \dot{\mathbf{r}}_i(s) T_{ij}\{\mathbf{R}(s, s')\} \dot{\mathbf{r}}_j(s') \tag{3.21}$$

and

$$T_{ij}\{\mathbf{R}(s, s')\} = \frac{\rho l^2}{12\pi} \frac{1}{|\mathbf{r}(s) - \mathbf{r}(s')|} \{\delta_{ij} + \mathbf{R}_i(s, s') \mathbf{R}_j(s, s')\} \tag{3.22}$$

and

$$\mathbf{R}(s, s') = (\mathbf{r}(s) - \mathbf{r}(s'))/|\mathbf{r}(s) - \mathbf{r}(s')|. \tag{3.23}$$

Thus the partition sum (3.18) for the single entangled chain can be written as

$$\begin{aligned} Z(\lambda, L, g) = \mathcal{N}_{\mathbf{A}}^{-1} &\int \mathcal{D}\mathbf{r}_\alpha \delta[\mathbf{r}_\alpha(0) - \mathbf{r}_\alpha(L_\alpha)] \\ &\times \exp\left\{-(3/2l) \int_0^{L_\alpha} \dot{\mathbf{r}}_\alpha^2 ds + \lambda F\{\mathbf{r}_\alpha\}\right\} \\ &\times \exp\left\{-\frac{1}{2}g^2 \int ds ds' W[\mathbf{r}_\alpha(s), \mathbf{r}_\alpha(s')]\right\}. \end{aligned} \tag{3.24}$$

The entanglement constraint has now appeared as a self-interaction term



$\{-g^2/2 \iint W ds ds'\}$ . The first term in  $W$ , given by (3.21), is familiar from electromagnetism as the self-inductance of a loop. The 'coupling constant  $g$ ' in this theory is conjugate to the linking number  $m$ .

#### 4. The entanglement constraint as a gauge-field theory

In § 3 we obtained the partition sum (3.18) for the average value of a single chain property  $F\{r_\alpha\}$  for the  $\alpha$ -chain in topological interaction with a large background chain ( $\beta$ -chain).

In this section we shall explicitly show that the statistical mechanics of an entangled polymer molecule can be described as a classical  $n$ -component gauge-field theory in the limit  $n \rightarrow 0$ . To this end we first consider an explicit form for the function  $F\{r_\alpha\}$  by considering the monomer-density of the entangled polymer at the space-point  $\mathbf{R}$ .

Therefore we set

$$F\{r\} = \delta[r(s_1) - \mathbf{R}] \quad (4.1)$$

where, for the sake of brevity, the  $\alpha$  subscript has been suppressed.

We then define the averaged monomer density of a chain of length  $L$  as

$$\rho(\mathbf{R}) = \int_0^L ds_1 \langle [\delta r(s_1) - \mathbf{R}] \rangle. \quad (4.2)$$

Next, we use equations (3.4), (3.6) and the partition function (3.18) to obtain the average value of the Dirac delta function in equation (4.2) as

$$\langle \delta[r(s_1) - \mathbf{R}] \rangle = \frac{\int_{-\pi}^{+\pi} dg \exp\{-igm\} G(\mathbf{R}, s; L, g)}{\int_{-\pi}^{+\pi} dg \int d^3R \exp\{-igm\} G(\mathbf{R}, s; L, g)} \quad (4.3)$$

where

$$G(\mathbf{R}, s; L, g) = \mathcal{N}_A^{-1} \int \mathcal{D}\mathbf{r}(s) \mathcal{D}\mathbf{A}(\mathbf{r}) \delta(\nabla \cdot \mathbf{A}) \delta[\mathbf{r}(0) - \mathbf{r}(L)] \delta[\mathbf{r}(s_1) - \mathbf{r}(0) - \mathbf{R}] \\ \times \exp\left\{-\frac{3}{2l} \int_0^L \dot{\mathbf{r}}^2(s) ds\right\} \exp\left\{ig \int_0^L \mathbf{A} \cdot \dot{\mathbf{r}}(s) ds - \mathcal{L}[\mathbf{A}]\right\} \quad (4.4)$$

and the normalisation factor  $\mathcal{N}_A^{-1}$  is given by equation (3.19).

Because of the closed-loop constraint on the polymer, it is possible to factorise the Wiener integrals in equation (4.4) into those with paths that begin at  $\mathbf{r}(0)$  and reach  $\mathbf{R}$  using an arc length  $s_1$ , and those with paths that begin at  $\mathbf{R}$  and reach  $\mathbf{r}(0)$  using an arc length  $(L - s_1)$ .

Thus the interaction term in (4.4) can be written as

$$\int_0^L \mathbf{A} \cdot \dot{\mathbf{r}}(s) ds = \int_0^{s_1} \mathbf{A}(\mathbf{r}(s)) \cdot \dot{\mathbf{r}}(s) ds - \int_0^{L-s_1} \mathbf{A}(\mathbf{r}'(s')) \cdot \dot{\mathbf{r}}'(s') ds' \quad (4.5)$$

where for  $s \geq s_1$  we have defined  $s' = L - s_1$  and  $\mathbf{r}'(s') = \mathbf{r}(s)$ . Next, we make a change of variable  $\mathbf{r} \rightarrow \mathbf{R} - \mathbf{r}(0)$  in the configurational Dirac delta functions appearing in (4.4), and factorise equation (4.4) thus:

$$G(\mathbf{r}, s; L, g) = \frac{\int \mathcal{D}\mathbf{A} \delta(\nabla \cdot \mathbf{A}) \exp\{-\mathcal{L}[\mathbf{A}]\} K(\mathbf{r}, s_1; [\mathbf{A}]) K(\mathbf{r}, s'; [-\mathbf{A}])}{\int \mathcal{D}\mathbf{A} \delta(\nabla \cdot \mathbf{A}) \exp\{-\mathcal{L}[\mathbf{A}]\}} \quad (4.6)$$

where we define

$$K(\mathbf{r}, s_1; [\mathbf{A}]) = \frac{\int_0^{s_1} \mathcal{D}\mathbf{r}(s) \delta[\mathbf{r}(s_1) - \mathbf{r}(0) - \mathbf{r}] \exp\{-\int_0^{s_1} ds [(3/2l)\dot{\mathbf{r}}^2(s) - i\mathbf{g}\mathbf{A} \cdot \dot{\mathbf{r}}]\}}{\int_0^{s_1} \mathcal{D}\mathbf{r}(s) \exp\{-(3/2l) \int_0^{s_1} \dot{\mathbf{r}}^2 ds\}}. \quad (4.7)$$

It is evident that  $K(\mathbf{r}, s_1; [\mathbf{A}])$  is a Markov process. Following Edwards (1968) we identify this Wiener integral with the Feynman integral for a charged particle moving in an electromagnetic vector potential field  $\mathbf{A}$ . The  $K(\mathbf{r}, s_1; [\mathbf{A}])$  is known to satisfy a Schrödinger-type equation

$$\{\partial/\partial s_1 - \frac{1}{2}l(\nabla - i\mathbf{g}\mathbf{A})^2\}K(\mathbf{r}, s_1; [\mathbf{A}]) = 0 \quad (4.8)$$

with

$$\lim_{s_1 \rightarrow 0} K(\mathbf{r}, s_1; [\mathbf{A}]) = \delta(\mathbf{r}).$$

The operator  $(\nabla - i\mathbf{g}\mathbf{A})$  is the familiar ‘minimal coupling’ term from scalar electrodynamics. Next we define the Laplace transform

$$\hat{K}(\mathbf{r}, \mu; [\mathbf{A}]) = \int_0^\infty ds_1 \exp\{-\mu s_1\}K(\mathbf{r}, s_1; [\mathbf{A}]). \quad (4.9)$$

We recall from (4.2) that we ultimately need to integrate over the arc length variables  $s_1$ , of the loop, in equation (4.6). This leads to the convolution

$$\int_0^\infty dL \exp\{-\mu L\} \int_0^L ds_1 K(\mathbf{r}, s_1; [\mathbf{A}])K(\mathbf{r}, L - s_1; [-\mathbf{A}]) = \hat{K}(\mathbf{r}, \mu; [\mathbf{A}])\hat{K}(\mathbf{r}, \mu; [-\mathbf{A}]) \quad (4.10)$$

and equation (4.8) becomes

$$[\mu - \frac{1}{2}l(\nabla - i\mathbf{g}\mathbf{A})^2]\hat{K}(\mathbf{r}, \mu; [\mathbf{A}]) = \delta(\mathbf{r}). \quad (4.11)$$

To exhibit the field-theoretic content of our formalism, we need to express  $\hat{K}(\mathbf{r}, \mu; [\mathbf{A}])$  in terms of functional integrals. However, because of the coupling of the polymer loop to the vector potential  $\mathbf{A}$  in the interaction term in (4.7), the loop is oriented. This orientation of the loop is preserved by the use of complex Gaussian random fields. We write

$$\begin{aligned} \hat{K}(\mathbf{r}, \mu; [\mathbf{A}]) &= \frac{\int \mathcal{D}\psi^*(\mathbf{r})\mathcal{D}\psi(\mathbf{r})\psi^*(0)\psi(\mathbf{r}) \exp\{-\mathcal{L}[\psi]\}}{\int \mathcal{D}\psi^*(\mathbf{r})\mathcal{D}\psi(\mathbf{r}) \exp\{-\mathcal{L}[\psi]\}} \\ &\equiv \langle \psi^*(0)\psi(\mathbf{r}) \rangle_{[\psi]} \end{aligned} \quad (4.12)$$

where

$$\mathcal{L}[\psi] = -\frac{1}{2} \int d\mathbf{r} \psi^*(\mathbf{r})[\frac{1}{2}l(\nabla - i\mathbf{g}\mathbf{A})^2 - \mu]\psi(\mathbf{r}). \quad (4.13)$$

Expression (4.12) represents a polymer ‘propagator’ that starts at  $\psi^*(0)$  and ends at  $\psi(\mathbf{r})$ . The transverse gauge condition (2.5) enables us to write

$$\hat{K}(\mathbf{r}, \mu; [-\mathbf{A}]) = \langle \psi(0)\psi^*(\mathbf{r}) \rangle_{[\psi]} \quad (4.14)$$

where  $\langle \dots \rangle_{[\psi]}$  is defined by equation (4.12). The generating functional is obtained by adding, to equation (4.13), a linear coupling of  $\psi^*\psi$  to an external source  $J(\mathbf{r})$ :

$$\mathcal{L}[J] = \mathcal{L}[\psi] - \int d\mathbf{r} J(\mathbf{r})\psi^*(\mathbf{r})\psi(\mathbf{r}). \quad (4.15)$$

Then

$$\hat{K}(r, \mu; [\mathbf{A}])\hat{K}(r, \mu; [-\mathbf{A}]) = \lim_{J \rightarrow 0} \frac{\delta}{\delta J(r)} \frac{\delta}{\delta J(0)} \ln \left\{ \frac{Z[J, \mathbf{A}]}{Z[0, \mathbf{A}]} \right\} \tag{4.16}$$

where

$$Z[J, \mathbf{A}] = \int \mathcal{D}\psi \mathcal{D}\psi^* \exp\{-\mathcal{L}[J]\}. \tag{4.17}$$

We recall from (4.6) that  $Z[J, \mathbf{A}]$  has to be averaged over the vector field  $\mathbf{A}$ ; the averaging over the logarithm in (4.16) can be performed by the use of the replica method (due to Edwards and Anderson 1975). Then, we may write (4.16) as

$$\hat{K}(r, \mu; [\mathbf{A}])\hat{K}(r, \mu; [-\mathbf{A}]) = \lim_{\substack{J \rightarrow 0 \\ n \rightarrow 0}} \frac{1}{n} \frac{\delta}{\delta J(r)} \frac{\delta}{\delta J(0)} \frac{Z^{(n)}[J, \mathbf{A}]}{Z^{(n)}[0, \mathbf{A}]} \tag{4.18}$$

where we define

$$Z^{(n)}[J, \mathbf{A}] = \prod_{\sigma=1}^n \int \mathcal{D}\psi_{\sigma} \mathcal{D}\psi_{\sigma}^* \exp\{-\mathcal{L}[J]_{\sigma}\} \tag{4.19}$$

and

$$\mathcal{L}[J]_{\sigma} = \int d\mathbf{r} \left\{ \frac{1}{12}l |(\nabla - i\mathbf{g}\mathbf{A})\psi_{\sigma}|^2 + \frac{1}{2}\mu |\psi_{\sigma}|^2 - J|\psi_{\sigma}|^2 \right\}. \tag{4.20}$$

$n$  is known as the replica index; the limit  $n \rightarrow 0$  is obtained by analytic continuation.

The Laplace transform of the Green function  $G(\mathbf{R}, s; L, g)$  in equation (4.6) can be written in obvious notation as

$$\begin{aligned} \hat{G}(\mathbf{R}, \mu; L, g) &= \lim_{\substack{J \rightarrow 0 \\ n \rightarrow 0}} \frac{1}{n} \frac{\delta}{\delta J(r)} \frac{\delta}{\delta J(0)} \\ &\times \frac{\int \mathcal{D}\mathbf{A} \delta(\nabla \cdot \mathbf{A}) \prod_{\sigma=1}^n \int \mathcal{D}\psi_{\sigma} \mathcal{D}\psi_{\sigma}^* \exp\{-\mathcal{L}_{\text{TOT}}(J)\}}{\int \mathcal{D}\mathbf{A} \delta(\nabla \cdot \mathbf{A}) \prod_{\sigma=1}^n \int \mathcal{D}\psi_{\sigma} \mathcal{D}\psi_{\sigma}^* \exp\{-\mathcal{L}_{\text{TOT}}(0)\}} \end{aligned} \tag{4.21}$$

where

$$\begin{aligned} \mathcal{L}_{\text{TOT}}(J) &\equiv \mathcal{L}[\mathbf{A}] + \mathcal{L}[J]_{\sigma} \\ &= \int d\mathbf{r} \{ (3/2\rho l^2)(\nabla \times \mathbf{A})^2 + \frac{1}{2}\mu |\psi_{\sigma}|^2 + \frac{1}{12}l |(\nabla - i\mathbf{g}\mathbf{A})\psi_{\sigma}|^2 - J|\psi_{\sigma}|^2 \}. \end{aligned} \tag{4.22}$$

The Lagrangian (4.22) is invariant under the group of transformations

$$\begin{aligned} \mathbf{A}' &\rightarrow \mathbf{A} + \nabla\Lambda(r) \\ \psi'_{\sigma} &\rightarrow \psi_{\sigma} e^{i\Lambda(r)} \\ \psi'^*_{\sigma} &\rightarrow \psi^*_{\sigma} e^{-i\Lambda(r)} \end{aligned} \tag{4.23}$$

where  $\Lambda(r)$  is an arbitrary  $r$ -dependent phase, and the phase factor  $\exp\{i\Lambda(r)\}$  is just the well known representation of the unitary group  $U(1)$ . The minimal coupling term appearing in the Lagrangian (4.22) is the covariant derivative which is  $U(1)$  gauge invariant.

Therefore, the problem of the entanglement of two polymer rings has now been transformed into an  $n \rightarrow 0$  gauge theory. Topological conservation of linking number of two rings has led to a reduction in the number of degrees of freedom that a ring may possess—a manifest consequence of gauge invariance. The Lagrangian (4.22) may be identified with the Lagrangian for scalar quantum electrodynamics (e.g. Coleman and Weinberg 1973). Stone and Thomas (1978) have obtained a similar Lagrangian for a system of polymer rings interacting with a Biot-Savart interaction, but with only a single-component field.

The inclusion of excluded volume interactions in the polymer problem is known to generate a further term  $v|\psi_\sigma|^4$  into the Lagrangian (e.g. des Cloizeaux 1974), so that equation (4.22) becomes

$$\mathcal{L}_{\text{TOT}}(J) = \int d\mathbf{r} \left\{ (3/2\rho l^2)(\nabla \times \mathbf{A})^2 + \frac{1}{12l} |(\nabla - ig\mathbf{A})\psi_\sigma|^2 + \frac{1}{2}\mu |\psi_\sigma|^2 + v|\psi_\sigma|^4 - J|\psi_\sigma|^2 \right\} \quad (4.24)$$

where  $v > 0$  is the excluded-volume parameter. The Lagrangian (4.24) is just the renormalised QED Lagrangian, as Coleman and Weinberg (1973) show that a renormalisation procedure, applied to the QED Lagrangian in the form of (4.22), generates a  $|\psi_\sigma|^4$  term. In the polymer case,  $v|\psi_\sigma|^4$  just takes into account the self-repulsion of the polymer, and it provides a correct weighting factor for the polymer configurational functional integral. The linking number constraint itself acts as a weak form of mutual repulsion by not allowing one chain to pass through another chain; however, it does not affect different monomers of the same chain. Hence for any realistic formulation of the entanglement problem of two chains, it is necessary to include the excluded volume effect.

A similar Lagrangian has been obtained by Hertz (1978) for a continuum spin-glass model. We hope to return to this analogy and the effect of entanglements on the critical indices associated with polymer configurations in a later paper.

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